APPLICATION OF KINETIC RELATIONSHIPS TO PHENOL REMOVAL IN THE ACTIVATED SLUDGE PROCESS

By

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CHAPTER I

INTRODUCTION

A great deal of time and money has been spent dealing with the world problem of cleaning up and improving our waters. Biological treatment (one possible means of attacking the problem) is often favored over other methods, such as physical-chemical treatment, due to the economics of operation which biological systems exhibit.

Two major types of biological treatment methods exist, fluidized-bed systems (activated sludge) and fixed-bed systems (trickling filters and bio-towers). Of these two major types, the former, the activated sludge system, has become very popular among researchers and practicing engineers because of its versatility and operational control features.

A flow diagram of the activated sludge process as shown in Figure 1, depicts raw sewage entering the primary clarifier. It is here the large solids are settled out while the primary clarifier effluent passes on into the aeration basin. In the aeration basin microorganisms attack the organic matter in the water, using part of it as an energy source and the remainder for synthesis of new cellular material. Following the organic removal in the aeration basin, the microorganism-liquid separation takes place in the secondary clarifier. A portion of the settled microorganisms (sludge) is recycled to the aeration basin in order to maintain the desired microorganism operating conditions, while the remainder of the sludge is wasted. The supernatent liquid from the

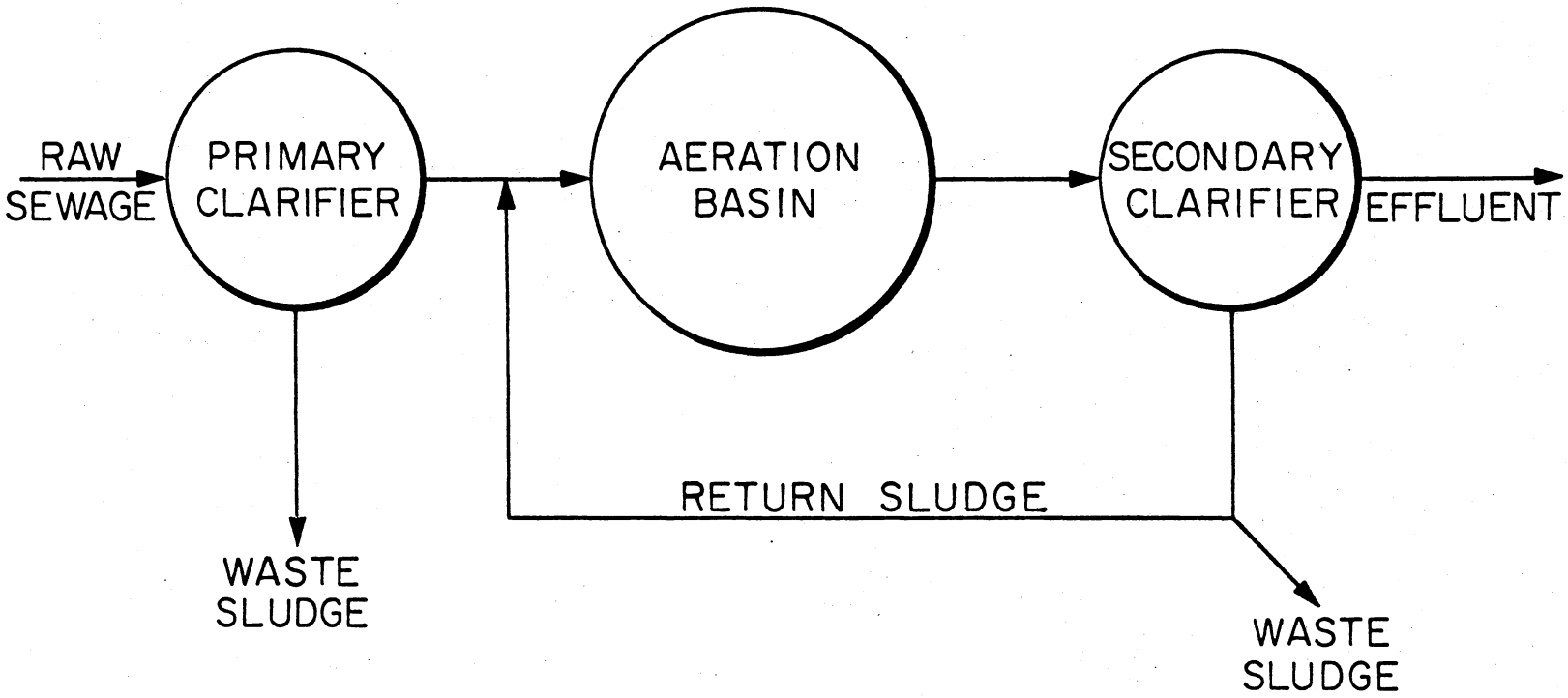

Figure 1. Typical Flow Diagram of the Activated Sludge Process

secondary clarifier is either given additional treatment or is discharged into a receiving water.

Recent trends in activated sludge research and design have been directed toward the operation of bench-scale units under steady state conditions and applying operational design equations to the data obtained. Steady state conditions are represented by nearly constant measurements of influent and effluent chemical oxygen demand, and aeration basin and effluent suspended solids. By wasting that amount of biomass which increases per unit time due to microbial growth, steady state conditions can be reached.

The operational aspects of the activated sludge process are of great importance due to the natural variations in the characteristics of the microorganisms used for the organic removal from the wastewater and the variations in the natural (operational) environment. The operational aspects for the completely mixed activated sludge process with cell recycle can be described by employing the following equations:

$$\theta_c = \frac{VX}{Q_w X_w + Q_{eff} X_{eff}}$$

and

$$Y_{obs} = \frac{\theta X}{\theta_c (C_o - C_{eff})}$$

where: Q, Q_w, and Q_{eff} are all volumetric flow rates of the influent, wasted, and effluent wastewater, respectively; X, X_w and X_{eff} are microorganism concentration in the aeration chamber, waste line, and effluent, respectively; V is aeration chamber volume; θ_c is sludge age or mean cell residence time; θ is hydraulic detention time, $\frac{V}{Q}$; and C_o and C_{eff} are influent and effluent substrate concentration, respectively.

This investigation encompassed an experimental study of the completely mixed activated sludge process with continuous internal recycle at the bench-scale level. Phenol was used as the sole carbon source. The underlying purpose of this investigation was the study of the kinetic relationships of phenol treatment in the completely mixed activated sludge process incorporating internal sludge recycle. Experimental results were analyzed through the application of the θ_c and Y_{obs} equations (given above) to determine the interrelationships of Y_{obs} and COD removal efficiency on values of θ_c.

CHAPTER II

LITERATURE REVIEW

A. Mean Cell Residence Time

Although treatment of sewage by the activated sludge process was developed in the early 1900's, it was not until the 1950's that the fundamentals of activated sludge process were studied in depth. Since the 1950's mean cell residence time or sludge age has been established as a useful parameter because of its basic relationship to bacterial growth rate and its accuracy and ease of use in design calculations. For these reasons mean cell residence time has been incorporated into many of the present activated sludge design models.

The mean cell residence time, or the average length of time the cells are in the system, is equal to the mass of microorganisms in the process divided by the rate at which the microorganisms are wasted from the process. It also takes into account the microorganisms which might leave the system via the effluent. The mean cell residence time is also the reciprocal of the microorganism specific growth rate which is used as a parameter in certain design equations.

In 1968 it was shown by Jenkins and Garrison (1) that effluent quality and nitrification could be regulated by controling sludge age. This study concluded that mean cell residence time is a kinetically rational basis for the control, operation, and design of activated sludge plants.

Walker (2) demonstrated that by applying a method of hydraulic control of mean cell residence time, solids changes in the system corresponded directly with changes in the influent substrate.

One of the more recent models which employs sludge age as a unifying parameter is one proposed by Lawrence and McCarty (3). They presented the idea that sludge age could be used as an independent parameter in biological treatment control and design, based on the fact that sludge age is related to the performance of the activated sludge process.

Sherrard, in a series of articles co-authored by Schoeder and Lawrence (4) (5) (6) (7) proposed a model for the completely mixed activated sludge process. These articles concluded that based on mean cell residence time it was possible to predict MLSS, sludge production, inorganic nutrient removal, sludge settling data, and treatment efficiency at different hydraulic loadings. Also by using a materials balance approach to describe biological reactions, observed yield (Y_{obs}), food to microorganism ratio (F/M), and specific utilization (U) were shown to be a function of mean cell residence time.

B. Yield

The observed yield coefficient is an important factor influencing the amount of microorganism production. Sherrard and Schroeder (6) discussed the factors which influence the magnitude of the yield coefficient in relation to a continuous flow biological treatment process. Their discussion was for both pure and heterogeneous cultures of microorganisms. The major influencing factors of cell yield are listed in Table I and are discussed below, with a major portion of the discussion taken directly from the paper by Sherrard and Schroeder (5).

TABLE I

INFLUENCING FACTORS OF CELL YIELD COEEFICIENT

1. Oxidation-Reduction State of the Carbon Source
2. Oxidation-Reduction State of the Nutrient Elements
3. Presence of Growth Factors; i.e., Amino Acids, Vitamins, etc.
4. Degree of Polymerization of the Substrate
5. Pathways of Metabolism
6. Net Microorganism Growth Rate
7. Physical Parameters of Cultivation
8. Predator Activities (Heterogeneous Cultures); i.e., Protozoa, Rotifiers, etc.

1. Oxidation-Reduction State of the Carbon Source

The potential energy available from the substrate influences yield and higher yields are associated with a substrate containing more energy. For the two-carbon atom molecules ethyl alcohol, (CH_3CH_2OH), acetaldehyde, (CH_3CHO), and acetic acid, (CH_3COOH) the highest yield would be expected with the ethyl alcohol and the lowest with the acetic acid. This can be further illustrated with the calculation of the mean oxidation number of the carbon atoms for each substrate. For the substrates cited, mean oxidation numbers of -II, -I, and 0 are found respectively.

2. Oxidation-Reduction State of the Nutrient Elements

Similar to case 1, a higher yield would be expected if nitrogen

were supplied as ammonia (-III) rather than nitrate (+V) because the nitrogen atom in ammonia is in a more reduced state.

3. Presence of Growth Factors

When growth factors are supplied, high yields are to be expected. Solutions containing amino acids and vitamins supply growth factors "ready-made" and therefore cellular energy need not be expended for synthesis because they are incorporated into cellular material directly from solution.

4. Degree of Polymerization of the Substrate

The length of the carbon-chained molecule affects the yield coefficient. Take for example the 3, 2, and 1 carbon atom substrates n-propyl alcohol, (CH_3CH_2COOH), ethyl alcohol, (CH_3COOH), and methyl alcohol, (CH_3OH). Each possesses carbon atom mean oxidation numbers of -II. The highest yield would be expected from n-propyl alcohol. The lowest yield would be found for methyl alcohol because this one carbon atom molecule would have to be further built into longer chained molecules found in the cell, a procedure requiring an additional expenditure of cellular energy.

5. Pathways of Metabolism

Magnitude of production of adenosine triphosphate (ATP) due to the metabolic pathway utilized by the microorganism affects the yield coefficient. Higher productions of ATP are associated higher yield coefficients.

6. Net Microorganism Growth Rate

Net microbial growth rate affects the magnitude of the yield coefficient because of the maintenance energy requirements. Cells growing rapidly expend most energy for growth and divert little energy for maintenance; however, a cell growing slowly must expend a greater portion of energy for maintenance. Maintenance energy reactions include factors such as molitity, maintenance of intracellular and extracellular concentration gradients, and the resynthesis of macromolecules that have been hydrolyzed within the cell.

