# THE USE OF MICROBIAL KINETICS IN MODELING KRAFT BLACK LIQUOR COD REMOVAL OVER A BIOLOGICAL TOWER

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THE USE OF MICROBIAL KINETICS IN MODELING

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OVER A BIOLOGICAL TOWER

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# CHAPTER I

# INTRODUCTION

## The Biological Tower

Since its crude beginnings around 1891 (1), the trickling filter (or biological tower, to use the preferred modern terminology) has become one of the most widely used and perhaps, after activated sludge, most appreciated of the available waste treatment processes. In this process, waste water is allowed to flow or trickle over a bed of rock or similar material, or, increasingly, over taller beds of wooden baffles or plastic media. Microbial populations soon coat the substratum, forming the zooglea which lives off of and consumes the soluble organic matter contained in the waste. When operated effectively under reasonable loadings, biological towers can produce very high degrees of purification.

With its relatively low maintenance and energy requirements and ease of operation the biological tower has many advantages over more slphisticated techniques, especially in small municipalities and in other situations in which large budgets and highly trained and conscientious operators are not available. There are some problems, however, the chief of which may be the lack of a really reliable design method. It seems relatively common to design and build a biological tower or trickling filter only to have it become grossly overloaded long before

its design life is reached. Unlike activated sludge, with a biological tower there is little operational control available to alleviate this difficulty. So it is perhaps even more important to have a rigorous design model for biological towers than for activated sludge.

Modeling a fixed bed reactor has proven much more difficult than modeling a completely mixed system. In spite of our fairly advanced knowledge of the biological aspects of waste removal, only recently has anyone attempted to base a design model for biological towers on this knowledge. The difficulties in modeling fixed bed reactors this way are probably the result of problems in quantifying the biomass, describing its growth and removal characteristics, and perhaps in describing the hydraulic characteristics of the flow and the possible existance of a substrate concentration gradient across a boundary layer next to the zoolea.

Of course, no progress can be expected in this area until some effort is expended. The research on biological towers has only recently begun to concentrate on describing the waste removal in biological terms. With continued effort, it can be hoped that this viable and must used process will soon be understood to the same extent as activated sludge is today, allowing it to be used more effectively than it is at present.

## Pulp and Paper Waste

Engineers in the field have often questioned the validity of laboratory studies conducted on synthetic waste (sucrose or glucose with nutrients) to real waste treatment situations. For this study the carbon source was pulp and paper waste, or more specifically, Kraft mill "black liquor". It is not the purpose of this thesis to study pulp and

paper waste treatment specifically, but a short description might be enlightening and should relieve any doubts as to the applicability of this study to real industrial treatment processes.

The purpose of chemical pulping is to dissolve the lignin, which acts as a binder in the wood, thereby freeing the cellulose fibers, which are the desired product. In the Kraft process, wood chips are steam-heated in a pressurized digestor with a cooking liquor. This cooking liquor is an aqueous solution of sodium hydroxide and sodium sulfide. At the end of the cooking phase (a number of hours usually or the process may be continuous) the liquor is discharged violently into a tank to break up the chips into individual fibers (pulp). The pulp is then removed from the "black liquor" (black because of the dissolved and degraded wood constituents) and washed free of all traces of the liquor, screened to remove large fragments, and passed to the stock tank, ready for bleaching or processing directly into paper products (2).

The black liquor is never wasted, as energy and chemical recovery from it is an important aspect to the economics of Kraft pulping. The wash waters, however, which are essentially diluted black liquor, form a significant portion of the total waste load of the pulp mill. In the black liquor one expects to find the solubilized lignin and all the other compounds, organic and inorganic, found in trees with the exception of cellulose. It has a very high COD and BOD and is very alkaline, with a pH of 10 or higher. It is however, lacking in essential nutrients. Much of the COD is contributed by carbohydrates. Of course, all compounds have been subjected to alkaline digestion. The "alkali lignin", or "Kraft lignin", which can be precipitated by acidification, is only very slowly biodegraded. This forms a large "residual COD" in pulp

waste water. Also from the black liquor comes color bodies, which are refractory to biological treatment, and small amounts of resin, fatty acids and other chemicals that result in foaming (3).

# CHAPTER II

## LITERATURE REVIEW

Prior to the development of microbial kinetics as applied to fixed bed reactors, biological towers were of necessity designed by empirical methods. Some authors attempted to derive the necessary filter area and depth by setting parameter ranges. Imhoff, for example, advocated sizing the filter on the basis of population (4). Ingram, on the other hand, believed in using parameters such as allowable hydrulic and organic loading rates to determine area and volume requirements (5).

A more popular method has been to collect data on a number of facilities and derive an empirical formula to fit that data. Two of the resulting formulas have been very widely used, those of the National Research Council and of Galler and Gotaas.

The National Research Council formula was developed from data collected from a number of military installations (6). For a single stage filter without recirculation the formula is:

$$E = \frac{100}{1 + C(\frac{W}{V})^{0.5}}$$

where E = % BOD removed

W = organic loading (lbs BOD/day)

V = filter volume (cubic feet)

C = constant, equal to 0.0561

Galler and Gotaas developed a formula by multiple regression analysis of data from existing treatment plants (7). Without recirculation:

$$L_e = \frac{1.3 L_o^{0.98} Q^{.12}}{(1+D)^{.66} T^{.15}}$$

where $L_e$ = BOD concentration remaining

$L_o$ = influent BOD concentration

$Q$ = hydraulic loading (mgd/acre)

$D$ = depth (feet)

$T$ = water temperature, °C

A third empirical formula developed by Fairall (8) has evidently not been so widely used.

Having recognized the need for a more sophisticated approach toward filter design, a number of workers proposed various theoretical relationships to be used. Phelps proposed that BOD removal would be first order with time (9):

$$Lt/L = 10^{-kt}$$

where $L$ = total initial removable BOD

$L_t$ = BOD at time t

$k$ = a rate constant, to be determined experimentally

Velz, equating depth in a filter with time, used a more applicable form (10):

$$L_D/L = 10^{-kD}$$

where $D$ = depth

$L_D$ = BOD at depth D

Gerber (11) and Schulze (12) combined the above first order

rate equation with empirical relationships to form new models. Schulze's formula is:

$$L_e/L_i = 10^{-kD/Q^n}$$

where $L_e$ = effluent BOD (mg/l)

$L_i$ = influent BOD (mg/l)

Q = hydraulic loading (mgd/acre)

D = filter depth (ft)

n = 2/3

k = 0.3 at 20°C

Howland, among others, studies this model and confirmed the value of n as 2/3 (13). The validity of this equation was confirmed on plastic media by Germain (14).

In 1957 Stack attempted a slightly different approach toward modeling trickling filters (15). Starting with the assumptions that (1) the trickling filter is a self-regenerating absorption tower, (2) each unit depth of filter will remove a constant fraction of the removable BOD applied to that depth, (3) removable BOD is the fraction of the observed BOD which can be removed by biosorption, and (4) the quantity of BOD that can be removed by one unit volume of a filter has a maximum limit. These assumptions were also used by Velz. Stack's formula, without recirculation, is:

$$R = fL[1 + (1-f) + (1-f)^2 \ldots (1-f)^{D-1}]$$

where R = fraction of removable BOD removed

D = number of unit depths in the filter

f = coefficient of biosorption (BOD removed/unit depth)

L = removable BOD loading applied

If enough removable BOD is applied to saturate a portion of the filter, the formula takes the form:

$$R = xfS = f(L-xfS)[1+(1-f)+(1-f)^2+ \ldots +(1-f)^{D-x-1}]$$

where x = number of unit depths saturated

S = removable BOD loading that must be applied to saturate a unit depth with BOD

L = removable BOD loading applied

Eckenfelder, expanding on the work of Velz, Schulze and Howland, developed a formula that allowed for BOD removal occurring non-uniformly with depth (the others had assumed that each unit depth removed a constant fraction of BOD) (16):

$$L_e/L_o = \frac{100}{1 + \frac{LD^{(1-m)}}{Q^n}}$$

where $L_e$ = effluent BOD

$L_o$ = influent BOD

D = depth (ft)

Q = hydraulic loading rate (mgd/acre)

(1-m), n = constants

Eckenfelder was concerned with the active biological portion of the filter, believing that the BOD removal was "related to the surface area of active film per unit volume of filter media." He commented on the relationship of the process to activated sludge and, further, defined the active biological film as being dependent upon the depth of film

through which aerobic conditions are maintained. Analyzing published data, Eckenfelder obtained the following values for the constants: $C = 2.5$, $(1-m) = 0.67$ and $n = 0.50$.

In 1968, Kornegay and Andrews laid the groundwork for a purely biological approach to filter modeling (17). The following assumptions were made: (1) complete mixing is achieved in the liquid phase, (2) substrate utilization from sources other than the attached microbial film is small and may be neglected, and (3) removal is described by a saturation function which incorporates the effect of diffusion and growth rate. To quantify the mass of microorganisms active in removal, they used:

$$M_o = (A)(x)(d)$$

where $M_o$ = mass of microorganisms

$A$ = surface area provided for growth

$x$ = microorganisms density in active layer

$d$ = active thickness

Using the above with the microbial growth model of Monod (18) they derived the following expression to describe substrate removal in their annular reactors:

$$F(S_o - S_1) = \frac{\mu_{max}}{Y} (A)(x)(d)\left[\frac{S_1}{k_s + S_1}\right]$$

where $S_o$ = influent substrate concentration

$S_1$ = effluent substrate concentration

$Y$ = cell yield

$\mu_{max}$ = maximum growth rate of population ($time^{-1}$)

$k_s$ = substrate concentration at which $\mu = \frac{1}{2}\mu_{max}$

As a result of this work, Kornegay and Andrews determined that $d = 70\mu$, independent of hydraulic or organic loading and DO concentrations, and that $x = 95$ mg/l, also constant. They were satisfied that their theoretical model could describe actual situations.

Having accomplished this much, Kornegay and Andrews developed a full-fledged design model in 1969, using this time a series of completely mixed, annular reactors to simulate a filter (19). Besides the assumptions used earlier, they assumed that (1) plug flow was achieved in the liquid phase and (2) the apparent yield remains constant with depth. The resulting formula is:

$$(S_o - S_e) + k_s \ln S_o/S_e = \frac{\mu_{max}}{F\ Y_{obs}} (a)(x)(d)(H)Z$$

which is very similar to the one used in this thesis. Here

a = specific area provided by the media (area/volume)

Z = depth

H = cross-sectional area

In 1970 Cook completed an exhaustive study on fixed bed reactor kinetics, using a realistic pilot plant, that supported a formula derived by making a materials balance around a unit volume of reactor (20). This formula was identical to the first one developed by Kornegay and Andrews for their single, annular reactors.

Kincannon and Sherrard, in 1973, proposed using the biological parameters of $\Theta_c$ or F/M ratio for evaluating biological towers (21). This way, the filter could be compared directly to an activated sludge system, since different systems operating with the same $\Theta_c$ or F/M ratio will give similar effluent quality and operational characteristics.

Having made this comparison, economic and operational considerations could be used in selecting the final design.

This proposal was supported by work done by Bentley, who found that biological parameters used in activated sludge processes could be used successfully to describe fixed-bed biological processes, and that in doing so a superior degree of understanding and control might result (22).

In 1974 the model presently being studied was put to its first test by Hapke (23). Using data obtained by Cook and Bentley, Hapke used the model to describe ΔCOD removal through a fixed bed reactor with good results.

In the same year, Williamson and McCarty presented an even more sophisticated model (24) (25). They assumed that the rate of reaction would be limited by a single substrate species, and developed a model using molecular diffusion descriptions coupled with the Monod equation. This model requires a number of assumptions and is so complicated as to have little immediate value as an engineering tool. It was used successfully, however, to predict substrate utilization rates of Nitrosomonas and Nitrosomonas-Nitrobacter enrichment cultures grown on plastic beads packed in columns.

# CHAPTER III

## KINCANNON'S MODEL

The removal of organic matter during any biological waste treatment process is the result of microorganisms, which metabolize organic compounds for growth and reproduction. The rate of organic removal is dependent, therefore, upon the number of microorganisms present, their growth rate, and their efficiency in converting the organic substrate into cellular matter (or the "yield" of new cell material per unit of substrate used). The growth rate, in turn, is dependent upon the substrate concentration, assuming that all inorganic nutrients (and any other growth factors) are present in sufficient quantities. This relationship between the growth rate and substrate concentration has been experimentally defined by Monod (18) as

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

where $\mu$ = growth rate ($time^{-1}$)

$\mu_{max}$ = maximum growth rate ($time^{-1}$)

$k_s$ = concentration of substrate at which $\mu=\mu_{max}$ (mass/volume)

$S$ = (initial) substrate concentration (mass/volume)

Chapter 4 of the M-3 Manual published by the Bioenvironmental Engineering Department of Oklahoma State University provides an excellent

development of microbial growth kinetics, and is highly recommended for the interested but unexposed reader (26).

These relationships have been used successfully to model completely mixed biological reactors, as is described in the M-3 Manual. Applying the same relationships to a fixed bed reactor requires some additional assumptions and information.

First of all, the hydraulic flow over the fixed bed reactor must be assumed to occur as plug-flow. One expects (and depends upon) a steady state being established, with the substrate concentration at any point in the system remaining constant as long as the influent substrate and hydraulic flow rate remain constant.

Also, the microbial population must be assumed to achieve a steady state. Ideally, the microorganisms, after reaching an optimum thickness of growth, would be sheared off at a rate equal to the rate of new growth. While this occurs sometimes (as it did during this project), the more usual procedure, apparently, is for rather large clumps of cells to slough off. This may not affect the kinetics in the long run, but it certainly increases the difficulties of rigorous biological modeling. To be more precise, it increases the difficulties of measuring accurately the amount of cell mass being generated over the tower, which is necessary for modeling.