7. Physical Parameters of Cultivation

Factors such as aerobic or anaerobic conditions, temperature, pH, salinity, etc., are included in this classification. Energetic considerations can be used to explain variation of yield as each of the above items is altered. Oxidized end products are found from aerobic environments, whereas reduced end products are derived from anaerobic environments. As a result, higher yields are obtained from aerobic conditions when compared with anerobic conditions. Maintenance energy requirements change with alterations of pH, temperature and salinity and under most circumstances only affect the yield to a small degree.

8. Predator Activities

While the first 7 factors discussed above were determined to affect the magnitude of the yield either in terms of the amount of energy supplied to or used by the microorganism(s), the factor of predator activities is concerned with the predator-prey interaction of heterogeneous cultures.

From an engineering viewpoint (given a specified organic wastewater complete with necessary nutrients) Sherrard (5) states that only two of the above factors can be regulated effectively: 1) physical parameters of cultivation, and 2) net microorganism growth rate. The design engineer has flexibility in selecting either an aerobic or an anaerobic environment making this the most easily regulated physical parameter. Once this condition is selected, the only remaining variable that can be regulated is net growth rate of the microorganisms. By controlling the wastage rate of microorganisms from a biological process the net growth rate can be regulated. High net growth rates are associated with low wastage rates and low net growth rates with low wastage rates. At slow net growth rates (large mean cell residence times) yield would be expected to be minimized because of increased maintenance activities and predator activities. At high net growth rates (small mean cell residence times) yield would be maximized because a greater portion of energy is used for growth rather than non-growth or maintenance energy reactions.

C. Phenolic Waste Treatment

Phenol, commonly known as carbolic acid, is the monohydroxy derivative of benzene. It ionizes to yield H^+ to a limited extent, and in concentrated solution it can be quite toxic to bacteria. It has been used widely as a germicide, and disinfectants have at one time been rated in terms of "phenol coefficients" relative to disinfecting power with respect to phenol (8).

Phenolic compounds probably act as an antimicrobial agent primarily by denaturing cell proteins and damaging cell membranes. Some phenolics greatly reduce surface tension, and this property undoubtedly contributes

to their antimicrobial action. Some phenolics are highly fungicidal though they are not sporicidal. Spores and viruses are more resistant to phenol than vegative bacteria. The antimicrobial activity of phenolics is greatly reduced at an alkaline pH and in the presence of organic material (9).

Phenol is recovered from coal tar, and considerable amounts are manufactured synthetically. It is used extensively in the synthesis of organic products, particularly phenolic type resins. It occurs as a natural component in industrial wastes from the coal-gas, coal-coking, and petroleum industries as well as in a wide variety of industrial wastes from processes involving the use of phenol as a raw material (8).

Phenols find their way to surface waters via wastewater discharges that contain industrial wastes. They can cause taste and odor problems in drinking water, particularly when drinking water is chlorinated (10). Trace amounts approaching one μg/L can impart objectionable taste to a water following marginal chlorination. Chlorine reacts with phenols to produce mono-, di-, or trichlorophenols which cause taste and odor problems. For this reason, the United States Public Health Service has placed a limit of one μg/L on phenolic materials in public water supplies and thus made the removal of phenols a serious challenge to the treatment plant (8).

There are a number of processes which can be used for coping with the problem of removing phenols from a water. These include such processes as biological treatment (since microorganisms do exist which degrade phenol).

Despite the widespread production of phenolic wastes arising from chemical and petrochemical operations, few studies have been done on the biological degradation of phenolic compounds, which can be far more

economical than physical and chemical treatment methods.

Usually where wastes containing phenol are treated biologically, it is a common practice to reduce phenol concentrations from a range of 1,000 - 10,000 milligrams per liter to 30 - 50 milligrams per liter before initiating biological treatment (11). There has been some research, though, conducted at the Dow Chemical Company plant in Midland, Michigan, and elsewhere, which has shown that phenol will serve as a bacterial food without serious toxic effects at levels as high as 500 mg/L. McKinney, et al.(12) were able to treat a wastewater containing 500 mg/L phenol in the laboratory by developing an acclimated, heterogeneous culture of aerobic microorganisms. This system consisted of a batch treatment process wherein phenolic waste was fed to the microorganisms on a "slug" basis each day.

Among other investigators reporting on the biological treatment of phenols, Harlow, et al.(13) found it possible to attain 90% removal efficiency from wastewaters containing 20 - 30 mg/L phenol. Coe (14) reported a phenol removal efficiency between 90% and 95% for a refinery wastewater containing 100 mg/L phenol which was treated in an activated sludge process with a 9 - 12 hour detention time.

Fairly recent and very extensive research on the mixed culture bio-oxidation of phenol was conducted by Pawlowsky and Howell (15). The initial purpose of their study was to determine kinetic parameters governing the growth of phenolic organisms by measuring growth rates in a batch culture.

Another recent and comprehensive investigation of activated sludge and phenol was published by Radhakrishnan and Ray (16). This study analyzed the kinetics and relationships of batch and once-through

systems by employing phenolic bacteria.

Other applications of kinetic parameters to phenol, especially the operational parameter of mean cell residence time, have not been attempted because of their relative recent development. Sherrard (11) has proposed, though, that by using the concept of mean cell residence time as a control parameter, criteria can be established to provide guidelines for treatment of phenolic compounds contained in wastewaters. This would be done by operating a bench-scale laboratory activated sludge unit under highly controlled conditions and collecting data for different phenol concentrations and different mean cell residence times.

CHAPTER III

MATERIALS AND METHODS

To study the influence of sludge age and stoichiometric relationships on phenol removal in the activated sludge system, a bench scale unit was operated under closely controlled conditions.

A description of the apparatus used, the feed solution, initial acclimation, daily protocol, analytical procedures, and methods of data analysis are presented separately for ease of presentation.

A. Laboratory Apparatus

An illustration of the type of model laboratory apparatus herein referred to as the reactor, which was used in this investigation, is shown in Figure 2. Two laboratory reactors of equal volume were used to perform simultaneous continuous flow experiments. The rectangular shaped reactors were made of $\frac{1}{4}$" plexiglass. Each reactor had two compartments (an aeration chamber and a settling basin) which were separated by an adjustable baffle. The aeration chamber and the settling basin volumes were 9.2 liters and 2.8 liters, respectively.

Continuous synthetic phenolic waste water was supplied to the respective reactors by means of a Milton-Roy dual, positive displacement pump (mini-pump, Model MM4-C-48R). The pumping rate of 18 liters per day was checked periodically by means of a graduated cylinder and timer. The 18 liters per day feed rate provided a hydraulic detention time of

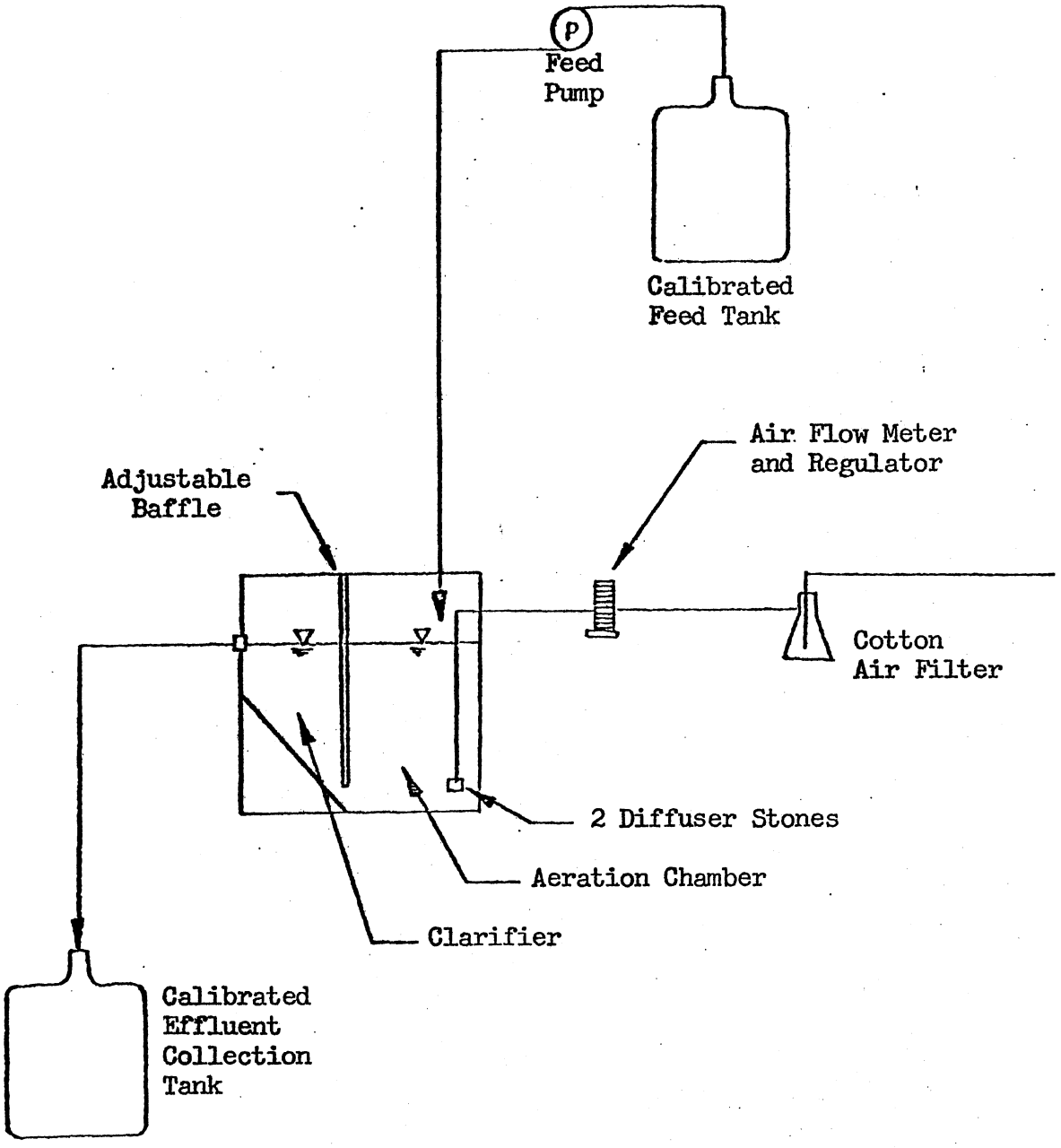

Figure 2. Experimental Activated Sludge Unit with Internal Recycle

12.3 hours in the aeration chamber and 3.7 in the settling basin.

Mean cell residence time or sludge age was controlled independently of hydraulic detention time by internal recycling. Solids which passed from the aeration basin were drawn back into the aeration basin by suction provided by two air diffusers. The mixed liquor suspended solids were wasted daily from the total reactor volume after removing the baffle and allowing the entire contents to mix. The wastage rates of the microorganisms were 670, 1,000, 1,500, 2,000 and 4,000 ml/day. Due to variance of effluent solids, it was possible in this study to obtain thirteen different θ_c steady state points from only the five wastage rates.

An airflow rate in excess of 5 liters per minute (monitored through a Gelman air flow meter) was used to provide sufficient oxygen for bacterial growth, good mixing, and a good recycle. A cotton filter was placed just before the airflow meter to prevent oil from entering the air lines and biological reactor which could contaminate the biological population.