Kornegay and Andrews, in developing a model very similar to Professor Kincannon's, determined that microbial films on a substratum reached a particular thickness after which an increase in thickness was not accompanied by an increase in substrate utilization or $O_2$ uptake (17). This particular thickness, called the "active thickness", was determined to be 70u, independent of flow rate, substrate concentration, or dissolved

oxygen. This value, along with the "specific area" (amount of surface area provided by a unit volume) of the particular substratum material used, can be used to quantitate the amount of biomass present in any given volume of the reactor.

Another assumption that must be accepted to obtain a reasonable model is that the yield (change in cell mass/decrease in COD) remains constant with depth. Kornegay and Andrews assumed that the observed yield, $Y_{obs}$, would remain constant, but this is demonstratably false. For this model, the true yield, $Y_t$, is assumed to remain constant.

The last assumption to be made is that all significant substrate removal must be accounted for by the microbial film. With volatile substrates, the possibility of stripping must be considered and accounted for separately.

Now imagine a volume of substratum, of unit cross-sectional area, and of depth Z. Consider a unit volume from the above, of depth dZ, with an influent substrate concentration of S+dS and an effluent concentration of S. Given steady state, the following substrate balance can be written across the differential depth, dZ:

$$F(S+dS) = FS + dMs/dt \qquad (2)$$

where $F$ = flow rate (volume/time)

$S$ = substrate concentration (mass/volume)

$M_s$ = mass of substrate (mass)

$t$ = time

The change in microbial mass is related to the decrease in substrate concentration by the yield, $Y_t$; and to time by the maintenance or "decay" coefficient, $k_d$ (with units of time$^{-1}$):

$$\frac{dM_o}{dt} = Y_t \frac{dM_s}{dt} - k_d M_o \quad (3)$$

where $M_o$ = mass of microorganisms

rearranging

$$\frac{dM_s}{dt} = \frac{dM_o/dt + k_d M_o}{Y_t} \quad (4)$$

The change in cell mass is related to the growth rate, $\mu$, and by:

$$\mu = \frac{dMo/dt}{Mo} + k_d \quad (5)$$

Substituting into (4):

$$\frac{dM_s}{dt} = \frac{\mu M_o}{Yt} \quad (6)$$

Substituting this into (2):

$$F(S+dS) = FS + \frac{\mu}{Yt} Mo \quad (7)$$

From the Monod relationship, equation (1):

$$F(S+dS) = FS + \left[\frac{\mu_{max} \cdot S}{K_s + S}\right] \frac{Mo}{Yt} \quad (8)$$

Rearranging:

$$\left(\frac{K_s + S}{S}\right)dS = \frac{\mu_{max} \cdot Mo}{F \cdot Yt} \quad (9)$$

As mentioned earlier, the mass of microorganisms can be quantitated if a steady state active thickness is accepted:

$$M_o = (a)(d)(H)(X)dZ$$

where $a$ = specific area (area/volume)

$d$ = active thickness (length)

$H$ = cross-sectional area of filter (length$^2$)

$X$ = microorganism density on dry weight basis in active film (mass/volume)

so

$$\left(\frac{K_s+S}{S}\right)dS = \frac{\mu_{max}}{F \cdot Yt}(a)(d)(H)(X)dZ \qquad (10)$$

integrating

$$k_s \ln \frac{S_i}{S_e} + (S_i - S_e) = \frac{\mu_{max}(a)(d)(H)(X)}{F\ Yt} Z \qquad (11)$$

which can be rearranged into a design oriented form:

$$Z = \frac{F\ Yt[k_s \ln(S_i/S_e) + (S_i - S_e)]}{\mu_{max}\ (a)(d)(H)(X)} \qquad (12)$$

where $S_i$ = influent substrate concentration

$S_e$ = effluent substrate concentration

This form allows the engineer to calculate the required depth for given biological constants and effluent requirements. It was stated above that the active thickness was determined to be 70u by Kornegay and Andrews, and that this value could be considered constant. These authors further determined that X was constant at 95 mg/cm$^3$. They also found $\mu_{max}$ and $Y_t$ constant over a wide range of F and $S_i$, while $k_s$ varied somewhat. These parameters, however, are functions of the specific microbial population present, which in turn is a function of the specific substrate being applied, the pH, operating temperature, and various other factors, some of which may not be appreciated in the present state of the

art. An additional assumption must be made, then, that the microbial population that develops for any specific waste and environmental conditions will remain at least stable enough to provide consistant values of the required biological constants. It is pretty well accepted that these biological constants have to be determined for each specific waste and treatment process being designed for.

This is done by operating a pilot plant, employing the desired treatment process and the exact waste to be treated, if possible. It is important with biological towers to use the exact substratum media in the pilot plant that will be used in the treatment facility. The pilot plant is operated at different flow rates and/or influent substrate concentrations, and steady state substrate and suspended solids concentrations are collected at different depths for each case. Generally, it is preferable to keep the influent substrate concentration constant and vary the hydraulic flow rate, as this makes it easier to directly compare the different levels of performance. With this data (from four or five different loadings) the biological constants can be determined.

First, the two parameters mean cell residence time, $\Theta_c$, and specific substrate utilization rate, U, must be calculated for each representative depth and flow rate:

$$\Theta_c = X_t/X_e \tag{13}$$

where

$X_t$ = total cell mass [ = (a)(d)(H)(X)Z](mass)

$X_e$ = effluent suspended solids at the specific depth (mass/time)

and

$$U = \frac{(S_i - S_e)F}{X_t} \tag{14}$$

These two parameters are related by:

$$\frac{1}{\Theta_c} = Y_t U - k_d \tag{15}$$

so that a plot of U versus $\frac{1}{\Theta_c}$ will give a Y intercept of $-k_d$ and a slope of $Y_t$. With $k_d$ known, the true growth rate, $\mu$, can be calculated for each known $\Theta_c$:

since

$$\frac{1}{\Theta_c} = \mu_n \tag{16}$$

and

$$\mu = \mu_n + k_d \tag{17}$$

then

$$\mu = \frac{1}{\Theta_c} + k_d \tag{18}$$

By the Monod relationship:

$$\frac{1}{\mu} = \frac{k_s}{\mu_{max}} \cdot \frac{1}{S} + \frac{1}{\mu_{max}} \tag{19}$$

so a plot of $\frac{1}{S}$ versus $\frac{1}{\mu}$ will give a Y intercept of $\frac{1}{\mu_{max}}$ and a slope of $\frac{k_s}{\mu_{max}}$. In working with biological reactors, $S_e$ is generally used for S. Having determined the necessary biological constants, the model is ready for use. The engineer has only to plug in influent substrate concentration, the required final effluent concentration, select the area of the filter, and the required depth is generated. Hapke presents an excellent treatment of the effect of varying the biological constants (23).

# CHAPTER IV

# MATERIALS AND METHODS

## Biological Tower Pilot Plant

In order to test the validity of the theoretical approach discussed in the last chapter, an existing pilot plant was operated. This pilot plant was constructed of clear plexiglass, in units of one foot square cross-sectional area. Growth modules containing three cubic feet (3 ft X 1 ft X 1 ft) of Air-X-Systems plastic media were separated by spacing units of four inch depth, which provided sampling ports and allowed adequate passive aeration. The plant was divided into two separate towers because of the total height required. The influent was applied at the top of the first tower, where it was dispersed evenly over the cross-sectional area by a splash plate and allowed to trickle down through five growth modules (separated by spacing units) and collected in a wet well at the bottom. The fluid collected in the wet well was continuously pumped to the top of the second tower, identical in every respect to the first, where it again trickled down through the modules. The effluent was discarded into the sanitary sewer system at this point. Thus a total height of thirty feet (30 cubic feet of volume) was provided for biological growth, divided into two towers, each of fifteen foot depth.

The Air-X-Systems media used was originally designed as cooling tower packing. This media is made of .020 inch thick PVC plastic,

formed into single sheets or "wafers" resembling misshapen honeycomb. The wall of each cell of this "honeycomb" is 1/4 inch deep and slanted about 30 degrees out of the vertical plane. Four sides of each hexagon are 7/8 inch long, the remaining two sides (which are opposite each other) are 1/2 inch long. This configuration allows the individual sheets to be turned and overlapped in such a way as to prevent any drop of water from falling far through the media without contacting a surface. As implied previously, enough of these sheets are packed into each growth module to occupy three cubic feet of space. Packed this way, the media has a void space of 95 percent and provides a specific surface area of 42 square feet per cubic foot of colume. The Air-X-Changers plastic media compares very favorably with other media (27).

Growth was already established on the tower at the time the project began. This growth had been maintained for several weeks on synthetic waste, with sucrose as the carbon source. When the black liquor waste was first applied the tower suffered a rather severe shock. Sewage was then applied twice a day for several days to aid in development of an adapted zooglea.

A "sampling wand" was used for the collection of samples. This was a piece of PVC pipe with one end plugged and the other connected to a piece of tubing. The upper portion of the pipe between the ends was cut out to form a sort of trough. This wand was inserted into a sampling port and liquid dripped from the bottom of the growth module above into the trough to run out through the tubing into a collection flask. The wand would be moved from side to side to obtain a representative sample. To insure an adequate sample, 200 to 500 mls would be collected at each point.

When cell populations corresponding to a particular depth were required (for growth studies), the sampling wand was inserted into the sampling port and a sturdy wire loop was used to scrape off portions of the zooglea into the wand.

The substrate used in this study was heat thickened spent Kraft black liquor (digestor blow-down liquor). This was obtained from the Weyerhaeuser Kraft mill near Valliant, Oklahoma. It was transported and stored in clean 55 gallon drums. This very thick, black and foul smelling material was diluted with water and nutrients to make up a concentrated feed solution, as described in the next chapter. This concentrated feed was pumped through a 1/4 inch line which connected to an influent water line just before it entered the top of the tower. The influent water line passed through a flow meter and could be adjusted at the hydrant to any desired flow rate. The feed pump could then be adjusted to give a feed flow rate necessary to yield the desired COD concentration.

## Experimental Protocol

The pilot plant was operated at four different hydraulic loadings, 658, 850, 1035 and 1700 gallons per day per square foot. At each loading rate, several sets of data were obtained after the tower had reached steady state (2 to 3 weeks, usually). The tower was assumed to be at steady state when comparable data was obtained over several consecutive days.

The data taken consisted of COD and suspended solids concentrations at various depths of the tower. Typically, samples were taken at 0 (influent), 6, 9, 15, 21 and 30 feet. Also, at each hydraulic loading

except 850 gal/day.ft$^2$, a growth study was run on cell populations collected at two different depths in the tower.

Suspended solids were measured by a membrane filter technique. Millipore filters (0.45μ pore size) were dried at 103°C for 2 hours, cooled to room temperature in a dessicator and weighed. Then a known volume of a sample (well mixed) was filtered through one of the filters, which was then again dried at 103°, cooled and weighed, yielding the suspended solids concentration of that particular sample. The filtrate was used for the COD determination, which was done by the method described in Standard Methods (28).

Growth studies were done in an attempt to characterize (and compare) populations at different depths and hydraulic loading by their biological constants, and also to compare the biological constants obtained in growth studies to those obtained from continuous flow data. To do a growth study vessels containing different initial substrate concentrations are innoculated with equal amounts of the population under study. The growth rate in the various vessels must then be measured. The most common method is to measure the change in optical absorbance of the different solutions with time, as the absorbance will decrease in direct proportion to the increase in cells. However, when the substrate itself is highly colored, as in the present study, this method cannot be used, since the optical properties of the solution will change during the growth of the microorganisms. Because the substrate is being measured in terms of oxygen demand, this difficulty can be overcome simply by using the Warburg apparatus to measure $O_2$ uptake with time. The $O_2$ uptake should be directly proportional to the substrate consumed, which in turn should be directly proportional to the increase

in cell mass, as long as the cell yield remains constant.

For this project, five different substrate concentrations were used for each population studied. Thirty-nine mls of the desired substrate solutions would be measured into special Warburg flasks, which would contain one ml of 20 percent KOH solution in the center wells. One ml of cell suspension would then be pipetted into the substrate solutions, the flasks connected to manometers and then placed into the 25°C water bath of a GME Lardy Model RWB3 Warburg apparatus. A blank, containing forty mls of distilled water, would be treated identically to adjust the subsequent readings for changes in barametric pressure. The $O_2$ uptake was then recorded for each flask at carefully measured time intervals.

# CHAPTER V

# RESULTS

## Introduction

From the beginning of this project the pupl and paper waste demonstrated the difficulties for which it has become so notorious. The undiluted black liquor was very thick, completely opaque (brownish-black color), odorous, and difficult to measure accurately because of its thick syrupy consistency. The COD was approximately 700,000 mg/l, the $BOD_5$ was around 278,000 mg/l. The pH was over 13. When this black liquor was diluted 1:2 with distilled water, the pH was 13.4. Titration with 10 N $H_3PO_4$ dropped the pH quickly (very little if any buffering effect), but when the pH approached 11, the lignin began to precipitate out. As the pH approached 9, $H_2S$ began to evolve; and at pH 7.5 there was vigorous foaming as copious amounts of $H_2S$ bubbled out of the solution, which by now was yellowish-brown and thick with precipitated material. Because of these difficulties, it was decided that no attempt would be made to neutralize the waste before applying it to the tower.

The second problem, also not uncommon with this waste, was foaming. On the first 15 feet of the tower there was little apparent foaming, but when the waste water was pumped to the top of the second tower, foaming began in earnest. This resulted in chronic short-circuiting problems which were never entirely relieved by rearranging the influent baffle and the influent line.

The concentrated feed solution was made by diluting the black liquor 1:3 with tap water, adding ammonium nitrate and phosphoris acid to give a BOD:N:P ratio of 100:5:1. This concentrated feed solution was pumped into the influent water line at a rate to give a COD of around 1000 mg/l. After adding the nutrients and diluting with water, the influent pH was always between 9.8 and 10.

After the initial shock during which most of the established growth on the tower fell off, an acclimated population was established very slowly. It was over three weeks before reliable samples could be taken. It was found that the pH dropped rather rapidly on the tower. Typically, with an influent pH of 10.0, at a depth of 6 feet the pH would be between 9.5 and 9.7, at 15 feet it would be close to 9.0 and by 30 feet it would be between 8.4 and 8.6. These values were remarkably constant over the entire range of flow rates studies, and even variation in the influent pH (resulting from variation in influent strength) had very little effect on the pH at the various sampling depths.

After the growth was established, the most troublesome operational problem was not a function of the black liquor, but rather, resulted from variation in the pressure of the influent water line. This almost constant variation made it impossible to get a consistant hydraulic flow over the tower. The feed pump and the feed solution, though, were both reasonably consistant and so, while the influent COD might vary quite a bit, the organic loading should have been constant, and it was assumed that the effect of this hydraulic variation would be minimal. A serious error would be introduced in modeling, however, if the flow rate was not accurately known. Before sampling, the hydraulic flow would be adjusted to the desired value, and at least 30 minutes allowed for equilization.

If it was found at the end of this time that the flow had again changed, that flow rate was recorded and the samples were taken anyway.

## ΔCOD

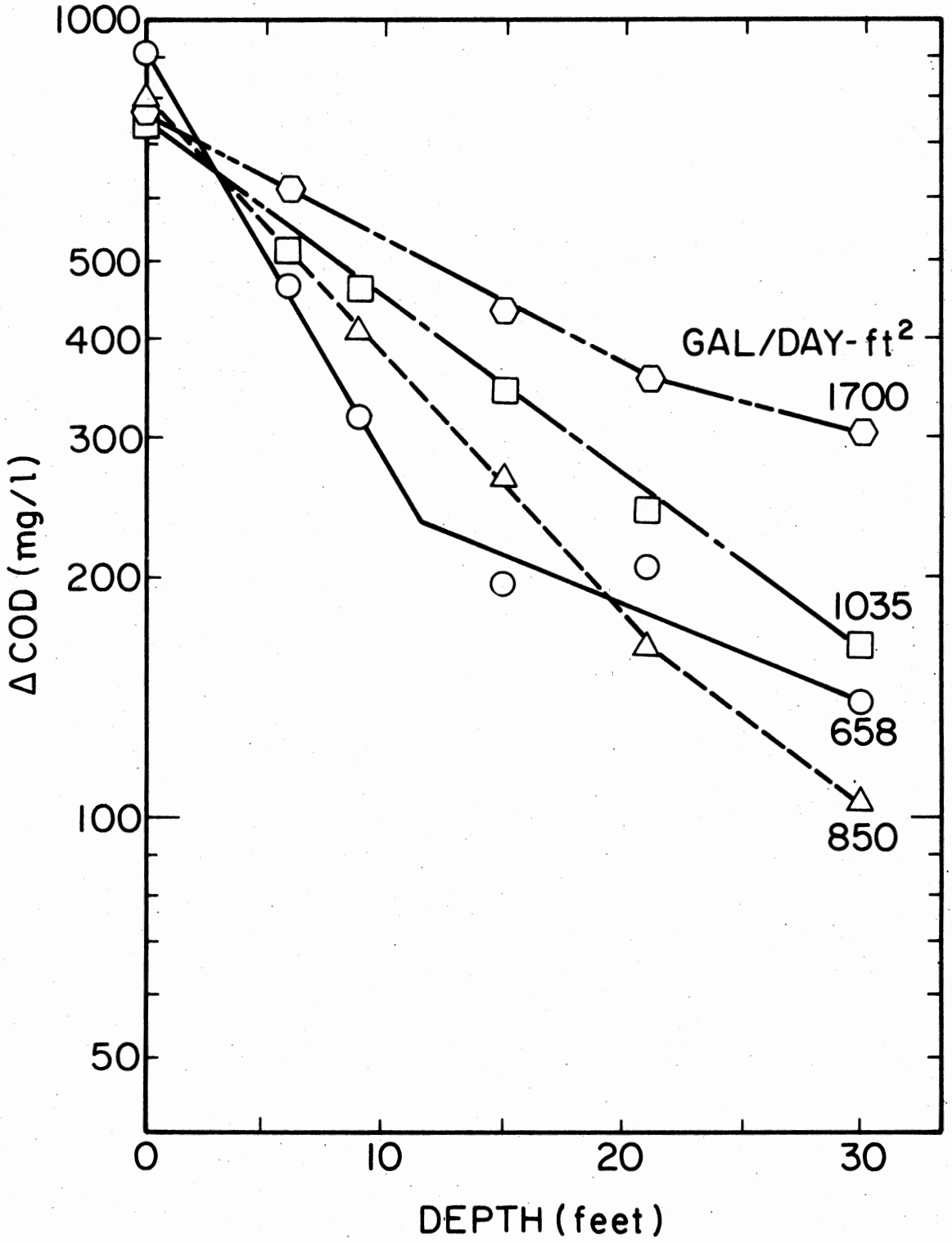
When using COD to evaluate biological systems, it is necessary to use only the "biologically degradable" portion, which is designated "ΔCOD". Numerous attempts were made to determine what proportion of the black liquor waste was non-biodegradable. When batch studies were attempted (following COD removal with time in shaker flasks), usually less than half of the soluble COD would be consumed. Often during this project the samples collected from the tower were put on the shaker and the remaining COD followed for several days, but the results were variable. The results from the tower were studied carefully to see if a minimum COD was reached. The maximum removal observed from the tower and from samples held over from the tower was around 70 percent, so the non-biodegradable portion was taken as thirty percent of the influent COD. This value was subtracted from the measured COD's to give the ΔCOD's.

## Continuous Flow Data

Several (3 to 6) sampling runs were made at each flow rate, measuring COD and suspended solids at different depths on the tower. The values were averaged to give one set of data for each flow rate. This data is presented in Figures 1 and 2.

Figure 1 shows the COD versus depth on the tower at four different hydraulic loadings, plotted on semi-log paper to illustrate that the COD

Figure 1. ΔCOD vs. Depth at Four Hydraulic Loadings on Biological Tower Pilot Plant

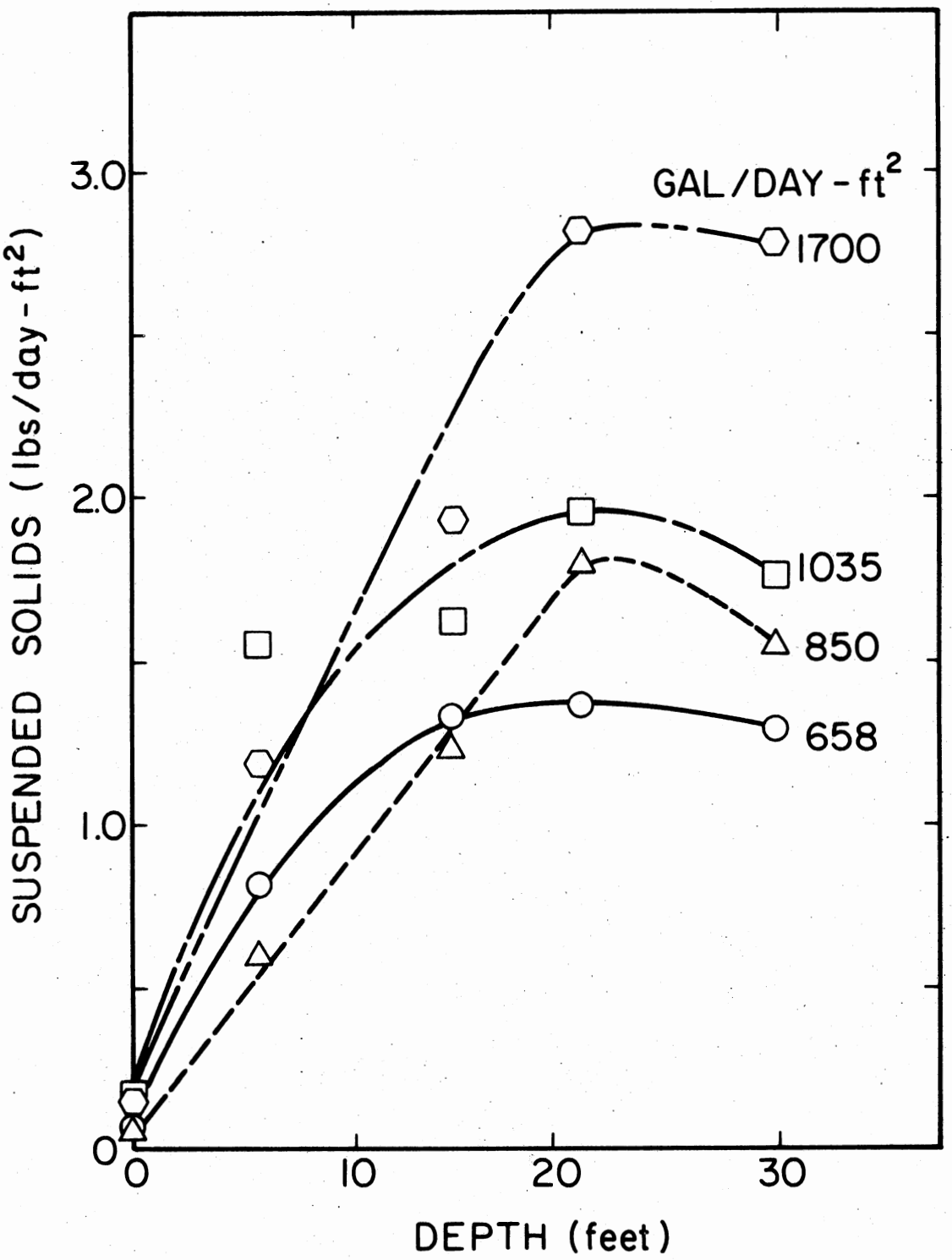

1000
500
400
300
200
100
50
ΔCOD (mg/l)
0
10
20
30
DEPTH (feet)
GAL/DAY-ft²
1700
1035
658
850

removal is clearly first order, at least initially. Note that the initial rate of removal consistently decreases as the flow rate (i.e., organic loading) increases. A tendency toward biphasic removal is indicated by the break in all but one of the curves, occurring between ten and twenty-one feet. It is quite possible that these curves represent two first-order removal sequences over the thirty foot depth of the tower, in which case difficulties in modeling have to be expected, as no model yet developed can account for this type of removal pattern.

In Figure 2, the suspended solids versus depth, a most interesting result is apparent. The first thing to note is that the suspended solids produced per day by the tower increases with increasing flow rate, as expected. The interesting result is the leveling off and actual decrease in suspended solids toward the deepest part of the tower, and this in spite of the fact that biodegradable COD is still present in significant amounts. Another interesting point is that this leveling off occurs at roughly the same depth as the break in the ΔCOD curve; that is at 21 feet, except for the lowest flow rate, where the suspended solids level off at around 15 feet and the ΔCOD curve breaks somewhere between 10 and 15 feet.

There was some difficulty with the suspended solids curves of the two higher flow rates, at around 6 feet. A smooth curve was drawn, but perhaps an 'S' shaped curve would be more appropriate, even though the author can think of no biological justification for this. One possible explanation would be that the 6 foot suspended solids contained precipitated lignin which was adsorbed onto the filter zooglea or redissolved before it reached the 15 foot sampling station. If this was the case, or if there was some consistent error in solids collection at this

Figure 2. Suspended Solids vs. Depth at Four Hydraulic Loadings on Biological Tower Pilot Plant


SUSPENDED SOLIDS (lbs/day-ft²)
3.0
2.0
1.0
0
0
10
20
30
DEPTH (feet)
GAL/DAY - ft²
1700
1035
850
658

station, then drawing the curve to minimize this influence is justifiable. More will be said about this problem in Chapter VI.