B. Feed Solution

The chemical composition of the wastewater and nutrients is listed in Table II. The wastewaters were designed to have a chemical oxygen demand of approximately 130 mg/L. This was achieved through the use of a concentrated stock solution of phenol as the sole carbon source. The various nutrients (magnesium sulfate, ferric chloride, manganese sulfate, calcium chloride, and ammonium sulfate) were added in proportion to the carbon source (phenol). A phosphate buffer solution was used as a means of controlling the pH in the system. This buffer, plus the

TABLE II

COMPOSITION OF PHENOLIC WASTE FOR 130 mg/L COD

Constituent	Stock Concentration (Per 2 L)	Quantity Stock Solution (Per 18 L)	Final Concentration (Per 18 L)
Phenol*			
C_6H_5OH	80 ml	25 ml	.06 ml/L
Ammonium Sulfate			
$(NH_4)_2SO_4$	200 grams	10 ml	55.56 mg/L
Potassium Phosphate Buffer			
Monobasic- KH_2PO_4	105.4 grams	50 ml	146.39 mg/L
Dibasic- K_2HPO_4	214 grams	50 ml	297.11 mg/L
Salts			
Calcium Chloride**			
$CaCl_2$	1.5 grams	20 ml	0.83 mg/L
Ferric Chloride			
$FeCl_3 \cdot 6\ H_2O$	0.1 grams	20 ml	0.06 mg/L
Magnesium Sulfate			
$MgSO_4 \cdot 7\ H_2O$	20.0 grams	20 ml	11.11 mg/L
Manganous Sulfate			
$MnSO_4 \cdot H_2O$	2.0 grams	20 ml	1.11 mg/L

*Phenol Liquified Reagent FW 94.11, Matheson, Coleman and Bell
**$CaCl_2$ must be added first when making stock salt solution

normal buffering effect of the tap water, maintained the feed pH between 6.8 and 7.1.

Considerable care was exercised in the making of the feed solution. Twelve liters of tap water were first placed in the 20-liter feed bottle. Following this, the stock solutions of ammonium sulfate, salts, and buffer were measured with a graduated cylinder and poured into the bottle. The phenol was then added by using a 25 ml pipette. The pipette was used to help achieve a consistence in the feed COD. Thus the variance of feed COD values can be attributed to the inaccuracies in running the COD tests and the inability to dilute the feed to exactly 18 liters each time. The feed solution was then diluted to the final volume of 18 liters. This method was incorporated into the study to help ensure adequate mixing of all the feed ingredients and consistent feed COD values.

C. Initial Acclimation and Startup

The original seed of microorganisms was taken from a well operating activated sludge system (similar to the one previously described, but using bacto-peptone as its sole carbon source) and placed into a 3 liter batch system. The bacto-peptone was kept as the major carbon source while the phenol concentration was increased very slowly. As the solids increased the volume of the batch system increased to maintain an approximate microorganism concentration of 1,000 mg/L. The initial stock phenol solution was one ml/L. One ml of this stock solution was added to the system along with the bacto-peptone and other nutrients. The phenol concentration was increased one ml per week until the one liter stock solution was completely used. This operation was repeated for stock phenol concentrations of 2, 4, 10, 20, and 40 ml/L. While the phenol

concentrations was increased, the bacto-peptone concentration in the feed was decreased, finally to the point of nonexistence. Thus, the microorganisms were growing with the phenol as the only carbon source. It should be pointed out that the initial bacto-peptone feed COD was 500 mg/L while the final phenol acclimated microorganisms used for this study were fed a phenol COD of 135 mg/L.

Once the phenol acclimated solids concentration reached the proximity of the desired concentration, the unit was switched to continuous flow operating conditions. Wasting of the mixed liquor was postponed until the solids concentration had built up to the desired value and the effluent solids reduced to an appropriate level. Having achieved these conditions, wasting of the mixed liquor at a previously determined rate was begun. Monitoring of the parameters noted in Table II was initiated.

D. Daily Protocol

A daily operating procedure was developed to aid in efficient and accurate data collection. Table III shows the parameters which were monitored.

1. Feed

The feed was prepared daily according to the proportions shown in Table II. A 20-ml sample of fresh feed was removed for the COD determination. The feed supply was then connected to the feed lines. The pH of the feed was checked periodically.

TABLE III

PARAMETERS MONITORED

1. Feed
   - A. COD
   - B. pH
2. Effluent
   - A. COD
   - B. Suspended solids concentration
   - C. pH
3. Reactor
   - A. Total system MLSS (Mixed liquor suspended solids)
   - B. Temperature
   - C. pH

2. Effluent

Approximately 100-ml of effluent was captured in a small beaker as it left the effluent line. Approximately 40-ml of this captured effluent was then filtered through a 45-μ millipore filter pad. From the filtrate a 20-ml sample was pipetted for COD analysis.

The 20-liter effluent collection bottle was shaken until the effluent solids were well mixed. A 50-ml sample was then pipetted from the bottle and filtered through a preweighed 45-μ millipore filter pad in order to determine the concentration of effluent suspended solids. The effluent pH which ranged between 7.4 and 7.8 was checked daily.

3. Reactor

After plugging the effluent discharge line, the baffle was removed and the entire MLSS was well mixed. A 25-ml sample was then pipetted and filtered through a preweighed 45-μ millipore filter pad in order to determine the MLSS concentration. Next, the desired waste volume of mixed liquor was removed. The baffle was replaced and the plug removed. The unit was then ready to continue operation.

During the course of this investigation, there was no real control over the temperature of the reactors. The reactor temperature was controlled principally by the room temperature and secondarily by the temperature of the tap water. Although the temperature of the tap water varied as much as 10°C during the various experiments, by the time the feed reached the reactor it was near room temperature. Since the reactors were located in a room with controlled temperature, the reactor temperatures remained fairly constant throughout the study. The daily reactor temperature varied between 22° and 24°C.

E. Analytical Procedures

To provide the necessary data for this investigation, the chemical oxygen demand, biological solids concentration, pH, and temperature were monitored. The following methods and equipment were used to measure these parameters.

1. Biological Solids

Biological solids determinations were performed by filtering the appropriate volume through 45-μ pore size filters (Millipore Filter Corp., Bedford, Mass.). The filter pads were placed in alluminum tare pans and dried at 103°C for two hours. Following cooling to room temperature in a desicator, the pans were tared to determine the initial weights. All weights were obtained by using a Mettler Instrument Corporation balance (No. 1-910). After filtration of the known volume of sample, the tared pans were placed back into the drying oven for two hours at 103°C, cooled in the desicator, and weighed to obtain the final weights.

2. Chemical Oxygen Demand

Feed and effluent COD determinations were made in accordance with Standard Methods (17). The standard method was used for the feed COD and the dilute method was used for the effluent COD.

3. Temperature and pH

The pH was determined by collecting at least 80 ml of liquid in a beaker which was then measured using a Beckman Expandomatic SS-2 pH meter. The temperature of the reactor was obtained by placing a

Sargent-Welch thermometer into the reactor for five minutes and then reading the temperature. The thermometer had a range from -20^{o} to 110^{o}C.

F. Methods of Data Analysis

The mathematical relationships for the completely mixed activated sludge system as presented by Sherrard, Schroeder, and Lawrence (7) were utilized for data analysis.

Treatment efficiency or COD removal efficiency was determined by the equation

$$E = \frac{100\ (C_o - C)}{C_o} \qquad (1)$$

where

E = COD removal efficiency, percent

C_o = Influent substrate concentration, mg/1 COD

C = Effluent substrate concentration, mg/1 COD

Mean cell residence time or sludge age was calculated according to the expression

$$\Theta_c = \frac{V\ X}{Q_w\ X + Q_{eff}\ X_{eff}} \qquad (2)$$

where

Θ_c = Mean cell residence time, days

V = Volume of total reactor, liters

X = Observed total reactor MLSS concentration, mg/1

X_{eff} = Observed effluent suspended solids concentration

Q_{eff} = Effluent liquid flowrate, liters/day

Q_w = Wasted MLSS flowrate (from total reactor), liters/day

The observed yield coefficient was obtained by applying the following equation

$$Y_{obs} = \frac{\theta X}{\theta_c (C_o - C)} \qquad (3)$$

where

Y_{obs} = Observed yield coefficient

θ = Total reactor hydraulic detention time, days

X = Observed total reactor MLSS, mg/L

θ_c = Mean cell residence time, days

C_o = Influent substrate concentration, mg/L COD

C = Effluent substrate concentration, mg/L COD

The food to microorganism ratio was calculated from the relationship

$$F/M = \frac{C_o}{\theta X} \qquad (4)$$

where

F/M = Food to microorganism ratio, $days^{-1}$

C_o = Influent substrate concentration, mg/L COD

θ = Hydraulic detention time, V/Q, days

X = Observed total reactor MLSS, mg/L

Specific utilization was obtained from the following expression

$$U = \frac{C_o - C}{\theta X} \qquad (5)$$

where

U = Specific utilization, $days^{-1}$

C_o = Influent substrate concentration, mg/L COD

C = Effluent substrate concentration, mg/L COD

θ = Hydraulic detention time, V/Q, days

X = Observed total reactor MLSS, mg/L

The rate of substrate utilization was determined by applying the following equation

$$\Delta S/\Delta t = \frac{C_o - C}{\theta} \qquad (6)$$

where

$\Delta S/\Delta t$ = Substrate utilization rate, mg COD utilized/L/day

C_o = Influent substrate concentration, mg/L COD

C = Effluent substrate concentration, mg/L COD

θ = Hydraulic detention time, V/Q, days

The amount of cell production was established by the relationship

$$\Delta X/\Delta t = \frac{X}{\theta_c} \qquad (7)$$

where

$\Delta X/\Delta t$ = Cell production mg cells produced/L/day

X = Observed total reactor MLSS concentration, mg/L

θ_c = Mean cell residence time, days

The total reactor microorganism concentration was calculated from the following expression

$$X = \frac{Y\,(C_o - C)\,\theta_c}{1 + b\theta_c\,\theta} \qquad (8)$$

where

X = Calculated total reactor MLSS concentration, mg/L

Y = Microorganism constant yield coefficient, mg/mg

C_o = Influent substrate concentration, mg/L COD

C = Effluent substrate concentration, mg/L COD

θ_c = Mean cell residence time, days

b = Microorganism mantenance energy coefficient, $days^{-1}$

θ = Hydraulic detention time, V/Q, days

Waste sludge production was determined by the relationship

$$P_x = \frac{V\,X}{\theta_c} \qquad (9)$$

where

P_x = Waste sludge production, mg/day

V = Volume of total reactor, liters

X = Calculated total reactor MLSS concentration, mg/L

θ_c = Mean cell residence time, days

CHAPTER V

RESULTS

Two laboratory activated sludge units were operated under closely controlled conditions, using mean cell residence time as the operating parameter. The hydraulic detention time was maintained at 16 hours. The influent substrate concentration was maintained at approximately 130 mg/L COD throughout the study. The mean cell residence time was varied between 2.9 days and 17 days. Summaries of the "steady state" data for thirteen different mean cell residence times are found in Tables IV and V.

A. COD Removal Performance

Changes in the mean cell residence time appeared to have little or no effect on the effluent COD and the COD removal efficiency for the θ_c range of 2.9 days to 17 days. Figure 3 illustrates the consistency of removal efficiency for θ_c's between 2.9 and 17 days was maintained around the 88% level. Figure 4 shows the effluent COD to be fairly constant for the entire range of θ_c's. The average was approximately 16 mg/L, with the difference of extremes being only 9 mg/L.