## Growth Studies

For each flow rate except the 850 gal/day·ft$^2$, a growth study was run on populations collected at two depths, as described in Chapter IV. The data from these experiments can be found in the Appendix. Generally, on a semi-log plot, a straight line curve was obtained starting somewhere between four and eight hours. A transition period would occur somewhere between twelve and twenty hours, and then another straight line portion was observed, demonstrating a rather complex removal sequence. The first straight line portion was taken as the representative uptake rate for that substrate concentration. An example of typical $O_2$ uptake curves is shown in Figure 3. The results of these studies are shown in Figures 4 through 6. Note the toxic effect of the substrate at the higher concentrations. In order to obtain a value for $\mu_{max}$ and $k_s$, the higher concentrations were ignored and the Linnweaver-Burke type plot was used, as was done by S.N.V. Ready in his study of phenol removal by biological populations (29). An example of this plot is shown in Figure 7. The results are presented in Table I. A disturbing aspect to this method is the fact that the calculated $\mu_{max}$ is significantly higher than the highest observed $\mu$. Note that there appears to be a significant variation in the biological constants with respect to depth. This will be discussed later. For the present work, the four values from the two higher flow rates were averaged to give a $\mu_{max}$ of 13.7 day$^{-1}$ and a $k_s$ of 510 mg/l, to be used in testing the model. The rationale for this was that the model, in its present form, must

Figure 3. Example: $O_2$ Uptake vs. Time from Warburg Studies

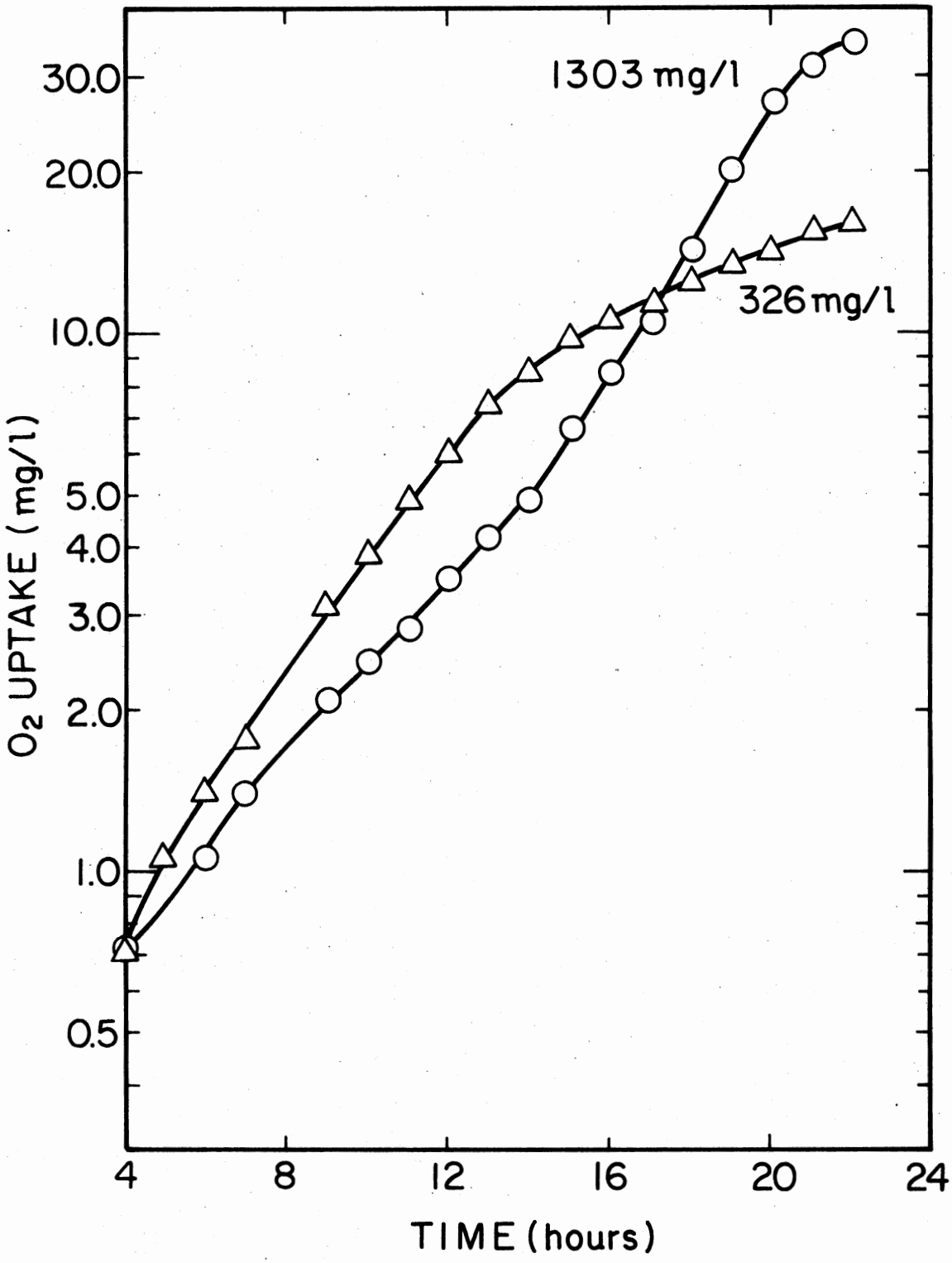

1303 mg/l
326 mg/l
30.0
20.0
10.0
5.0
4.0
3.0
2.0
1.0
0.5
O2 UPTAKE (mg/l)
4
8
12
16
20
24
TIME (hours)

Figure 4. Growth Rate vs. Substrate Concentration for Two Populations at 1700 gal/day.ft$^2$

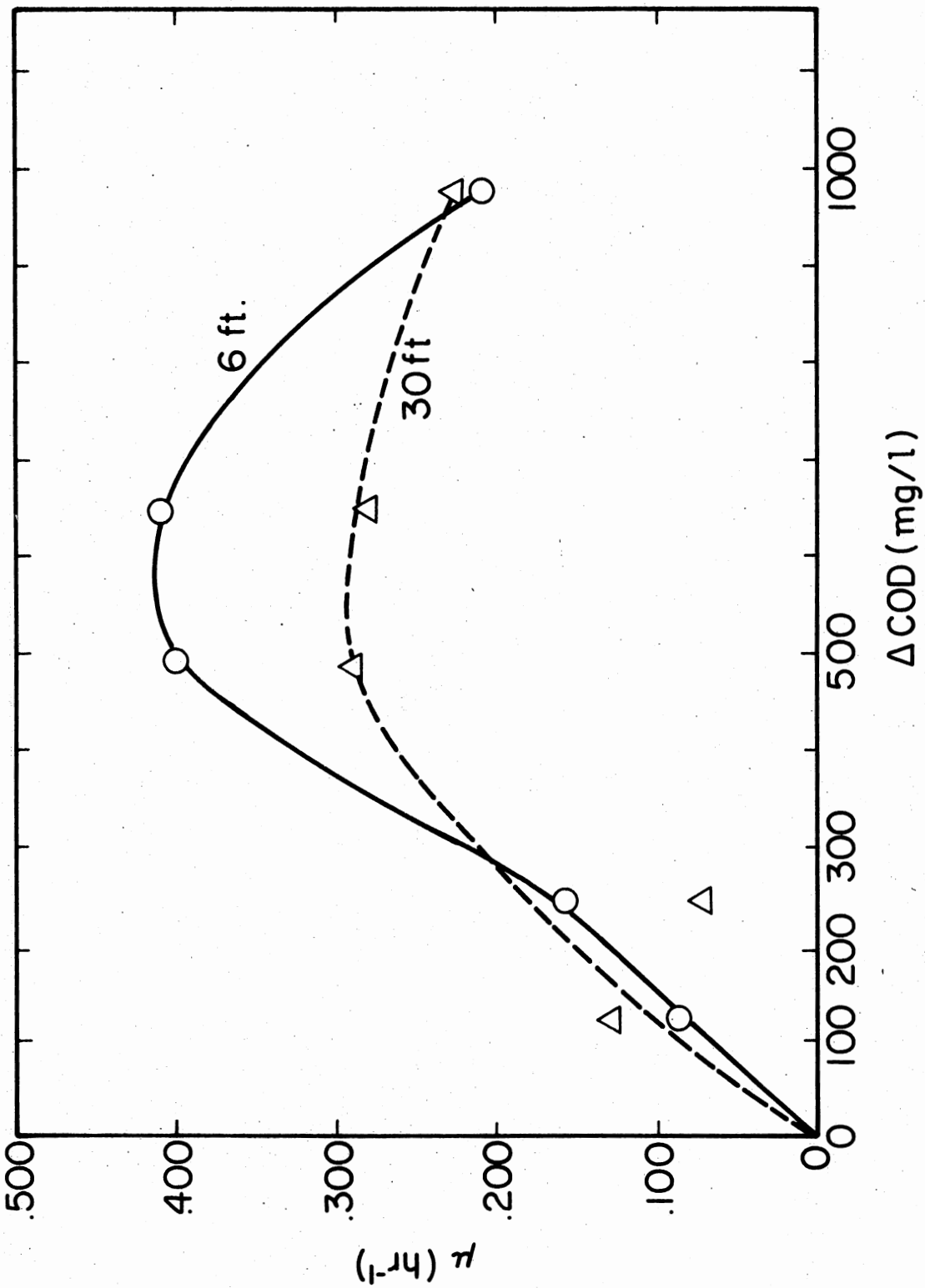

6 ft.
30 ft
μ (hr⁻¹)
.500
.400
.300
.200
.100
0
0
100
200
300
500
1000
ΔCOD (mg/l)

Figure 5. Growth Rate vs. Substrate Concentration for Two Populations at 1035 gal/day·ft$^2$

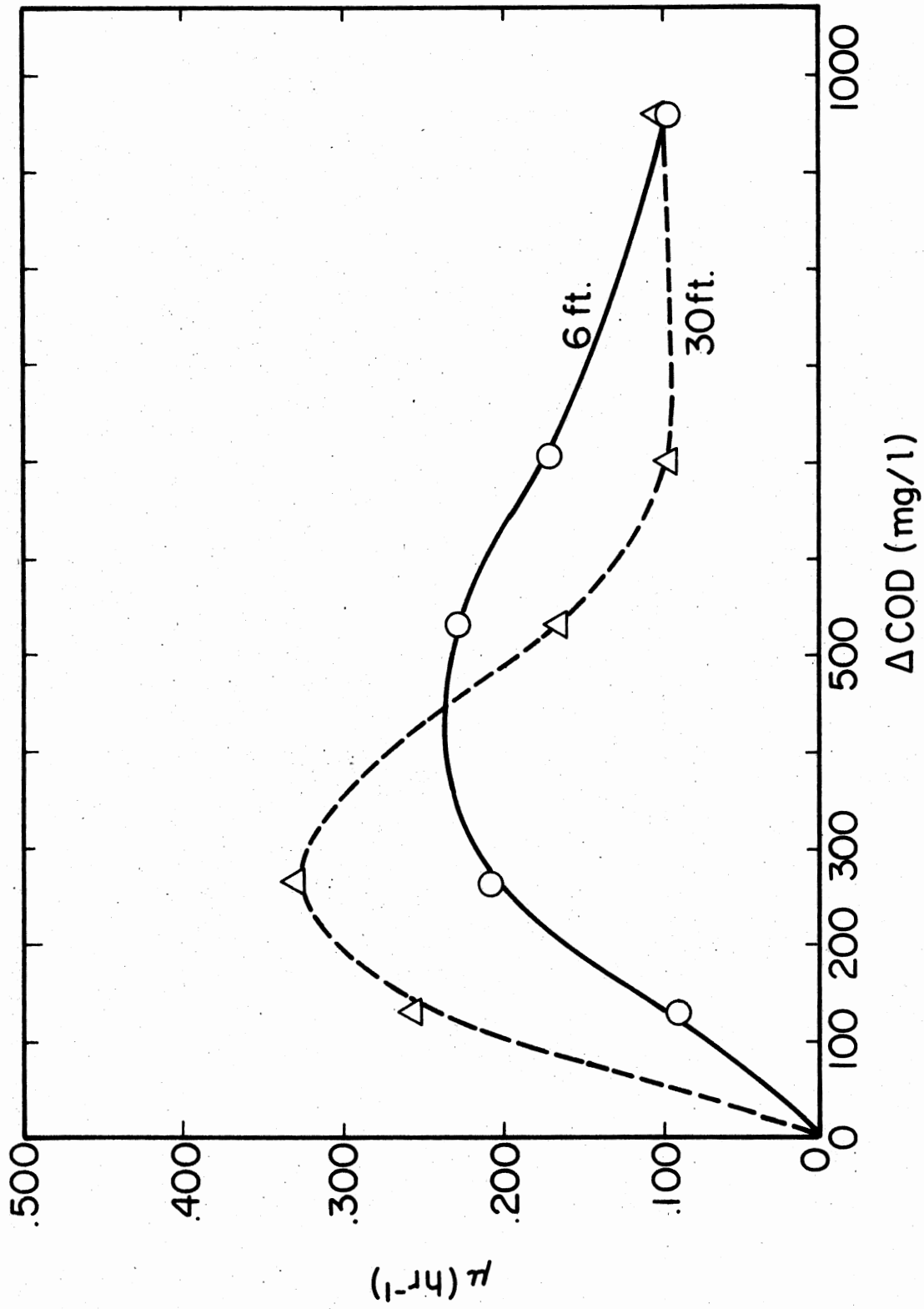

μ (hr⁻¹)
.500
.400
.300
.200
.100
0
0
100
200
300
500
1000
ΔCOD (mg/l)
6 ft.
30ft.