Figure 5 shows that substrate utilization is not a function of cell production. As the sludge production varies, substrate utilization remains fairly constant for the entire range. Values for substrate utilization varied between 167 and 183 mg COD L^{-1} Day^{-1} with the average

TABLE IV

SUMMARY OF STEADY STATE DATA

	θ_c, days					
	2.9	4.3	5.1	5.5	6.1	7.1
Feed COD, mg/L	133	139	130	130	132	132
Effluent COD, mg/L	15	17	13	19	17	16
Removal efficiency, %	89	88	90	85	87	88
Observed total reactor MLSS, mg/L	350	476	519	561	606	616
Solids wasted/day, mg	1499	952	1038	1122	909	924
Effluent MLSS, mg/L	3	23	12	7	17	7
Observed P_x, mg/day	1442	1320	1230	1234	1190	1040
Y_{obs}, mg/mg	0.682	0.605	0.580	0.613	0.576	0.499
F:M, $days^{-1}$	0.570	0.410	0.376	0.348	0.327	0.321
U, $days^{-1}$	0.506	0.348	0.341	0.297	0.285	0.282
ΔS, mg COD/L/day	177	183	177	167	173	174
ΔX, mg/L/day	121	110	102	102	99	87
Calculated total reactor MLSS, mg/L	354	457	506	527	557	602
Calculated P_x, mg/day	1465	1275	1191	1149	1096	1017
$1/Y_{obs}$, mg/mg	1.47	1.65	1.72	1.63	1.74	20
$1/\theta_c$, $days^{-1}$	0.345	0.233	0.196	0.182	0.164	0.141

TABLE V

SUMMARY OF STEADY STATE DATA

	θ_c, days						
	9.8	10.6	11.5	11.9	14.1	15.7	17.0
Feed COD, mg/L	134	131	132	129	134	134	130
Effluent COD, mg/L	18	10	14	15	19	16	15
Removal efficiency, %	87	92	89	88	86	88	88
Observed total reactor MLSS, mg/L	1614	1840	1706	1840	1842	1919	2043
Solids wasted/day, mg	1614	1840	1706	1840	1234	1279	1369
Effluent MLSS, mg/L	21	14	4	1	19	11	4
Observed P_x, mg/day	1971	2078	1774	1857	1563	1470	1438
Y_{obs}, mg/mg	0.947	0.956	0.838	0.904	0.757	0.691	0.697
F:M, $days^{-1}$	0.125	0.107	0.116	0.105	0.109	0.105	0.096
U, $days^{-1}$	0.108	0.099	0.104	0.093	0.094	0.092	0.084
ΔS, mg COD/L/day	174	182	177	171	173	177	173
ΔX, mg/L/day	165	174	148	155	131	122	120
Calculated total reactor MLSS, mg/L	1651	1713	1777	1809	1934	2015	2073
Calculated P_x, mg/day	2022	1939	1854	1819	1646	1540	1463
$1/Y_{obs}$, mg/mg	1.056	1.046	1.193	1.106	1.321	1.447	1.435
$1/\theta_c$, $days^{-1}$	0.102	0.094	0.087	0.084	0.071	0.064	0.059

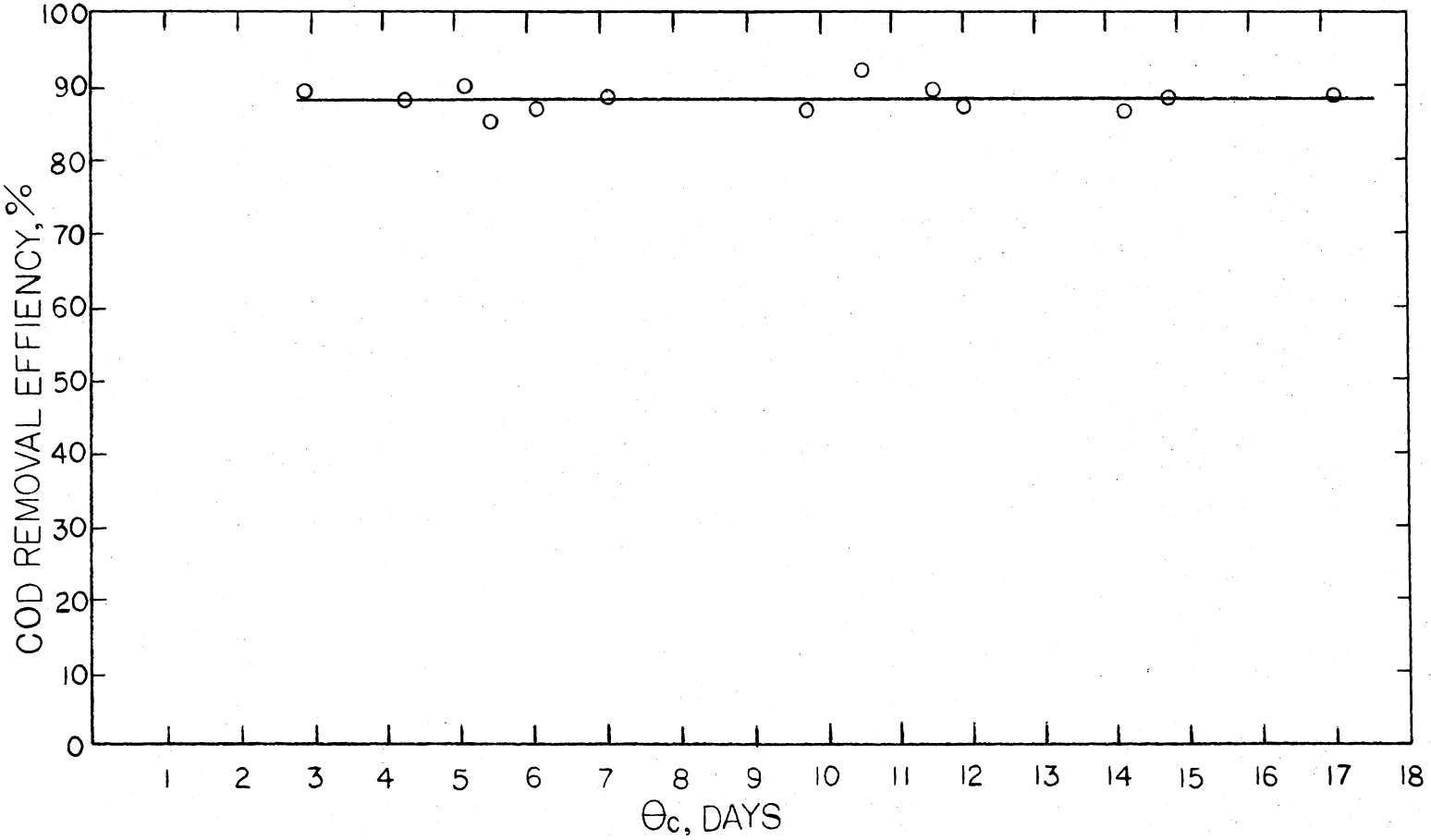

Figure 3. Treatment Efficiency versus θ_c

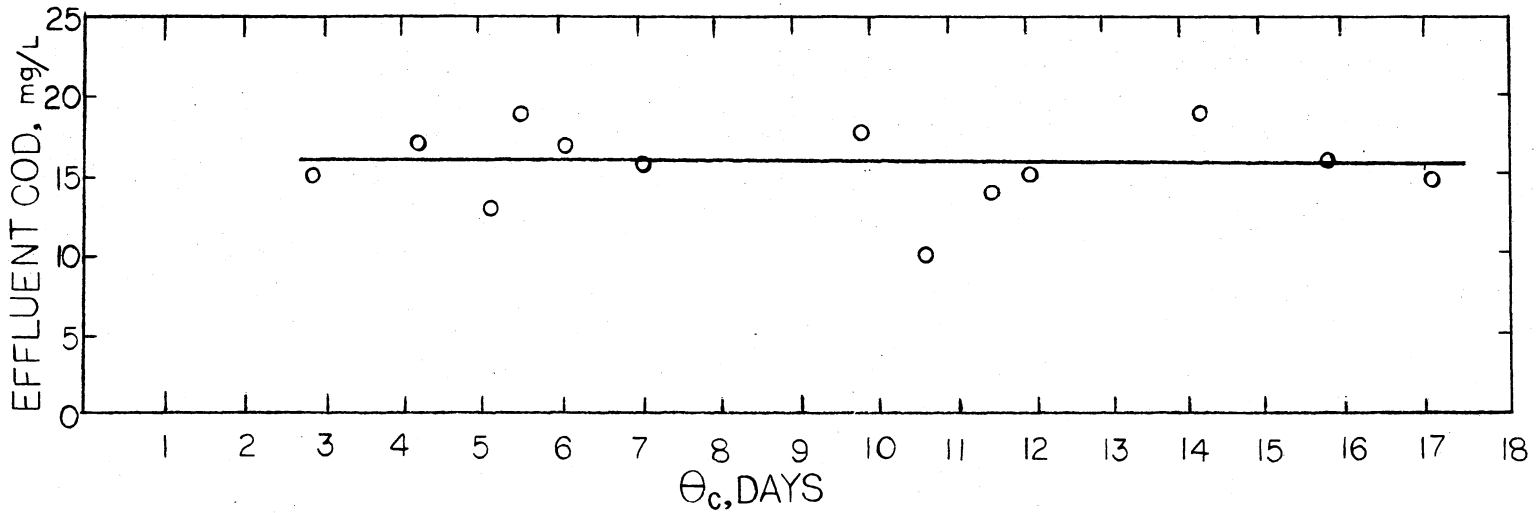

Figure 4. Effluent COD versus Θ_c

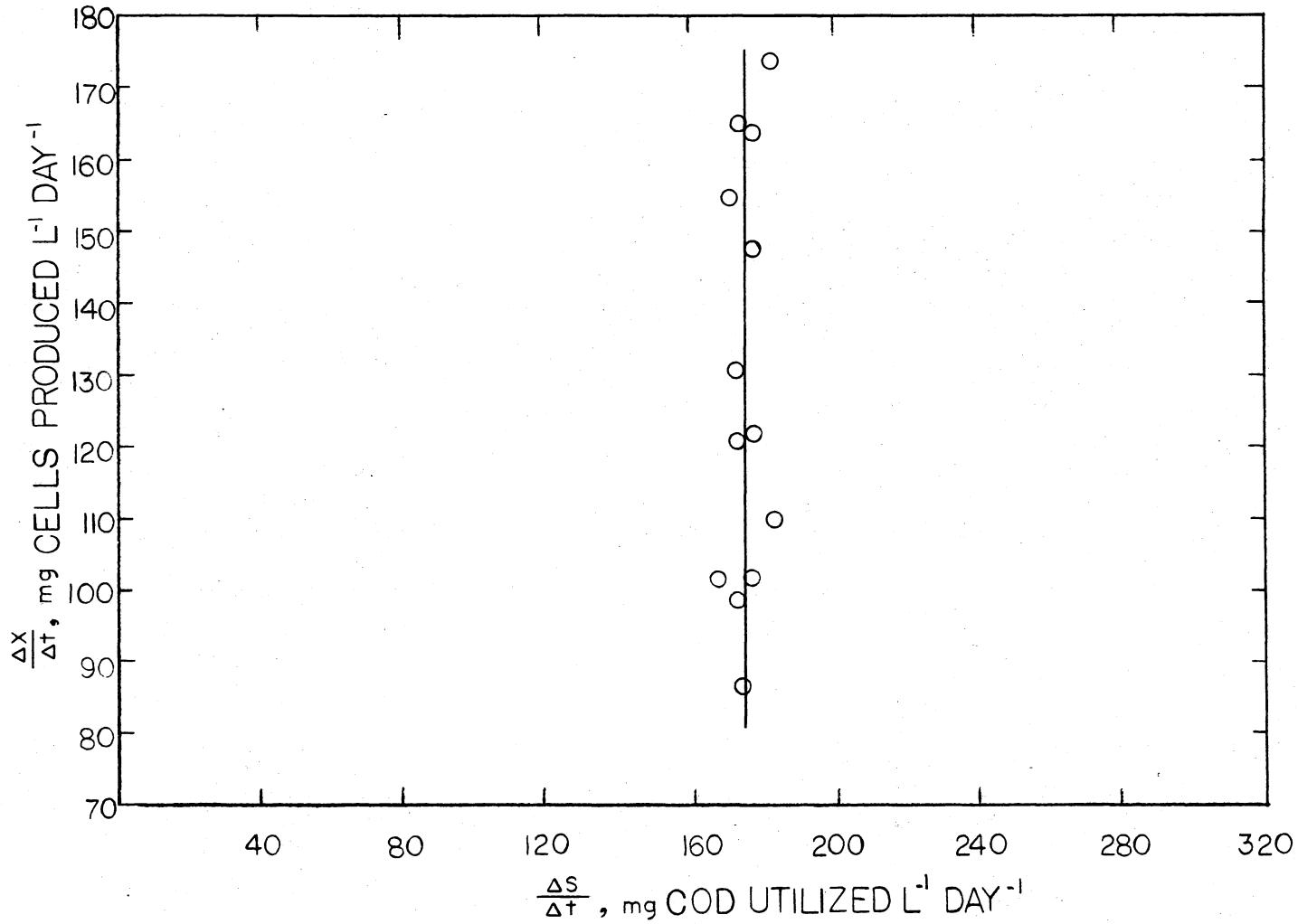

Figure 5. Cell Production versus Substrate Utilization Rate

being 175. Cell production ranged between 87 and 174 mg cells L^{-1} Day^{-1}.

B. Observed Yield

An observed yield coefficient was calculated on the basis of COD, not phenol, for each mean cell residence time (See Equation 3). Results of the relationship between observed yield and mean cell residence time are shown in Figure 6, which clearly indicates the presence of two distinct curves. The two distinct curves are a significant variance from previous investigations which indicated or at least assumed the presence of only one continuous yield curve over the 1 to 17 day θ_c range. The first curve, A, appears between θ_c's of 2.9 to 7.1 days and the second curve, B, occurs between 9.8 and 17 days. When analyzing the two curves independently each curve decreases as θ_c increases. This has been the accepted relationship between Y_{obs} and θ_c from previous works. The two curves also illustrate relative high yields which range between 0.5 to 0.96.

The observed yield data was then linearized by using the relationship

$$\frac{1}{Y_{obs}} = \frac{1}{Y_{max}} + \frac{b\theta_c}{Y_{max}}$$

Figure 7 illustrates the linearization of the reciprical of Y_{obs} vs θ_c. It further illustrates and substantiates the idea that the system under study projected to separate yield curves. The slope intercept form of the above equation was used in establishing values of Y_{max} and b for the two curves. For Curve A values of 1.0 and .149 were found for Y_{max} and b, respectively. Curve B yielded values of 2.0 and .113 for Y_{max} and b, respectively.

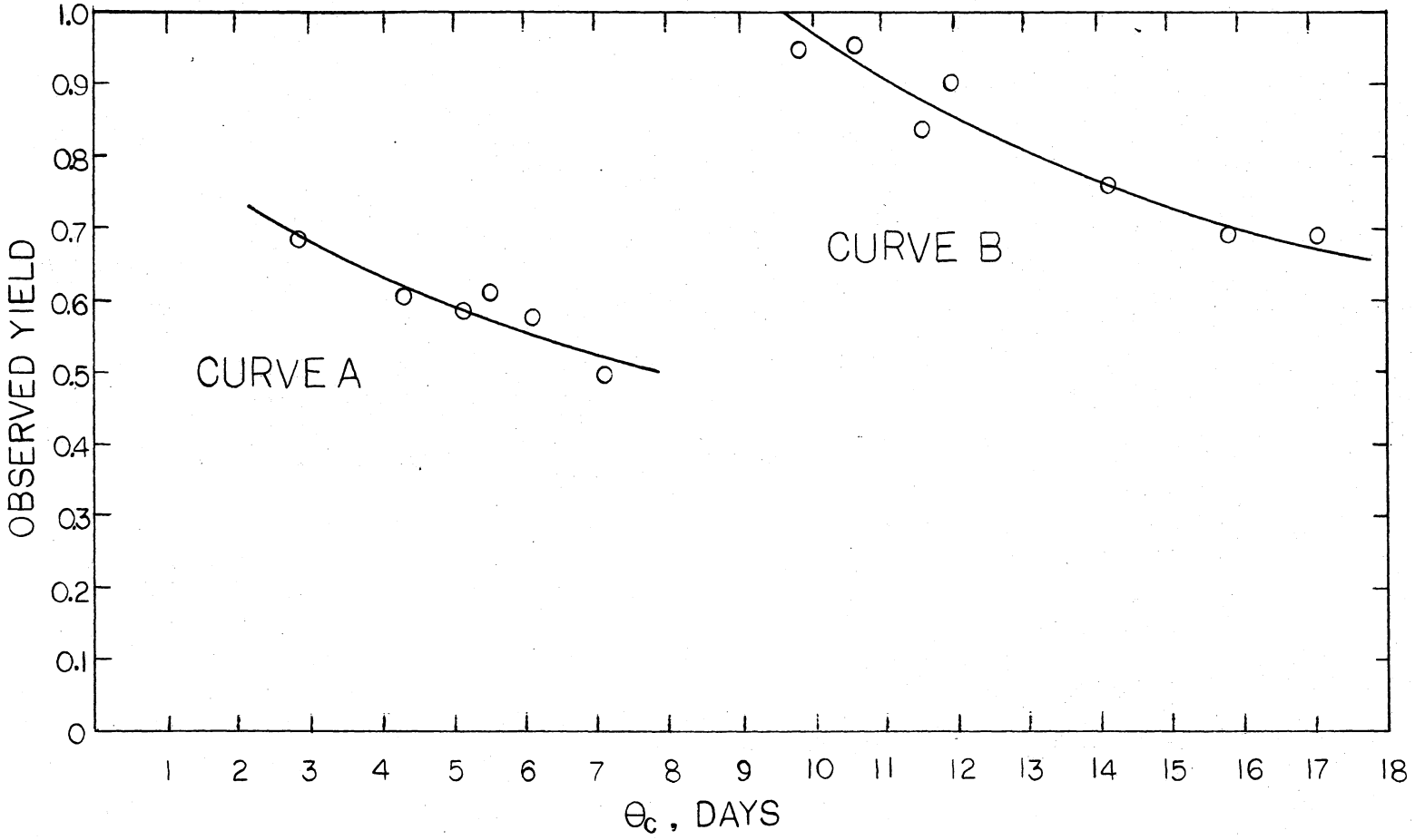

Figure 6. Observed Yield versus θ_c

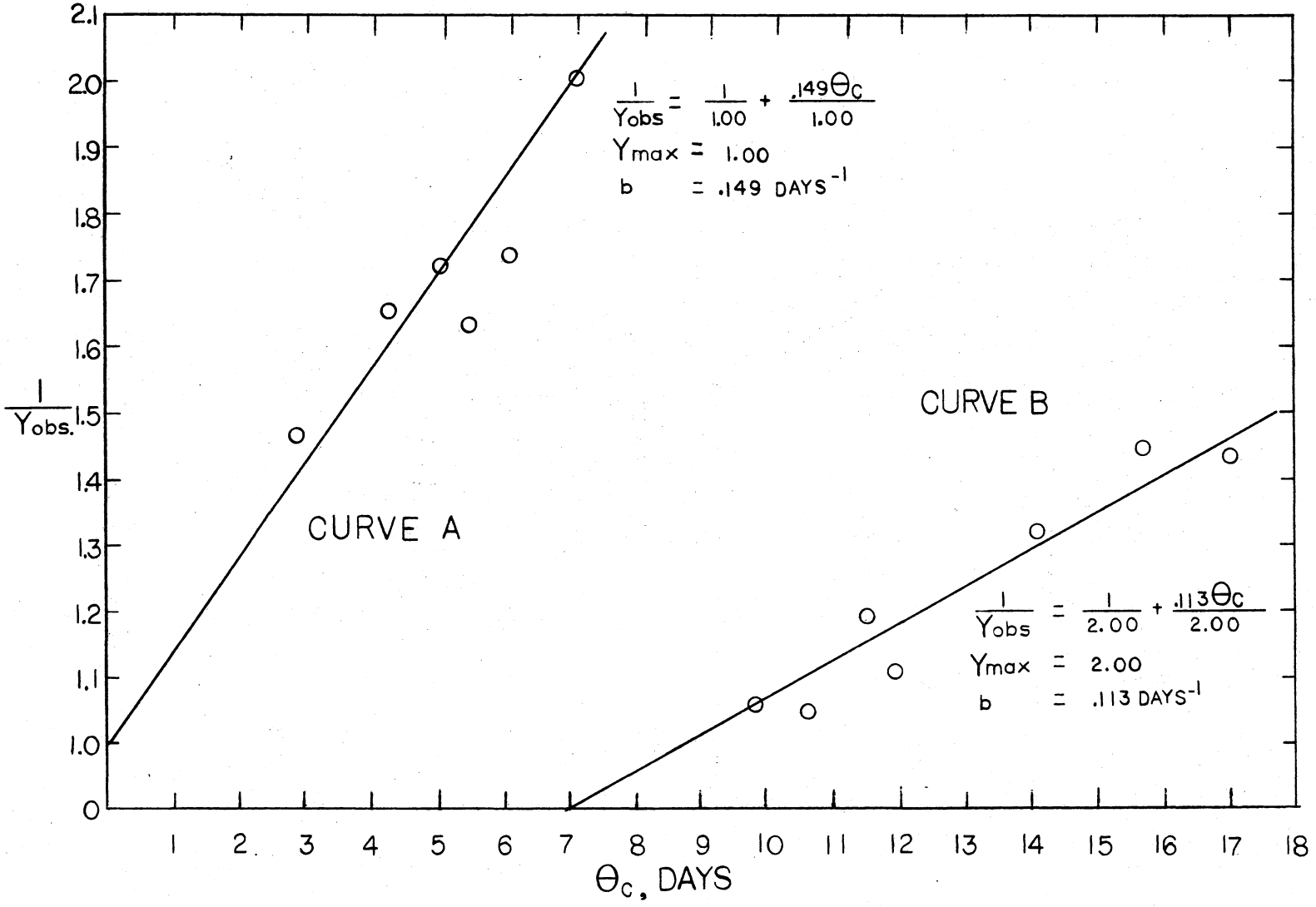

Figure 7. Reciprocal of Observed Yield versus θ_c

A second linear relationship was obtained according to the equation

$$\frac{1}{\theta_c} = YU-b$$

The specific growth rate, $1/\theta_c$, was plotted as a function of specific utilization, U, as shown in Figures 8 and 9. Maximum yield, Y_{max}, is represented by the slope of the straight lines passing through the experimental datum points. The Y-intercepts represent the maintenance energy coefficient, b. The values for Y_{max} were the same as those derived from Figure 7 while the values for b varied only slightly between the two graphs.

C. Specific Utilization

Specific utilization is the rate of the substrate utilized per day and the microorganism concentration. The relationship between specific utilization and mean cell residence time is given in Figure 10. As shown, specific utilization decreases as θ_c increases. Although not as clearly as Figures 6 - 8, Figure 10 does indicate two separate curves with a distinct break occurring between θ_c's of 7.1 and 9.8 days.