Figure 6. Growth Rate vs. Substrate Concentration for Two Populations at 658 gal/day·ft$^2$

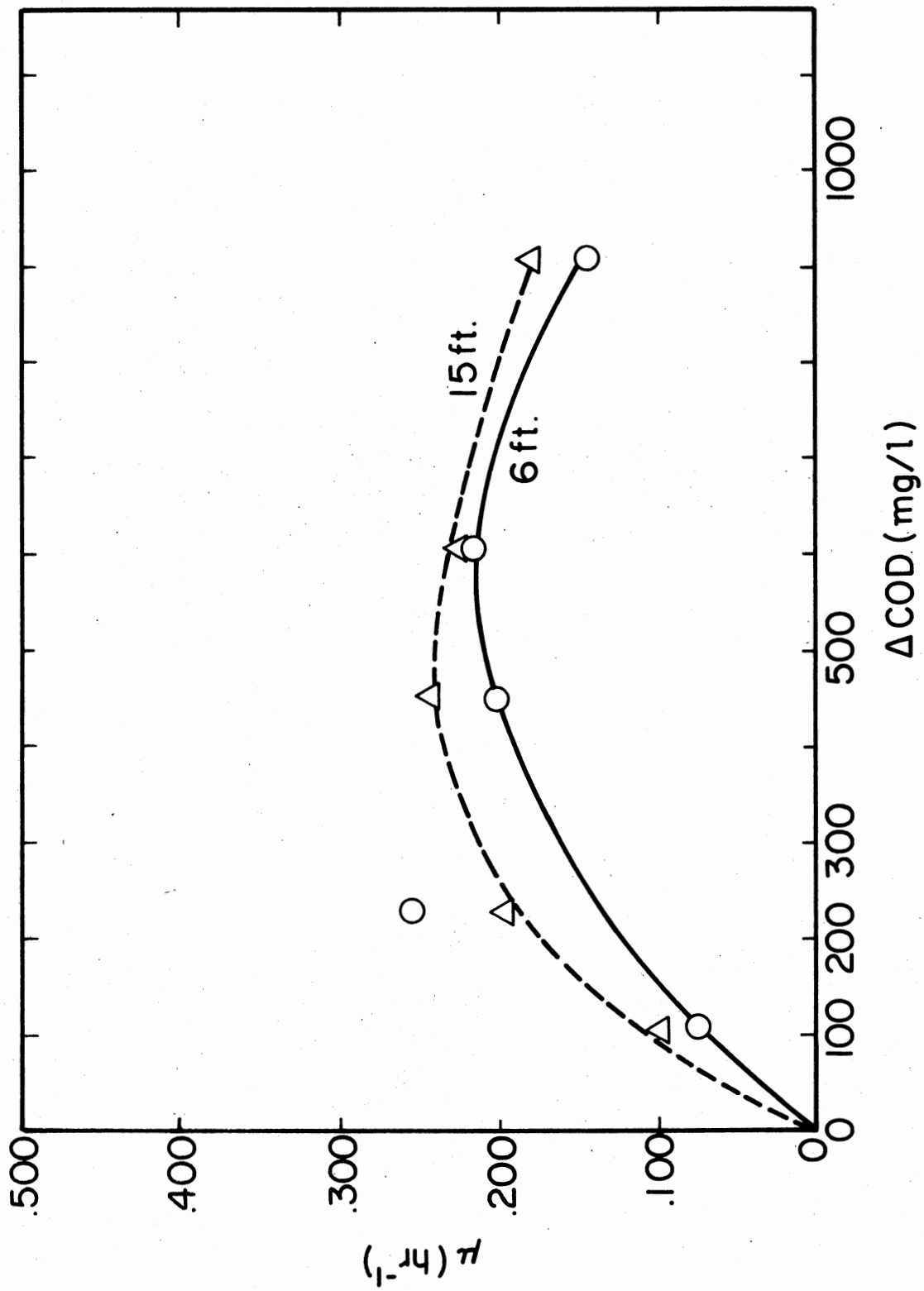

μ (hr⁻¹)
.500
.400
.300
.200
.100
0
0
100
200
300
500
1000
ΔCOD (mg/l)
15 ft.
6 ft.

Figure 7. Example: Linnweaver-Burke Plot from Warburg Study

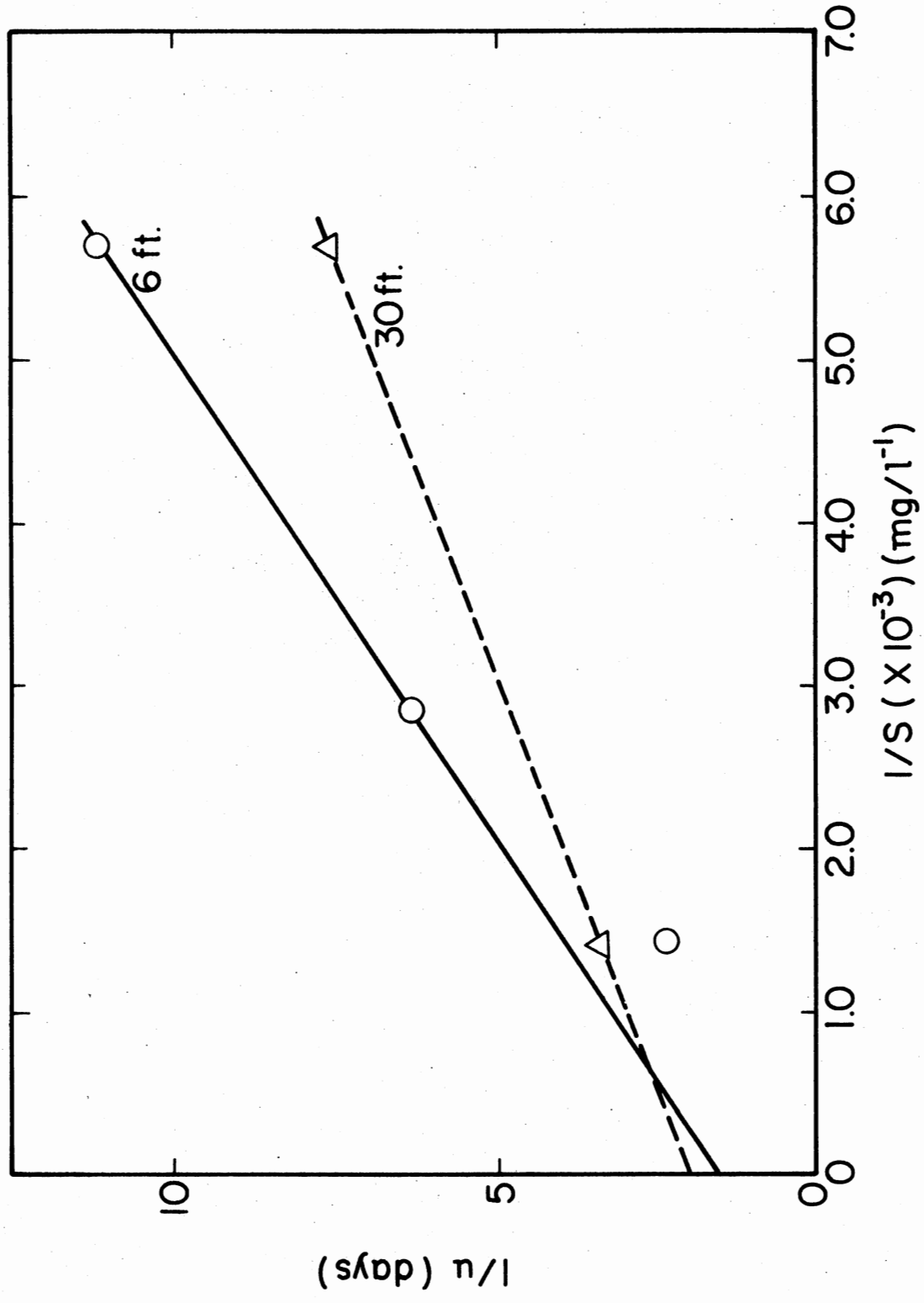

6 ft.
30 ft.
0
5
10
1/u (days)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
1/S (X 10⁻³) (mg/l⁻¹)

TABLE I

BIOLOGICAL CONSTANTS OBTAINED
FROM WARBURG STUDIES

| $F(gal/day \cdot ft^2)$ | Depth from which population was collected (feet) | $\mu_{max}$ $(day^{-1})$ | $k_s(mg/l)^{\Delta COD}$ |
|---|---|---|---|
| 1700 | 6 | 16.1 | 792 |
| | 30 | 11.5 | 325 |
| 1035 | 6 | 16.8 | 824 |
| | 30 | 10.3 | 97 |
| 658 | 6 | 10.1 | 496 |
| | 15 | 9.81 | 332 |

represent the "average" biological population, it cannot describe removal resulting from a varying population. The values from the two highest flow rates were used because they agreed rather closely with each other, while the values from the lowest flow rate (which did not include a population from the lower part of the tower) did not correspond well with the previously determined values. In fact, the values from both 6 and 15 feet at the lowest flow rate might correspond to the 30 foot values of the higher flow rates.

## Biological Constants from Continuous Flow Data

The required biological constants can also be obtained directly from the tower data, as described in Chapter III. The necessary calculated parameters are tabulated in Table II. Figure 8 shows the plot of U versus $\frac{1}{\Theta_c}$, which by linear regression yields the values: $Y_t = .53$ and $k_d = .45\ day^{-1}$. With these values, the growth rate, $\mu$, can be determined ($\mu = \frac{1}{\Theta_c} + k_d$), as has been done in the last column of Table II. Now the Linnweaver-Burke plot can be used, Figure 9, with linear regression to obtain $\mu_{max} = 4.63\ day^{-1}$ and $k_s = 304$ mg/l.

As was mentioned earlier, there was some problem with foaming and subsequent short-circuiting on the second tower. It was advisable, therefore, to examine the first tower separately, in case these problems had some effect on the kinetics of the COD removal. This was done by simply repeating the above steps using only the data collected between 0 and 15 feet (the end of the first tower). This gave $\mu_{max} = 5.26\ day^{-1}$, $k_s = 553$ mg/l, $Y_t = .42$, and an inappropriate $k_d$ of $-0.15\ day^{-1}$, which was suppressed. The $k_d$ was taken to be zero, which is really not too unreasonable considering the $\Theta_c$ values.

TABLE II

BIOLOGICAL PARAMETERS FROM CONTINUOUS FLOW DATA

| F | D | $S_e$ | $X_e$ lbs/day | $X_T$ | $\Theta_c$ (days) $x_c/x_e$ | $\frac{U}{(S_c-S_e)F}{Xt}$ | $Y_{ob}$ | $\frac{\mu}{\Theta_c+k_d}$ |
|---|---|---|---|---|---|---|---|---|
| 658 | 0' | 909 | 0.99 | ---- | --- | -- | -- | -- |
| | 6' | 407 | 0.81 | .343 | .42 | 7.07 | .33 | 2.83 |
| | 9' | 320 | --- | -- | -- | --- | -- | -- |
| | 15' | 197 | 1.33 | .856 | .64 | 4.56 | .34 | 2.01 |
| | 21' | 203 | 1.36 | 1.20 | .88 | 3.23 | .35 | 1.59 |
| | 30' | 140 | 1.29 | 1.71 | 1.32 | 2.47 | .31 | 1.21 |
| 850 | 0' | 798 | 0.78 | -- | -- | --- | -- | -- |
| | 6' | 510 | 0.60 | .343 | .57 | 5.95 | .29 | 2.20 |
| | 9' | 405 | --- | -- | -- | -- | -- | -- |
| | 15' | 265 | 1.23 | .856 | .70 | 4.41 | .32 | 1.88 |
| | 21' | 163 | 1.79 | 1.20 | .67 | 3.75 | .40 | 1.94 |
| | 30' | 104 | 1.54 | 1.71 | 1.11 | 2.88 | .31 | 1.35 |
| 1035 | 0' | 741 | 0.17 | -- | -- | -- | -- | -- |
| | 6' | 516 | 1.55 | .343 | .22 | 5.66 | .80 | 5.00 |
| | 9 | 460 | -- | -- | -- | -- | -- | -- |
| | 15' | 344 | 1.61 | .856 | .53 | 4.00 | .47 | 2.34 |
| | 21' | 241 | 1.95 | 1.20 | .62 | 3.60 | .45 | 2.06 |
| | 30' | 164 | 1.76 | 1.71 | .97 | 2.91 | .35 | 1.48 |
| 1700 | 0' | 756 | 0.14 | -- | -- | -- | -- | -- |
| | 6' | 617 | 1.19 | .343 | .29 | 5.74 | .60 | 3.90 |
| | 9' | 547 | -- | -- | -- | -- | -- | -- |
| | 15' | 432 | 1.94 | .856 | .44 | 5.37 | .42 | 2.72 |
| | 21' | 358 | 2.82 | 1.20 | .42 | 4.70 | .50 | 2.83 |
| | 30' | 304 | 2.78 | 1.71 | .62 | 3.75 | .43 | 2.06 |

Figure 8. Reciprocal Mean Cell Residence Time vs. Substrate Utilization Rate from Continuous Flow Data