D. Food to Microorganism Ratio

The food to microorganism ratio, F:M, is equal to the amount of substrate applied per amount of microorganisms under aeration per day. Figure 11 shows a plot of the F:M ratio vs θ_c. Figure 11 illustrates the same type of a break between 7.1 days θ_c and 9.8 days θ_c as appeared in Figure 9. The decreasing slopes of the two curves in Figure 10 can be explained when considering the change in total MLSS vs θ_c shown in Figure 11. While maintaining C_o and θ as constants, the total MLSS are

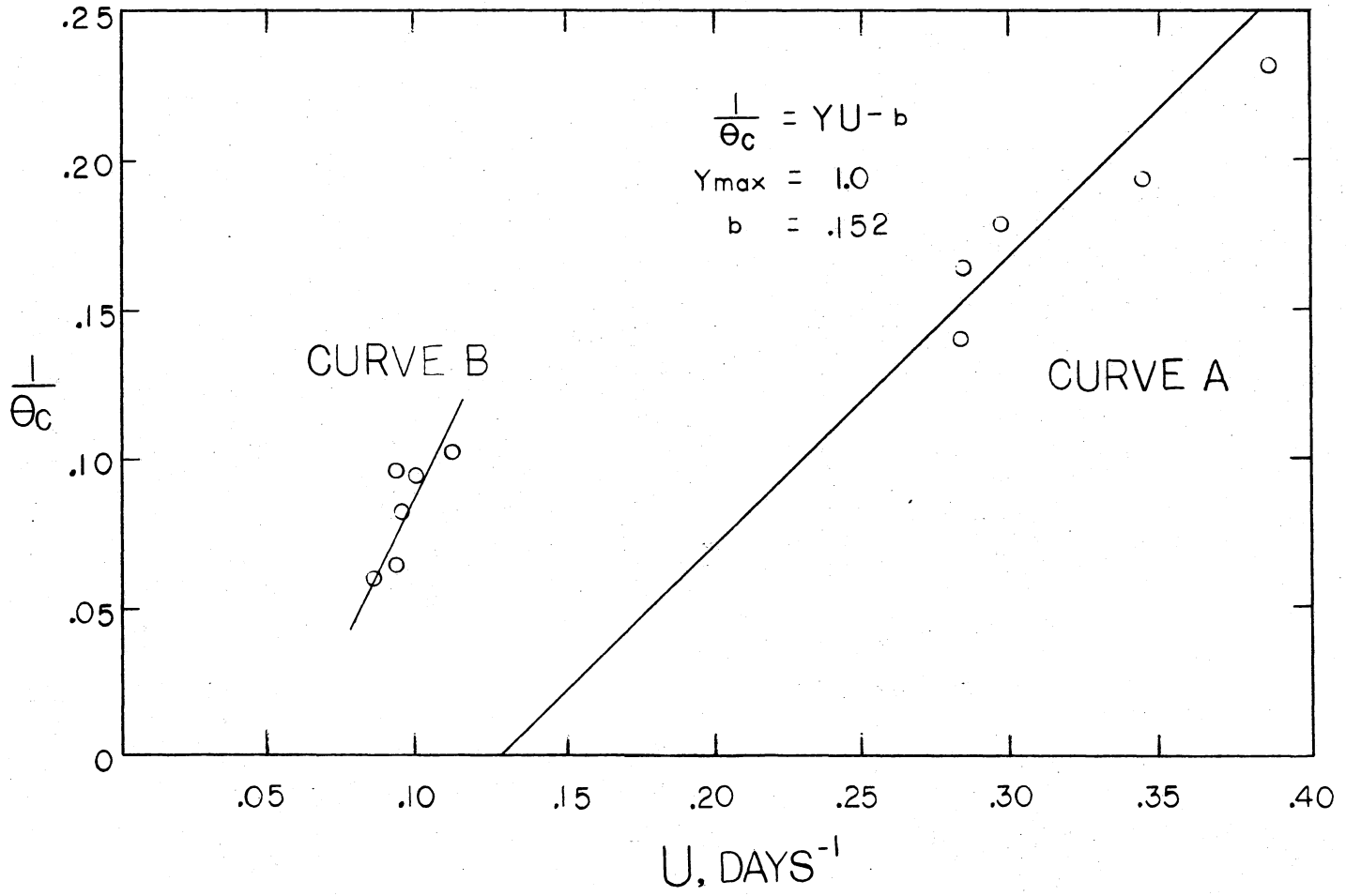

Figure 8. Specific Growth Rate versus Specific Utilization Rate

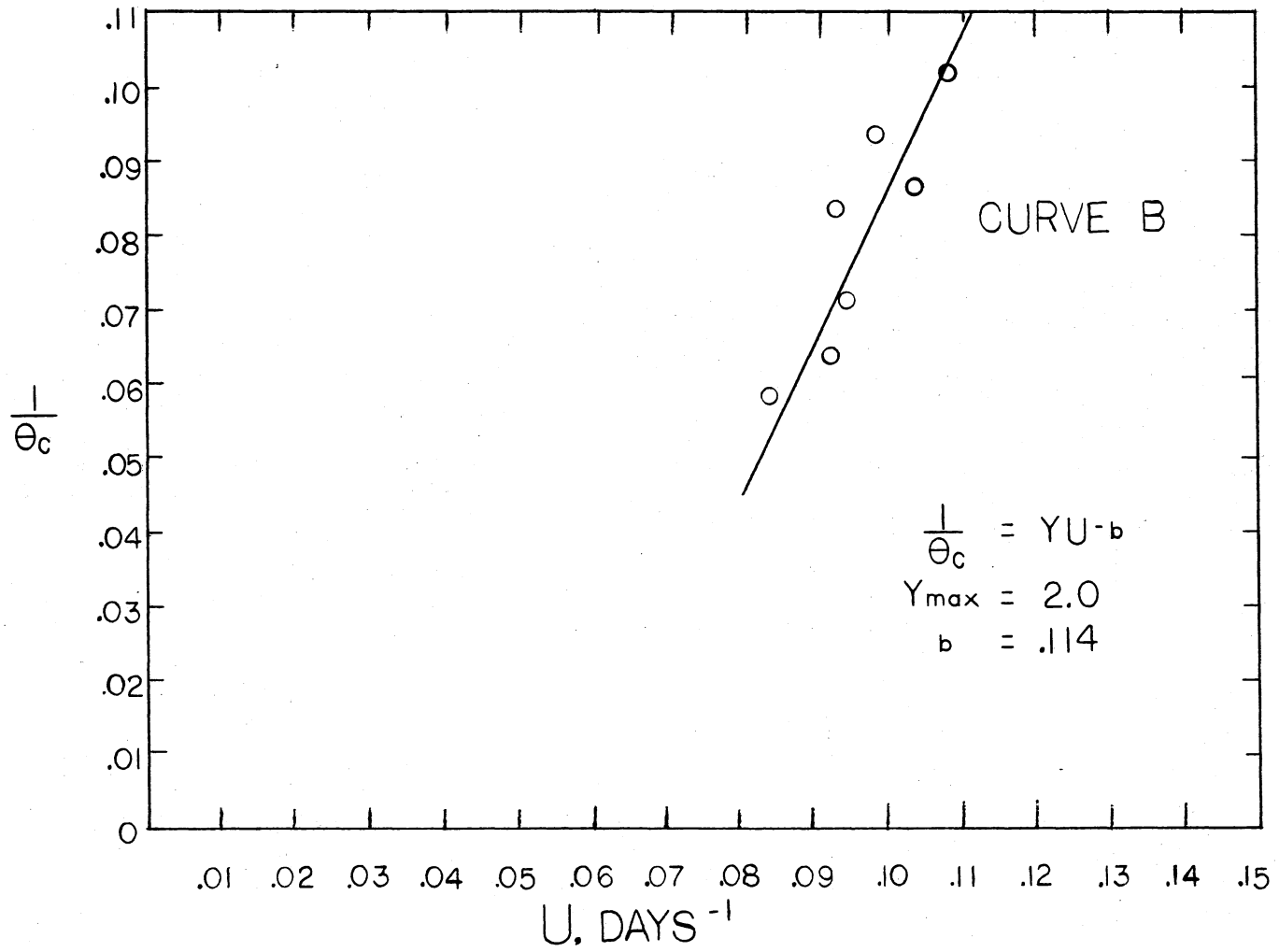

Figure 9. Specific Growth Rate versus Specific Utilization Rate

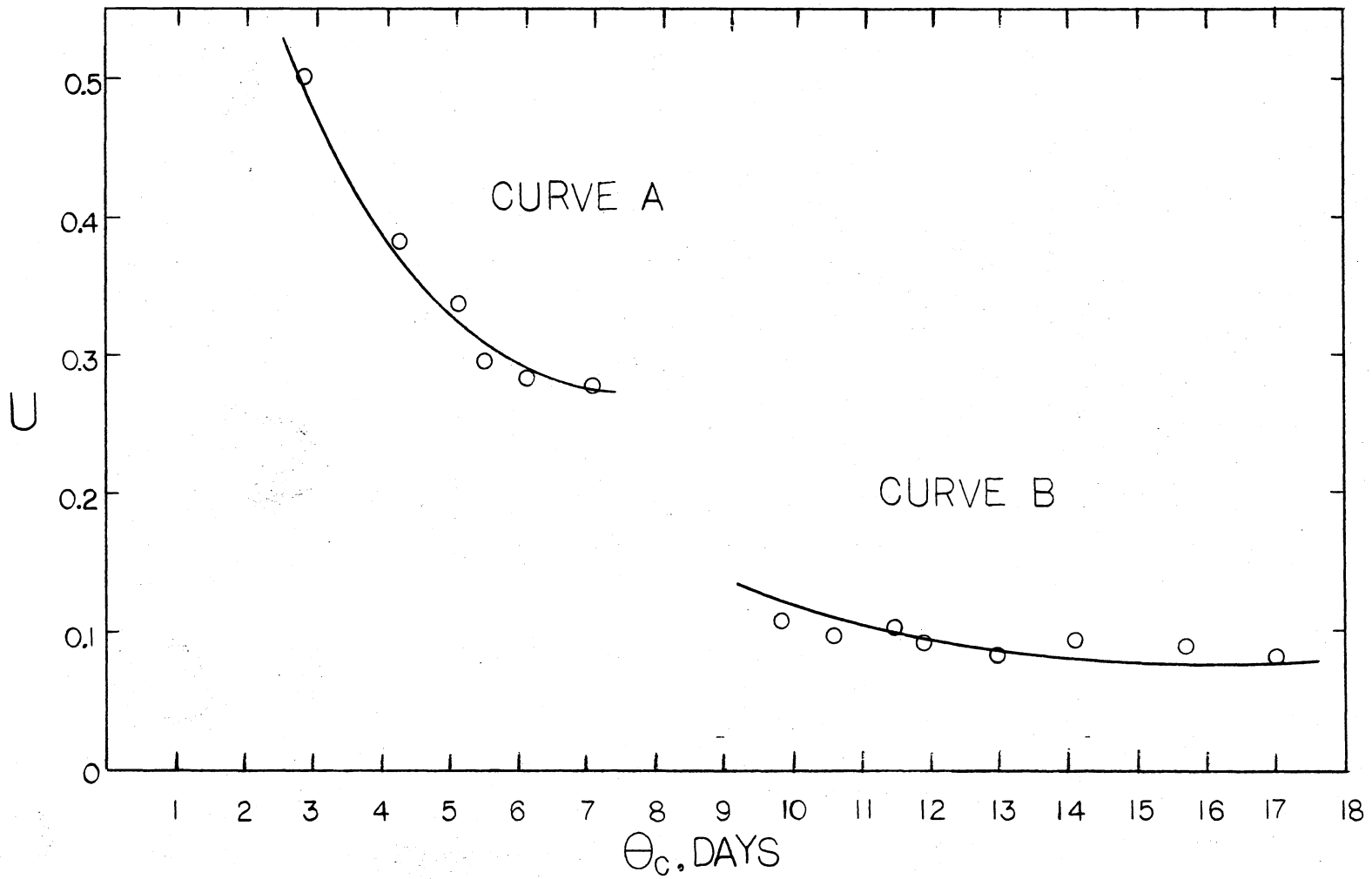

Figure 10. Specific Utilization Rate versus θ_c

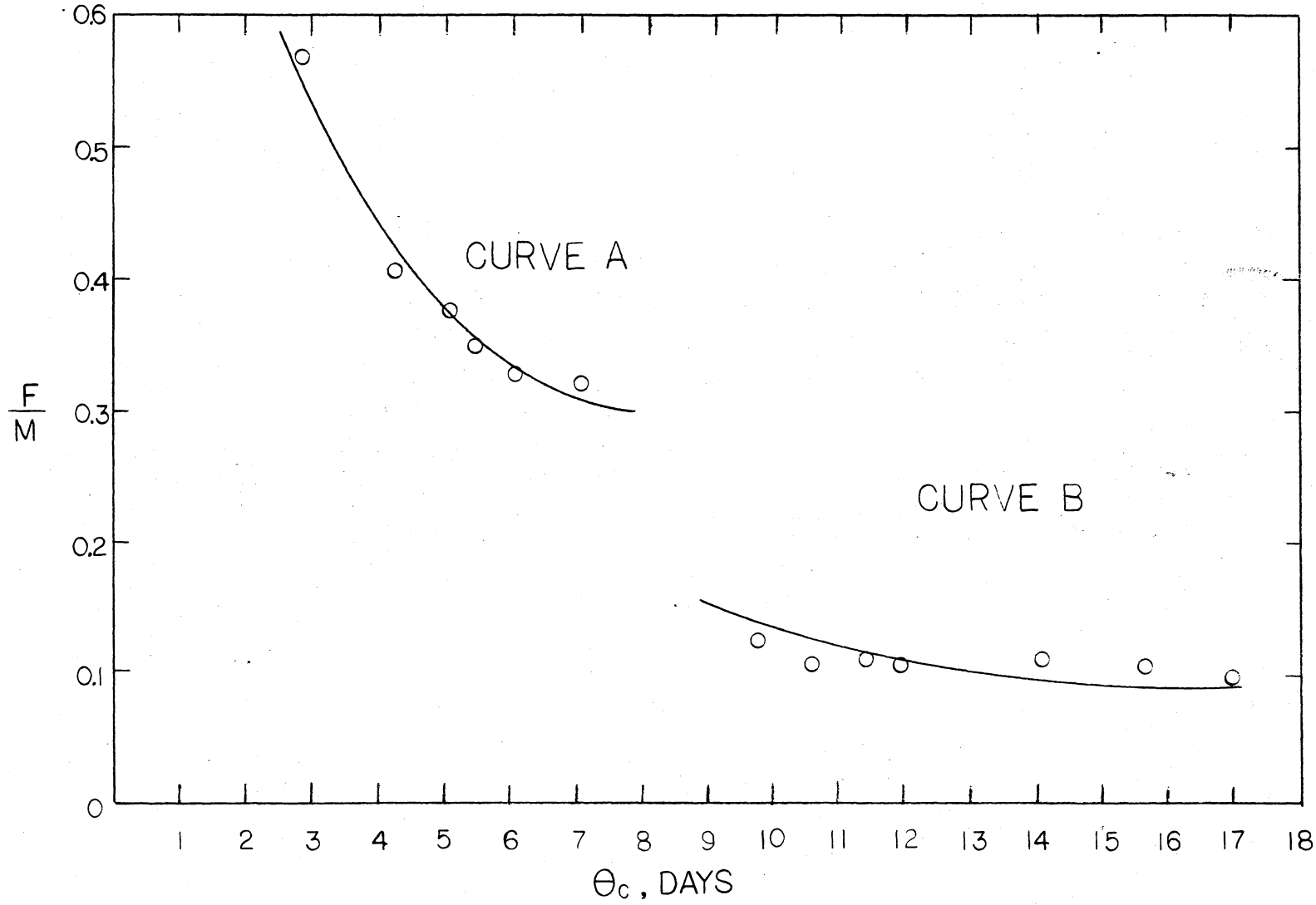

Figure 11. Food to Microorganism Ratio versus θ_c

shown to increase with increases in θ_c.

E. Total Reactor Microorganism Concentration

The relationship between the total reactor microorganism concentration and mean cell residence time is shown in Figure 12. Illustrated very clearly is the existence of two distinct MLSS curves. The predicted values of MLSS calculated from equation (8) are represented by the two solid curves, while the actual observed MLSS concentrations are plotted as points along the curves. The dashed portions of the curves are extensions showing how each curve would have projected had the