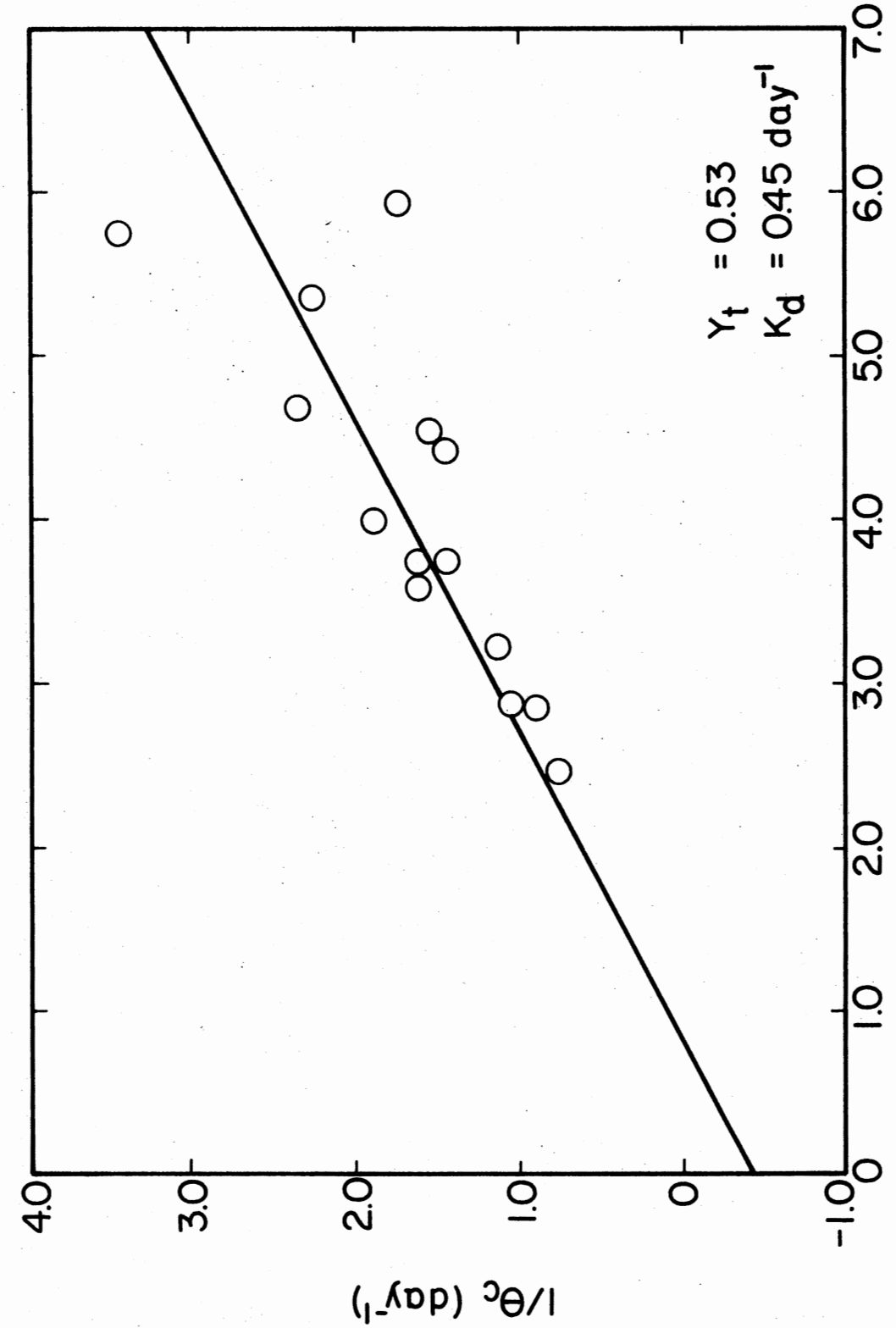
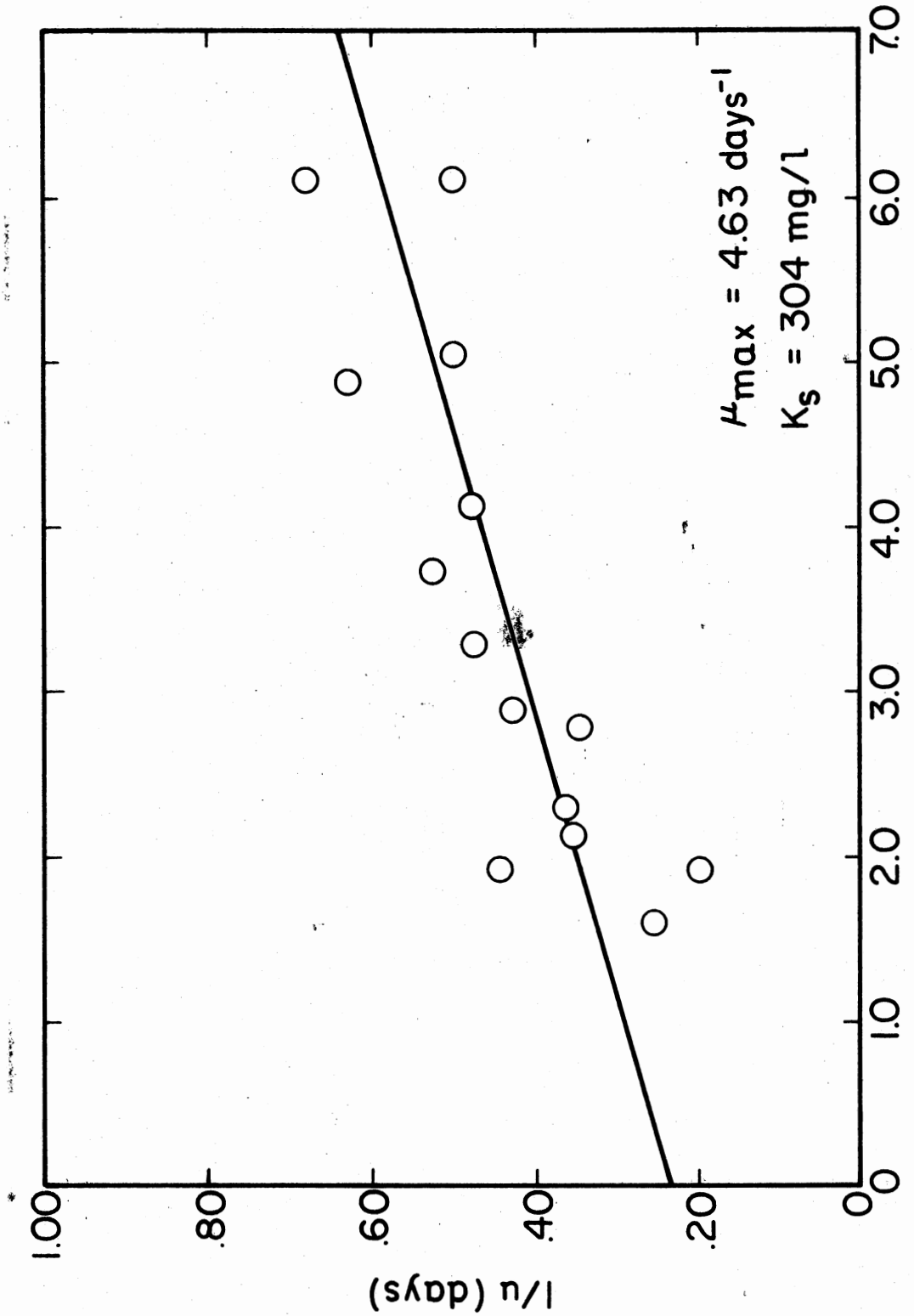

$Y_t$ = 0.53
$K_d$ = 0.45 day$^{-1}$
1/$\Theta_c$ (day$^{-1}$)
U (day$^{-1}$)
4.0
3.0
2.0
1.0
0
-1.0
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0

Figure 9. Linnweaver-Burke Plot from Continuous Flow Data


1/u (days)
1.00
.80
.60
.40
.20
0
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
1/S (mg/l$^{-1}$) (X 10$^{-3}$)
$\mu_{max}$ = 4.63 days$^{-1}$
$K_s$ = 304 mg/l

There was also the phenomenon of biphasic COD removal to examine, clearly indicated in Figure 1. To accomplish this, the data was split into first phase and second phase removal sequences. The end of the first phase was taken to be 21 feet for all flow rates except 658 gal/day·ft$^2$, for which 15 feet was considered the end of first phase removal. The ΔCOD value at the end of the first phase was used as the initial substrate concentration for the second phase. Otherwise, the biological constants were again determined exactly as above, giving, for the first phase: $\mu_{max}$ = 4.17, $k_s$ = 345, $Y_t$ = .45 and $k_d$ = 0 (the actual Y intercept was .008). For the second phase: $\mu_{max}$ = 3.89, $k_s$ = 204, $Y_t$ = .57 and $k_d$ = .55.

## Testing the Model

These then, are the values that were used in checking the performance of the model against the actual data. For each set of biological constants a ΔCOD removal curve was generated with the model to correspond with each flow rate. Some of these curves are presented in Figures 10 through 13, with explanations as to the origin of each.

The curves generated with constants obtained by the Warburg studies are obviously of no value in predicting ΔCOD removal over the tower. It should be added that the $Y_t$ and $k_d$ used in this case were those derived using all the tower data (i.e., $Y_t$ = .53, $k_d$ = .45), as the Warburg studies gave only $\mu_{max}$ and $k_s$. $Y_t$ can be determined from special batch studies, but $k_d$ can be obtained only from continuous flow data, as the growth rates obtained during batch studies are always high enough to mask any maintenance requirements. It is clear, however, that the $\mu_{max}$'s obtained in the growth studies are much too high to use in modeling, as

Figure 10. Theoretical ΔCOD Removal Compared to Actual Data at 658 gal/day·ft$^2$

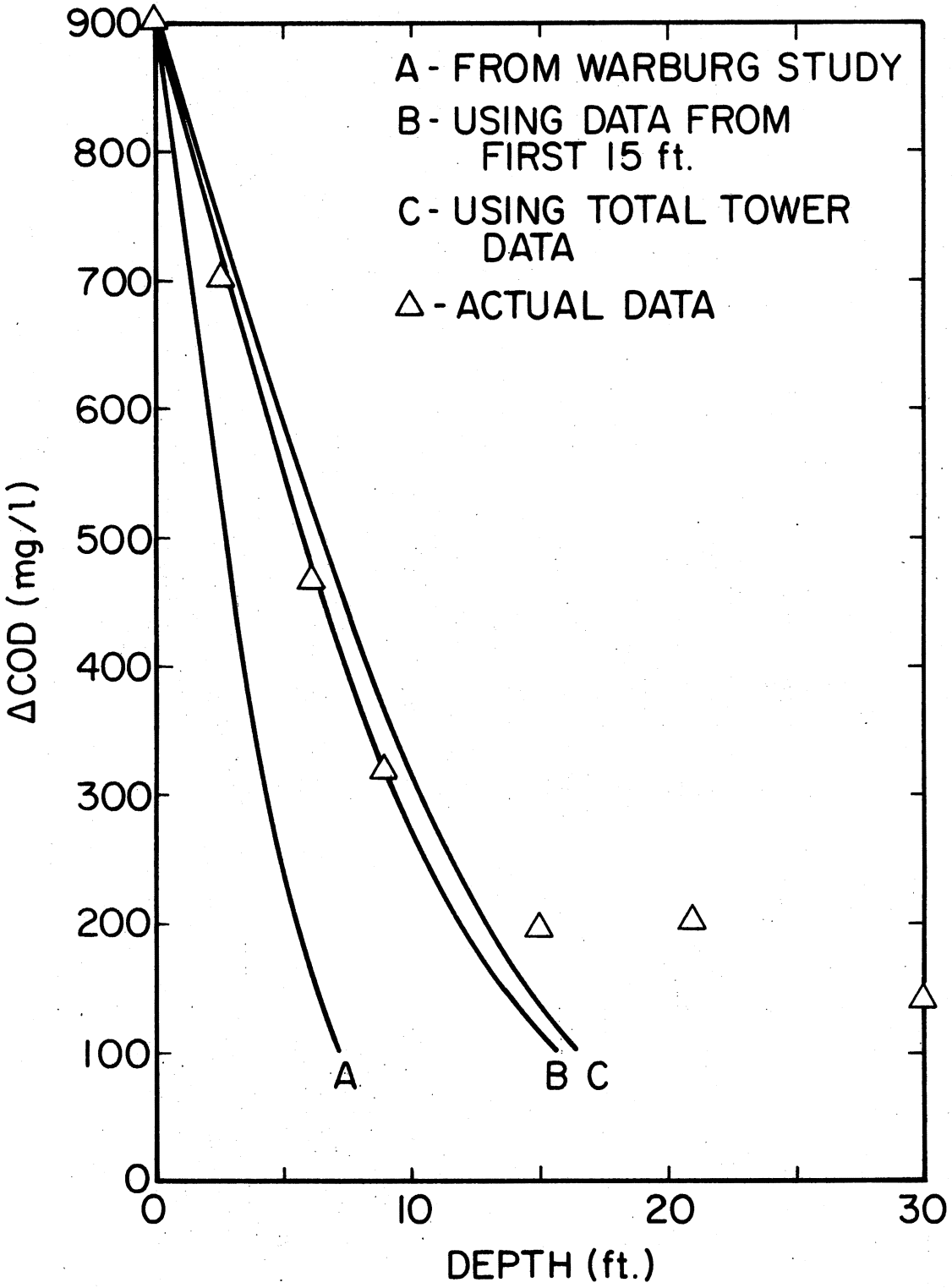

A - FROM WARBURG STUDY
B - USING DATA FROM FIRST 15 ft.
C - USING TOTAL TOWER DATA
△ - ACTUAL DATA
ΔCOD (mg/l)
900
800
700
600
500
400
300
200
100
0
0
10
20
30
DEPTH (ft.)
A
B C

Figure 11. Theoretical ΔCOD Removal Compared to Actual Data at 850 gal/day·ft$^2$

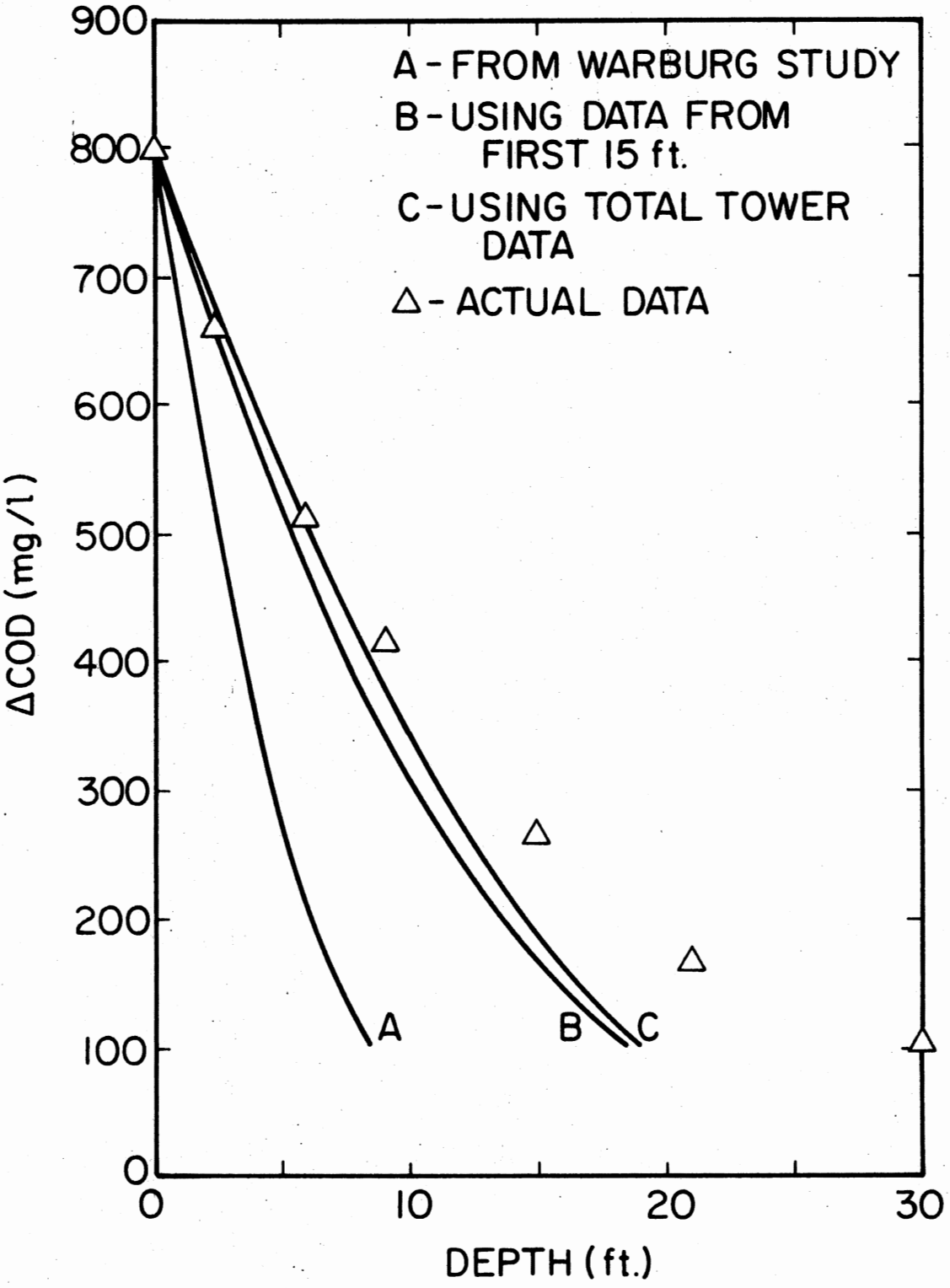

A - FROM WARBURG STUDY
B - USING DATA FROM FIRST 15 ft.
C - USING TOTAL TOWER DATA
△ - ACTUAL DATA
ΔCOD (mg/l)
DEPTH (ft.)
900
800
700
600
500
400
300
200
100
0
0
10
20
30
A
B
C

Figure 12. Theoretical ΔCOD Removal Compared to Actual Data at 1035 gal/day·ft$^2$

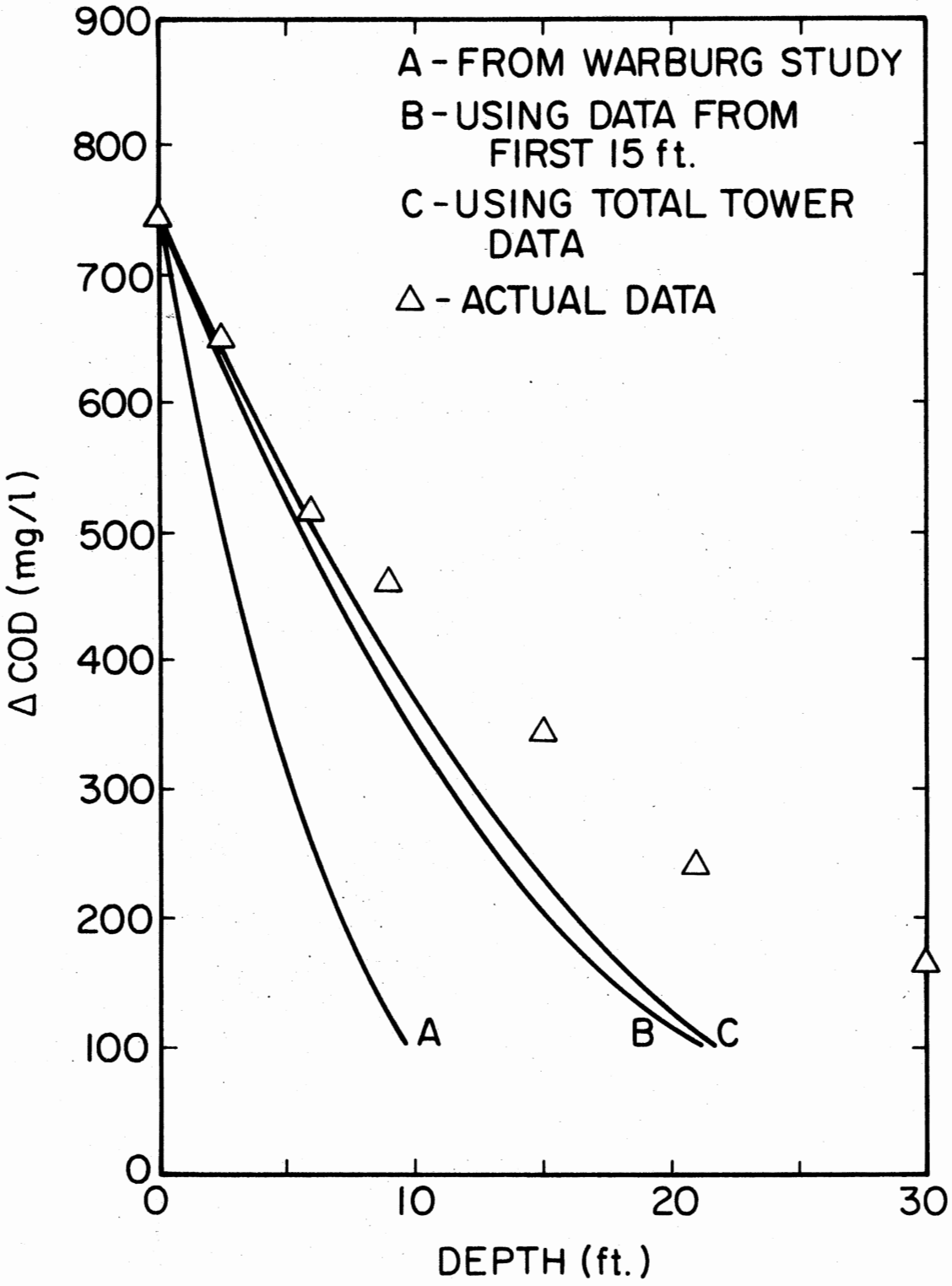
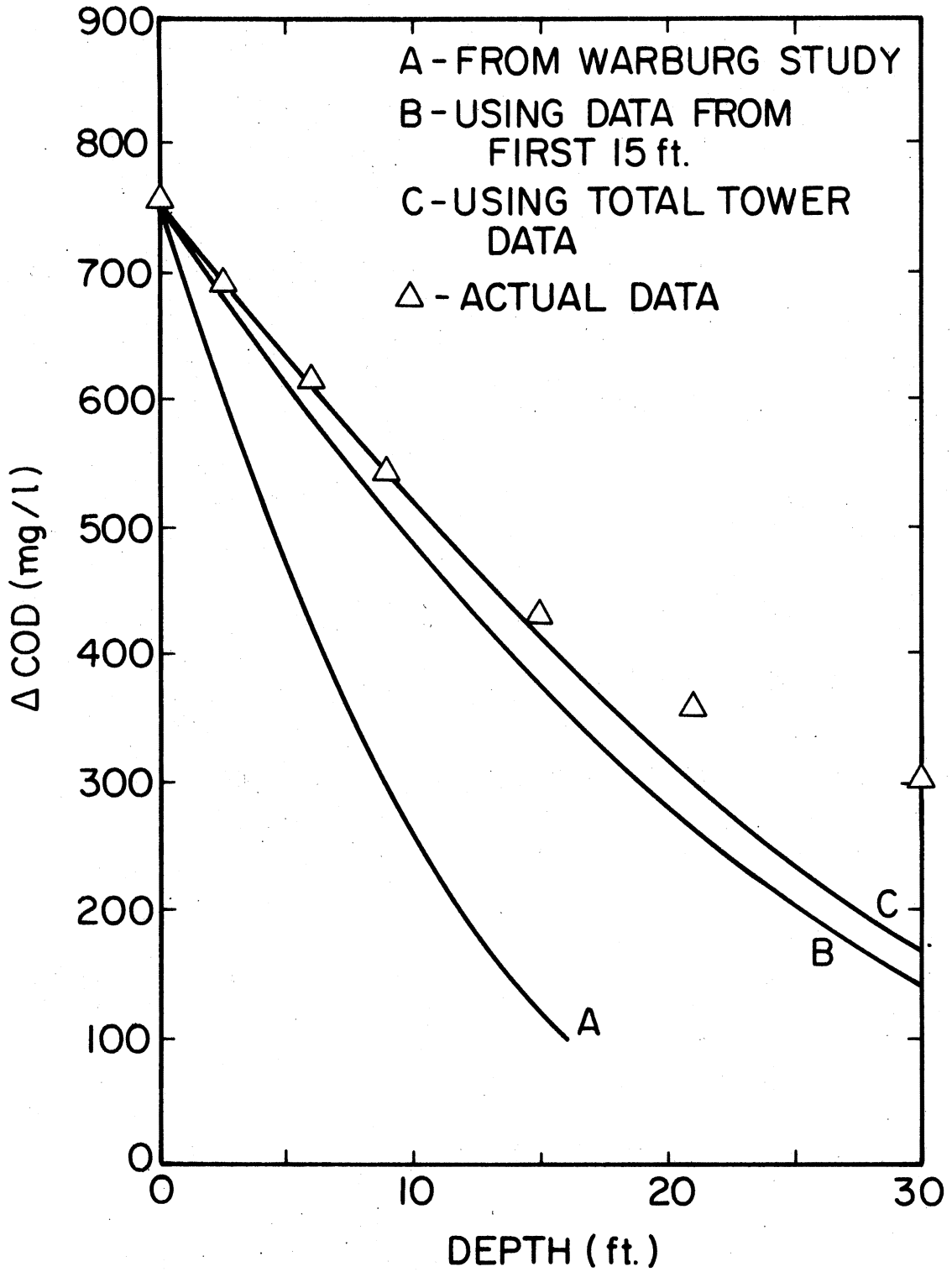

A - FROM WARBURG STUDY
B - USING DATA FROM FIRST 15 ft.
C - USING TOTAL TOWER DATA
△ - ACTUAL DATA
Δ COD (mg/l)
DEPTH (ft.)
900
800
700
600
500
400
300
200
100
0
0
10
20
30
A
B
C

Figure 13. Theoretical ΔCOD Removal Compared to Actual Data at 1700 gal/day·ft$^2$


A - FROM WARBURG STUDY
B - USING DATA FROM FIRST 15 ft.
C - USING TOTAL TOWER DATA
△ - ACTUAL DATA
900
800
700
600
500
400
300
200
100
0
Δ COD (mg/l)
0
10
20
30
DEPTH (ft.)
A
B
C

no reasonable value of $Y_t$ or $k_d$ will improve a removal curve much with a $\mu_{max}$ that high.

All of the curves obtained directly from the continuous flow data fell rather close together. The curve obtained using the "first phase removal" data fell between the curves generated from constants obtained using the total tower data and the data from the first 15 feet only, so it is not included in the figures.

These curves are close enough together that they cannot really be distinguished with the available data. It is apparent that none of these curves fully describes the actual ΔCOD removal. If only the first six to ten feet of the tower is considered, then the theoretical curves might be said to approximate the actual removal, but after that point they diverge radically from the experimental data.

Considering only the first ten feet, the constants obtained using the total tower data give the best fitting curve for the three higher flow rates, while the lowest flow rate is very closely approximated with constants obtained using only the data from the first fiteen feet.

# CHAPTER VI

# DISCUSSION

The failure of the curve obtained using constants from the growth studies to describe ΔCOD removal over the tower is not really surprising. Values for $\mu_{max}$ obtained from growth studies are almost always much higher than those obtained using continuous flow data (30). A possible explanation for this is that conditions provided in growth flasks may select for the fastest growing organisms, which then contribute disproportionately to the measured parameters (substrate removal, increasing cell numbers or mass, $O_2$ uptake, etc.), while continuous flow conditions may provide completely different selective pressures, such as ability to adhere to surfaces (or to each other), to avoid predators, to compete with the established population for food, to endure temperature, pH, substrate and/or toxic substances concentration variations, etc. At any rate, the $\mu_{max}$'s from the Warburg studies do not match at all the $\mu_{max}$'s from the continuous flow data, and could not be expected to from previous experience, and thus cannot describe growth and substrate removal in a continuous flow system.

The failure of the continuous flow data is more disturbing, especially as the divergence of the theoretical curves from the experimental data cannot be attributed entirely to biphasic removal, as the point of divergence occurs before the end of the first phase removal sequence in the three higher flow rates. It was not expected that the

model could mimic biphasic removal, but it was hoped that the first phase could be described.

As it turns out, the real significance of this study may be the depth of the tower studied. Previous investigators in this department, who were successful in using this model to describe their experimental ΔCOD removal, used much shallower towers. Hapke used data taken from towers of only four feet. As mentioned in the last chapter, if this study had been confined to ten feet, a fair degree of success would have been reported. It is unfortunate, in this case, that the study should be complicated with a complex substrate. High priority, in any following work, must be given to verifying or refuting the results of this thesis using a simple substrate. If these results are duplicated with a simple waste, then the model will have to be modified somehow. If success is obtained in modeling the simple substrate removal, then the difficulties encountered in the present study can be attributed to the nature of the substrate used. There are, indeed, properties of the Kraft black liquor that could create or aggravate problems in modeling.

Since this model uses only one value each for $\mu_{max}$, $k_s$, $Y_t$ and $k_d$, it obviously does not describe a system in which the biological population varies greatly with depth or flow rate. One of the assumptions in model development was that any population developing on any specific waste would yield consistant biological constants with respect to depth and flow rate. The biological constants used with the model must be descriptive of the 'average' population. The removal curve derived using this average population can be expected to fit the data closely if all the actual populations on the tower have biological constants close to those of the average population. The greater the variations in the

populations, the less likely it becomes that the model will describe the actual situation. So any factor tending to create variation in the biota of a system will adversely affect the ability of the model to describe that system.