transition between 7.2 and 9.8 days θ_c not occurred. Figure 12 shows the predicted values and the actual observed values for the total reactor microorganism concentration to correlate very closely when evaluating the two curves independently.

F. Sludge Production

The predicted values of sludge production calculated from equation 9 were compared with the actual values of sludge production observed ($Q_w X_w = Q_{eff} X_{eff}$). Figure 13 shows both the observed and actual values of sludge production and how they relate to θ_c. The two distinct curves are representative of the calculated values while the actual values are plotted as points along the curves. Figure 13 shows there to be an insignificant difference between the predicted values and the actual values. When analyzing the two curves independently, each curve appears to decrease as θ_c increases. This characteristic has been observed in previous works. It is the presence of the two distinct curves which cause Figure 13 to vary greatly from previous investigations.

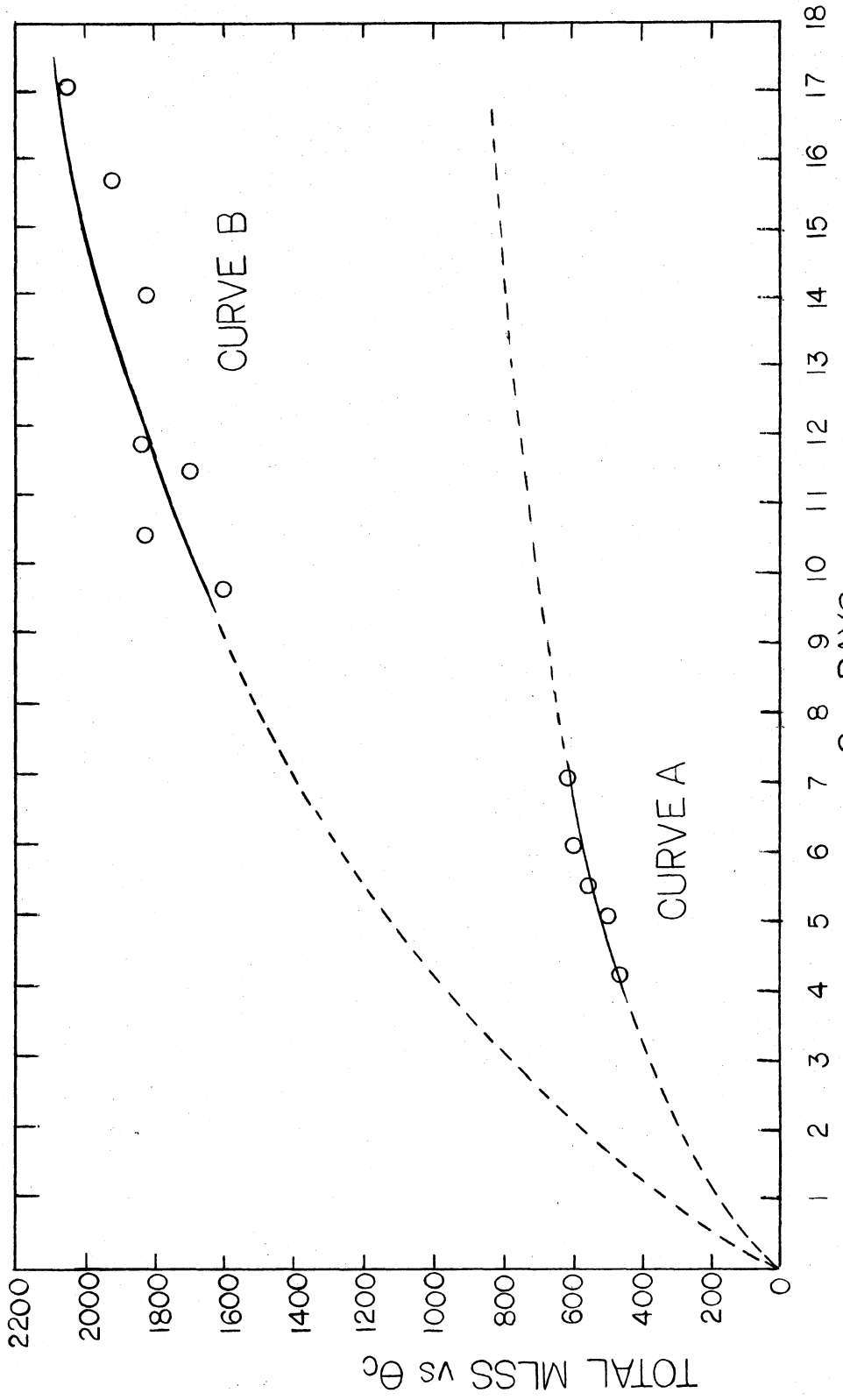

Figure 12. Total MLSS versus θ_c

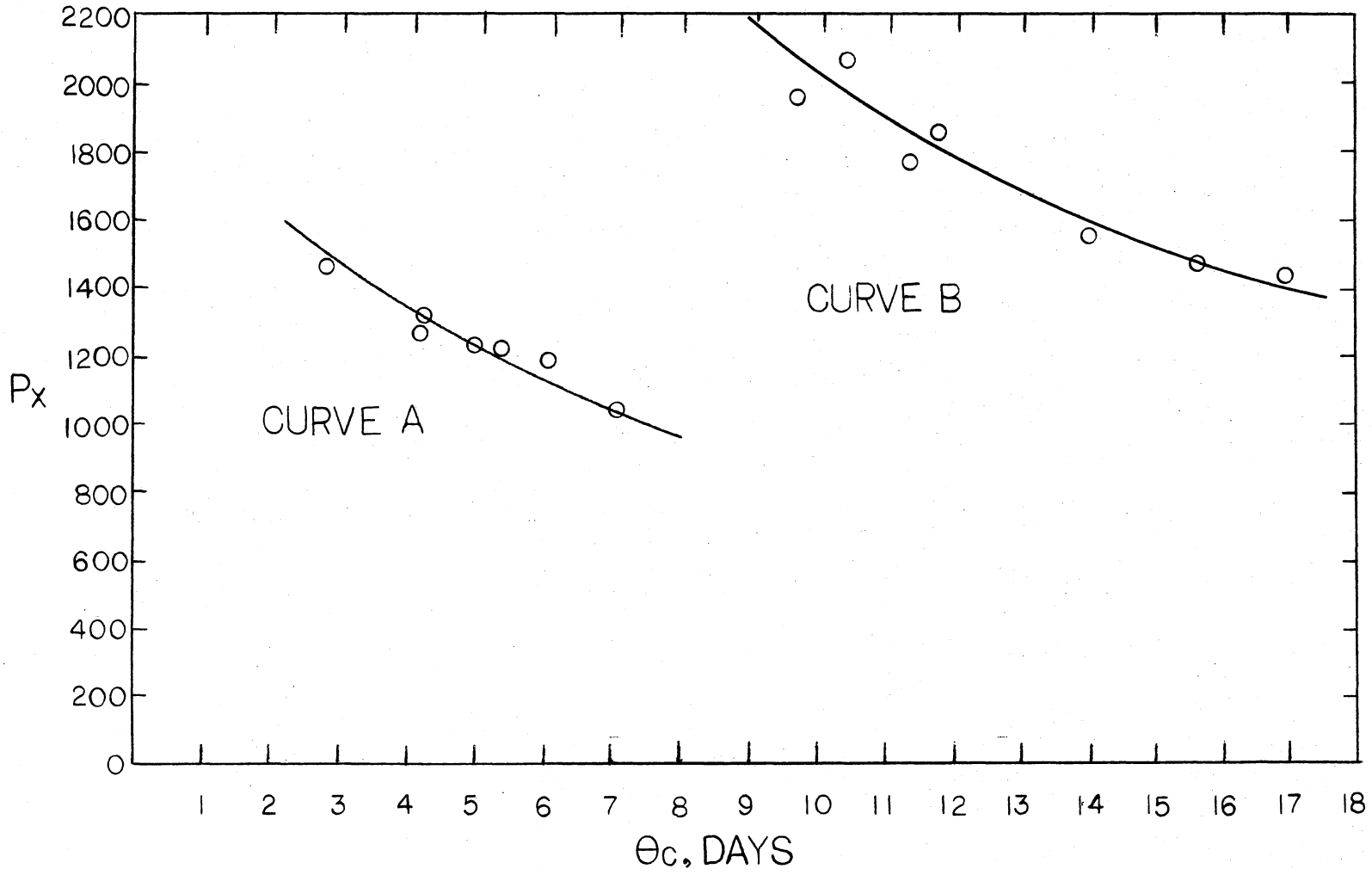

Figure 13. Sludge Production versus θ_c

CHAPTER VI

DISCUSSION

The purpose of this investigation was to apply wastewater kinetics to an activated sludge process which utilized phenol as its sole carbon source. By varying the sludge wastage rate, the operational parameter of mean cell residence time was varied between 2.9 and 17 days.

An analysis of COD removal (Figures 3, 4 & 5) shows, as was previously discussed in the literature review, that it is possible to biologically remove phenol from certain wastewaters while maintaining a relative high efficiency level. This study also illustrates that a relative high efficiency level of 88% can be maintained over the normal operating range for wastewater treatment.

Upon evaluation of the observed yield, Y_{obs}, this investigation takes a new direction from previous works. First, some exceptionally high Y_{obs} values (in excess of 0.9) were observed. The second and most important variation is the fact that two Y_{obs} curves were observed for the system instead of one. Figures 6, 7 & 8 illustrate this fact.

As noted in Figure 6, both curves A and B increase as θ_c is decreased. In one case, Y_{obs} begins to approach 1.0 as θ_c approaches 10 days from higher values. As θ_c was decreased from 9.8 to 7.1 days there was a "transitional drop" in Y_{obs} from 0.96 to 0.5. At 7.1 days Y_{obs} starts increasing as θ_c decreases until it reaches a θ_c of 3.0 days. At three days what appeared to be another transitional phase was experienced.

The yield appeared to reach a peak, drop off, and then begin rising again but washout conditions in the system made it impossible to be sure.

The author would like to mention here that he has no concrete conclusions which can explain the phenomena of the two yield curves, only a few theories of which all, a part, or none may be the case.

A predominance change due to washout conditions was first thought to be the reason for the transitional phase between Curves A and B as θ_c was decreased below 10 days. But when the θ_c was increased back beyond 10 days, the data correlated very closely to the initial data for curve B and was not an extension of Curve A as would been expected if the initial organisms had been washed out in the change. There is the possibility, though, that the organisms went dormant at the lower θ_c's and came back into predominance at the higher θ_c's, as could be the case of certain autotrophic bacteria such as nitrifying organisms.

While most microorganisms obtain their energy from the oxidation of organic matter, the autotrophic bacteria obtain their energy from the oxidation of inorganic compounds. Considering the autotrophs which could have influenced this study, the nitrifying bacteria seem to be the most likely candidate. Although no tests were run to determine the amount of nitrogen in the feed, it can be assumed there was an ample nitrogen supply due to the addition of ammonium sulfate.

Nitrifying organisms do not compete well with heterotrophs except when there is a low concentration of soluble organic matter. For this study, even the initial substrate concentration was small which was then reduced substantially. Thus giving the nitrifyers a chance to compete.

Washout conditions for nitrifyers occur at a θ_c of approximately three days, which may have been the case in this study. A definite

washout was observed at approximately three days.

Nitrifying organisms can maybe explain why Curve B values were duplicated after the θ_c was reduced and then extended back beyond ten days. It has been shown by other studies in the OSU Bioenvironmental Engineering laboratory that nitrifying organisms have the ability to go dormant under certain conditions and then start back up again when the conditions are conducive to their growth.

In reviewing the literature concerning one stage nitrification in the activated sludge process, a ten day θ_c seemed to be a significant value. At this value accomplishment of near complete nitrification along with maximum removal efficiency of soluble organics has been reported. Below the ten day value nitrification has been shown to drop off. It is at this ten day point, though, where the idea of nitrifyers being present in the system becomes a little shakey. Nowhere in the literature was there found a case where there was such a sharp drop in nitrification at ten days as would be necessary to explain what happened in this study. Previous works show nitrification to decrease gradually as θ_c is decreased, until at three days washout conditions occur. In this study there was a sharp transitional drop right below ten days, with a gradual increase in yield until at around three days a washout occurred. Thus the nitrifyers can be used to explain what happened at three days, but it is much more difficult to relate them to the sharp break at ten days.

An important fact which opposes the theory of nitrifyers affecting the system is that the effluent pH was consistently higher than that of the buffered feed, exactly opposite of what would be expected.

There is also the possibility of a shift of a change in the metabolic processes which the microorganisms utilize. This could most

definitely cause a change in the amount of energy an organism could utilize and/or produce. This can only be a guess since only the gross energy reactions are understood and little is known about the exact energy patterns of the organisms.

Specific utilization, U, and the food to microorganism ratio, F:M, were both plotted against θ_c (Figures 10 and 11). The resulting plots of the two graphs were very similar. Both of the graphs had decreasing curves as θ_c was increased which is to be expected. The importance in this study, though, was the fact they illustrated two separate curves with a distinct break occurring between 7.1 and 9.8 days. The separate curves were not as pronounced as in Figures 6 - 9 but the sharp drop is obvious.

Graphs of the microorganism concentration and the amount of sludge produced are shown in Figures 8 and 9, respectively. The observed data appeared to indicate two separate graphs in each case. Theoretical values were then calculated and plotted on the same graphs to help clarify the observed values. The results turned out to be very similar and to also clarify the fact that two microorganism growth curves did exist.

CHAPTER VI

CONCLUSIONS

The operation of a continuous flow activated sludge unit using phenol as the sole carbon source and θ_c as the principal operational parameter has led to the following conclusions:

1. The activated sludge process provided high treatment efficiency for the biological removal of phenol.

2. The effect of θ_c on the effluent quality was insignificant over the normal range of operation.

3. Discontinuous kinetics were observed between 7.1 and 9.8 days θ_c. When plotting Y_{obs} vs θ_c this caused two separate and unique curves.

CHAPTER VII

SUGGESTIONS FOR FUTURE STUDY

Based on the findings of this study, the following suggestions are presented for further studies of phenol removal in the activated sludge process:

1. To study more fully the effects of autotrophic organisms on observed yield values.

2. Conduct studies to determine if the same properties which existed in this study would be present in other systems of biological treatment of phenol (bio-towers, trickling filter, activated sludge with constant X_R).

3. Study the effects that varying substrate concentrations would have on the system.

4. Study the microbial populations and types that exist at different Θ_c's.

5. Study the effects that varying nitrogen concentrations would have on the system.

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APPENDIX

TABLE VI

RAW DATA FOR A 4 LITER/DAY WASTAGE RATE

DATE	SOLIDS			Θ_c	COD		
	TOTAL S.S., mg/1	EFF. S.S. mg/1	WASTE S.S. QwXw, mg	TOTAL SYSTEM Days	FEED mg/1	EFFLUENT mg/1	REMOVAL EFF. %
5-75	400	1	1600	3	131	13	90
	360	6	1440	2.8	137	17	88
	344	1	1376	3	131	13	90
	332	1	1328	3	131	14	89
	312	6	1248	2.8	137	17	88
AVG	350	3	1400	2.9	133	15	89

TABLE VII

RAW DATA FOR A 2 LITER/DAY WASTAGE RATE

DATE	SOLIDS			Θ_c	COD		
	TOTAL S.S., mg/l	EFF. S.S. mg/l	WASTE S.S. QwXw, mg	TOTAL SYSTEM Days	FEED mg/l	EFFLUENT mg/l	REMOVAL EFF. %
10-74	524	8	1048	5.3	127	16	87
	492	10	988	5.1	131	12	91
	540	16	1080	4.9	131	12	91
	536	14	1072	5.0	131	14	89
	504	12	1008	5.0	131	13	90
AVG.	519	12	1038	5.1	130	13	90
2-75	476	30	952	4.0	139	18	87
	480	28	960	4.1	139	18	87
	480	16	960	4.7	139	15	89
	468	16	936	4.7	139	15	89
AVG.	476	23	952	4.3	139	17	88
3-75	544	10	1088	5.2	131	19	86
	552	4	1104	5.7	131	20	85
	572	4	1144	5.7	131	20	85
	576	8	1152	5.4	127	18	86
AVG.	561	7	1122	5.5	130	19	85

TABLE VIII

RAW DATA FOR A 1.5 LITER/DAY WASTAGE RATE

DATE	SOLIDS			Θ_c	COD		
	TOTAL S.S., mg/1	EFF. S.S. mg/1	WASTE S.S. QwXw, mg	TOTAL SYSTEM Days	FEED mg/1	EFFLUENT mg/1	REMOVAL EFF. %
3-75	628	20	942	6.0	135	16	88
	608	18	912	6.0	131	21	84
	604	14	906	6.4	124	18	86
	576	18	864	6.0	133	16	88
	616	14	924	6.4	137	16	89
AVG.	606	17	909	6.1	132	17	87
3-75	608	10	912	6.8	137	16	89
	584	10	876	6.7	130	23	82
	596	10	894	6.8	130	15	88
	612	6	918	7.2	130	15	89
	652	2	978	7.7	130	13	90
	616	4	924	7.5	131	14	89
	632	4	948	7.5	135	15	89
	600	6	900	7.2	135	17	87
	648	8	972	7.0	131	17	87
AVG.	616	7	924	7.1	132	16	88

TABLE IX

RAW DATA FOR A 1 LITER/DAY WASTAGE RATE

DATE	SOLIDS			Θ_c	COD		
	TOTAL S.S., mg/l	EFF. S.S. mg/l	WASTE S.S. QwXw, mg	TOTAL SYSTEM Days	FEED mg/l	EFFLUENT mg/l	REMOVAL EFF. %
8-74	1576	24	1576	9.5	134	23	82
	1580	18	1580	10.1	138	18	87
	1588	24	1588	9.5	134	20	85
	1640	24	1640	9.6	138	18	87
	1648	18	1648	9.9	134	17	88
	1652	16	1652	10.3	127	11	91
AVG.	1614	21	1614	9.8	134	18	87
8-74	1700	12	1700	10.7	131	10	92
	1704	2	1704	11.8	123	12	90
	1752	1	1752	11.9	143	16	89
	1668	1	1668	11.9	131	16	88
AVG.	1706	4	1706	11.5	132	14	89
5-75	1748	12	1748	10.7	127	15	88
	1784	14	1784	10.6	133	6	95
	1800	12	1800	10.8	133	9	93
	1916	14	1916	10.7	128	8	94
	1948	18	1948	10.4	133	8	94
	1844	14	1844	10.3	134	11	92
AVG.	1840	14	1840	10.6	131	10	92
5-75	1760	1	1760	11.9	127	18	86
	1844	1	1844	11.9	127	17	87
	1836	2	1836	11.8	130	11	92
	1920	1	1920	11.9	130	13	90
AVG.	1840	1	1840	11.9	129	15	88

TABLE X

RAW DATA FOR A 0.67 LITER/DAY WASTAGE RATE

DATE	SOLIDS			Θ_c	COD		
	TOTAL S.S., mg/l	EFF. S.S. mg/l	WASTE S.S. QwXw, mg	TOTAL SYSTEM Days	FEED mg/l	EFFLUENT mg/l	REMOVAL EFF. %
8-74	1824	18	1222	14.3	130	20	84
	1860	20	1246	14.0	138	17	88
AVG.	1842	19	1234	14.1	134	19	86
8-74	1836	12	1230	15.3	130	18	86
	1908	10	1278	15.8	142	18	88
	1988	12	1332	15.5	138	13	91
	1948	12	1305	15.5	131	17	87
	1916	8	1284	16.2	127	13	90
AVG.	1919	11	1279	15.7	134	16	88
8-74	2000	4	1340	17.0	127	12	90
	2016	2	1351	17.5	131	14	89
	2004	2	1343	17.5	131	15	88
	2096	6	1404	16.7	131	18	86
	2100	4	1407	17.1	131	14	89
AVG.	2043	4	1369	17.0	130	15	88

VITA[2]

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Master of Science

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