It must be expected, in a tower of this depth especially, that the variations in environmental conditions between the top and bottom will result in a variation in the biological population over the same distance. With a simple substrate, these conditions, and hence the biological variation, might be minimized. In this case, the major variation might be one of substrate concentration, with metabolic by-products or end products also contributing somewhat to environmental differences. Since we are dealing with aerobic conditions, these products (with a simple waste) will most likely be non-toxic and biodegradable, often by the same organisms which produced them. The biota toward the deeper parts of the tower are also constantly reinforced with organisms from the shallower portions, which may be able to adapt to the slightly altered conditions in the deeper portions. All of this might be expected to minimize biological variations.

As the organic loadings increase, then, only the concentration of substrate (and products) increases, and the biological population can remain relatively constant (but with an increased growth rate). With Kraft black liquor (and perhaps many other complex wastes) there are complicating factors. The two most obvious ones are pH and toxicity.

While the pH at different points in the tower remained surprisingly stable with varying flow rates, it varied greatly over the depth of the tower. Organisms, and especially bacteria, which develop at extreme pH values, are notoriously poor at adapting to or competing with other

organisms at more neutral values of pH. The biota at various points in this tower, then, would not be receiving the constant viable reinforcement expected under more ideal conditions. Instead, points at different depths on this tower might be expected to develop distinct populations with very variable biological characteristics. This is supported by the growth studies run of populations at different depths on this tower. An attempt at averaging these characteristics for modeling might well result in the complete failure of that model, even if it is confined to a single removal phase.

The problem of toxicity is even more difficult to handle. The Warburg studies clearly demonstrated that this waste is toxic. The toxicity of a waste may either decrease or increase (or remain constant) with depth over a tower, depending on whether the toxic substance(s) is consumed or stripped, or added to in the form of toxic metabolic by-products or end products. Either of these situations will result in enforced biological variation over the depth of the tower. Also, as the organic loading increases, the amount of toxic material is correspondingly increased, dictating another probable variation in biological population with flow rate.

It might be possible to overcome these problems by determining the biological constants at a number of points on the tower and using a series of curves rather than just one curve. This would probably be inappropriate from an engineering standpoint, as it would be very difficult and expensive to obtain adequate data for this. Attempts to reach such a solution in the present thesis failed; it was impossible even to obtain reasonable biological constants when using data from two points located close together on the tower. This was probably due to

inadequacies in the accuracy of the data. As the differences in suspended solids and COD concentration with depth decrease, any error will become increasingly disruptive. A possible problem in the suspended solids data was briefly discussed in Chapter V.

The measurement of suspended solids is critical for the determination of the continuous flow biological constants. The gravametric measurement employed is simple but susceptible to several errors, one of which was mentioned in Chapter V. That is, there is no way to distinquish between biological suspended solids (the desired parameter) and suspended solids that are something other than microorganisms. There is no simple solution for this problem, unless the extraneous suspended solids happen to be non-volatile, which is not the case with lignin, or any other substance likely to cause variations in suspended solids over the depth of a tower.

A second problem, mentioned in Chapter III, is the possibility of non-uniform suspended solids release from the filter zooglea. Although in this study there appeared to be no significant variation in the suspended solids release over a time period of several days, the possibility of sporadic releases of large masses of cells cannot be entirely discounted. Clarifiers have been employed by some previous workers in an attempt to collect all the solids produced per day, but only at the end of the tower. This would have been useful in the present case only as a check on the accuracy of the sampling. The constant use of clarifiers at each sampling station seems unjustifiable, not only because of the technical problems, but because of the danger of modifying the biological structure of the tower. The possibility of large periodic releases of solids has caused some workers to doubt the validity of any model that does not consider this (31).

This second problem leads naturally to a discussion of a third problem, which affects not only suspended solids measurement, but the COD measurement as well. That is the problem of adequate sampling from the tower. The method of sampling presently used was described in Chapter IV. In situations of completely uniform flow and suspended solids release, this method is completely satisfactory. Uniform flow in this instance means with respect to cross-sectional area, that is, the absence of any short circuiting. In most instances, however, it would be very desirable to be able to collect the entire flow at any specific depth in the tower. This could be accomplished by providing a sampling slot, rather than a round port, in which a collecting tray (connected by a tube to a collection flask) could be inserted to intercept the entire flow. This would relieve any sampling problems caused by non-uniform flow and would also allow the use of a clarifier, if desired.

## Note on BOD

Although $BOD_5$ is the official parameter in the waste water field, $\Delta COD$, as used in this study, is the accepted design parameter in this department and for most research applications everywhere. It would have been absolutely necessary to use $\Delta COD$ in this case in any event, because of the toxicity of the waste. Toxicity creates the phenomenon of "sliding BOD", in which the measured BOD increases with increasing dilution. Although $BOD_5$'s were measured in this study, the results are not presented and were not used because of their questionable reliability.

# CHAPTER VII

## CONCLUSIONS

1. Biological constants obtained from Warburg studies do not correspond well to the same constants obtained from continuous flow data, when the substrate is Kraft black liquor.

2. Kincannon's model, when used with biological constants obtained from Warburg studies or from continuous flow data collected from fifteen feet or more of a biological tower, will not adequately describe Kraft black liquor $\Delta$COD removal beyond the first ten feet of that tower.

3. It cannot be concluded, at present, whether this failure is a result of the relatively great depth over which the study was attempted, or of the complicating factors of the Kraft black liquor.

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# APPENDIX

# $O_2$ UPTAKE DATA FROM WARBURG STUDIES

F = 1700 gal/day·ft$^2$

| t (hrs) | Cells from 6' | | | | | Cells from 30' | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | *175 | 350 | 700 | 930 | 1400 | 175 | 350 | 700 | 930 | 1400 |
| 2.5 | 2.29 | 3.75 | 3.55 | 2.98 | 1.68 | 2.65 | 1.96 | 1.40 | 0.88 | 1.40 |
| 3.75 | 3.52 | 6.43 | 6.39 | 5.60 | 2.61 | 3.88 | 3.93 | 2.81 | 1.95 | 2.28 |
| 5.5 | 4.93 | 8.75 | 11.9 | 10.2 | 2.05 | 5.30 | 7.14 | 4.91 | 3.19 | 3.16 |
| 7.95 | 6.86 | 12.5 | 20.2 | 20.3 | 4.85 | 7.41 | 11.4 | 10.2 | 6.02 | 5.26 |
| 9.85 | 7.92 | 15.4 | 25.2 | 27.8 | 9.32 | 9.35 | 13.9 | 17.2 | 10.3 | 8.07 |
| 11.05 | 8.10 | 16.6 | 27.7 | 31.2 | 11.9 | 9.53 | 15.0 | 21.2 | 14.9 | 10.5 |
| 14.95 | 9.50 | 20.2 | 35.0 | 40.4 | 30.0 | 10.8 | 18.9 | 28.4 | 31.9 | 28.8 |
| 17.65 | 9.86 | 21.6 | 38.9 | 45.0 | 38.8 | 10.8 | 22.8 | 32.3 | 37.0 | 38.2 |
| 18.75 | 10.2 | 22.1 | 40.3 | 46.7 | 41.6 | 10.8 | 23.7 | 33.5 | 38.9 | 42.5 |

*Initial ΔCOD (mg/l)

$F = 1035\ gal/day \cdot ft^2$

| t (hrs) | Cells from 6' | | | | | Cells from 30' | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | *189 | 378 | 758 | 1010 | 1515 | 189 | 378 | 758 | 1010 | 1515 |
| 1.4 | .714 | .528 | .536 | .525 | .746 | .176 | 0 | .176 | .531 | .526 |
| 2.25 | 1.43 | .88 | .714 | .875 | .932 | .176 | 0 | .176 | .708 | .878 |
| 4.0 | 2.32 | 1.58 | 1.07 | 1.22 | 1.49 | .706 | .357 | .526 | 1.06 | 1.40 |
| 4.9 | 2.86 | 1.94 | 1.25 | 1.22 | 1.49 | .706 | .357 | .526 | 1.06 | 1.40 |
| 6.67 | 4.28 | 3.52 | 1.96 | 1.92 | 2.24 | 1.06 | .714 | .878 | 1.59 | 1.76 |
| 8.4 | 5.36 | 4.93 | 2.50 | 2.1 | 2.42 | 1.76 | .892 | 1.05 | 1.95 | 2.28 |
| 10.75 | 6.43 | 8.10 | 3.75 | 2.98 | 2.98 | 3.18 | 1.07 | 1.05 | 2.12 | 2.46 |
| 11.5 | 7.50 | 10.0 | 4.46 | 4.02 | 3.36 | 3.88 | 1.61 | 1.40 | 2.48 | 2.98 |
| 12.0 | 7.50 | 10.7 | 5.18 | 4.2 | 3.36 | 4.41 | 1.61 | 1.58 | 2.48 | 2.98 |
| 13.0 | 8.4 | 11.8 | 6.25 | 4.9 | 3.54 | 5.47 | 2.14 | 1.58 | 2.66 | 3.16 |
| 14.0 | 9.28 | 13.4 | 8.75 | 6.65 | 4.48 | 6.53 | 3.21 | 2.28 | 3.36 | 3.86 |
| 15.0 | 10.0 | 14.8 | 11.8 | 8.58 | 4.85 | 7.41 | 4.10 | 2.46 | 3.72 | 4.04 |
| 16.0 | 10.7 | 16.2 | 15.2 | 11.2 | 5.22 | 8.12 | 5.89 | 2.81 | 4.07 | 4.39 |
| 16.5 | 11.1 | 16.5 | 17.3 | 12.6 | 5.60 | 8.47 | 7.14 | 3.16 | 4.25 | 4.74 |
| 18.5 | 12.1 | 18.0 | 25.2 | 20.3 | 6.34 | 9.18 | 11.4 | 3.86 | 4.60 | 5.09 |
| 19.5 | 13.0 | 19.0 | 27.5 | 23.8 | 7.09 | 9.53 | 12.0 | 4.39 | 4.96 | 5.09 |
| 20.0 | 13.0 | 19.0 | 28.0 | 25.2 | 7.09 | 9.53 | 12.1 | 4.39 | 4.96 | 5.26 |
| 20.8 | 13.4 | 19.7 | 29.6 | 28.9 | 8.02 | 10.1 | 12.7 | 4.91 | 5.13 | 5.62 |

*Initial $\Delta$COD (mg/l)

$F = 658\ gal/day \cdot ft^2$

| t (hrs) | Cells from 6' | | | | | Cells from 15' | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | *163 | 326 | 652 | 869 | 1303 | 163 | 326 | 652 | 869 | 1303 |
| 1.0 | 0 | 0 | 0 | 0 | 0 | .353 | 0 | 0 | 0 | 0 |
| 2.0 | 0 | 0 | 0 | 0 | 0 | .353 | 0 | 0 | 0 | 0 |
| 3.0 | .714 | .352 | .357 | .350 | .373 | 1.06 | .356 | .351 | 0 | .351 |
| 4.0 | 1.07 | .704 | .714 | .700 | 1.12 | 1.76 | .712 | .702 | .708 | .712 |
| 5.0 | 1.43 | 1.06 | 1.07 | .700 | 1.12 | 2.12 | 1.07 | 1.05 | 1.06 | 1.05 |
| 6.0 | 1.43 | 1.41 | 1.43 | 1.05 | 1.12 | 2.82 | 1.42 | 1.40 | 1.06 | 1.05 |
| 7.0 | 1.78 | 1.76 | 1.43 | 1.05 | 1.49 | 3.18 | 1.42 | 1.76 | 1.42 | 1.40 |
| 9.0 | 3.21 | 3.17 | 2.50 | 2.10 | 2.24 | 4.94 | 2.85 | 3.16 | 2.48 | 2.10 |
| 10.0 | 3.57 | 3.87 | 2.86 | 2.10 | 2.24 | 5.30 | 3.56 | 3.86 | 3.19 | 2.46 |
| 11.0 | 4.28 | 4.93 | 3.57 | 2.80 | 2.61 | 6.00 | 4.27 | 5.26 | 3.89 | 2.81 |
| 12.0 | 4.28 | 5.98 | 4.28 | 3.15 | 2.61 | 6.71 | 5.34 | 6.32 | 4.96 | 3.51 |
| 13.0 | 4.64 | 7.39 | 5.36 | 3.85 | 3.36 | 7.41 | 6.41 | 8.42 | 6.02 | 4.21 |
| 14.0 | 5.00 | 8.45 | 5.71 | 4.55 | 3.73 | 7.77 | 7.48 | 10.5 | 7.79 | 4.91 |
| 15.0 | 5.71 | 9.86 | 7.14 | 5.95 | 4.48 | 8.82 | 9.26 | 13.7 | 10.3 | 6.67 |
| 16.0 | 6.07 | 10.6 | 8.92 | 7.35 | 5.60 | 9.53 | 10.7 | 17.2 | 13.8 | 8.42 |
| 17.0 | 6.07 | 11.3 | 10.0 | 8.40 | 6.34 | 9.53 | 11.7 | 20.0 | 17.7 | 10.5 |
| 18.0 | 6.78 | 12.7 | 12.5 | 11.6 | 8.21 | 10.24 | 13.2 | 22.8 | 22.3 | 14.4 |
| 19.0 | 7.14 | 13.4 | 14.6 | 15.8 | 10.4 | 10.2 | 14.2 | 24.2 | 25.8 | 20.0 |
| 20.0 | 7.85 | 14.1 | 17.1 | 20.3 | 13.4 | 10.6 | 15.3 | 26.0 | 29.7 | 27.0 |
| 21.5 | 8.21 | 15.5 | 20.7 | 24.8 | 19.8 | 10.9 | 16.7 | 28.4 | 34.0 | 33.0 |
| 22.0 | 8.21 | 15.8 | 21.4 | 25.9 | 22.8 | 10.9 | 17.1 | 28.8 | 34.7 | 34.7 |
| 27.8 | 9.64 | 19.7 | 27.8 | 36.4 | 48.5 | 12.6 | 20.6 | 35.1 | 43.5 | 52.3 |

*Initial ΔCOD (mg/l)

VITA 2

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