METHODOLOGICAL INVESTIGATION ON WASTE TREATABILITY AND OXIDATION RATE IN BATCH REACTORS

By

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CHAPTER I

INTRODUCTION

It is widely recognized that organic matter contained in effluent streams of municipal and industrial origin cause oxygen depletion in receiving waters due to microbial utilization of the organic matter as carbon source for growth. Thus, there is a growing trend throughout the world to require that such biodegradation of these carbon sources be conducted in well-engineered bioreactors prior to recycling the effluent to the water resource. In the design of such bioreactor plants, e.g., activated sludge plants, it is essential to characterize the organic matter and to determine its "treatability." Prominent among the needed parameters is the measurement of the amount of carbon source in the waste which is available to the microorganisms. In most cases in the past, the 5-day BOD test has been employed. The so-called "ΔCOD" test has recently been recommended, based upon studies conducted in the bioenvironmental engineering laboratories of Oklahoma State University. This test measures the amount of biologically available carbon source in the waste as the difference between initial and final COD when the waste is metabolized by an acclimated population. Thus, it provides a direct measure of the waste strength in terms of carbon source (expressed in terms of O_2 uptake). Also, in these laboratories there has been recent research on an open reactor procedure for measuring the O_2 uptake (i.e., BOD) of a waste in systems of low organic concentration.

The purpose of the present study was to gain insight into practical means of performing treatability studies in batch reactors. The ΔCOD test was employed as a measure of the strength of the waste. In these studies, a synthetic waste of rather high strength and known composition was employed in order to determine the repeatability of results of the test and by estimating the reaction characteristics of the system (the liquid and the batch reactor), and by measuring the dissolved oxygen profile during the course of running the ΔCOD test, it was possible to determine if the open reactor technique could be used to assess the O_2 uptake (BOD exertion) in these high strength systems. It was also the purpose of this study to compare both the ΔCOD results and the O_2 uptake results with results obtained using other analytical techniques for measuring these parameters. The overall aim of the study was to provide practical recommendations for making treatability studies.

CHAPTER II

LITERATURE REVIEW

Since Frankland (1) ran the first modern biochemical oxygen demand (BOD) test in 1870, this test has been widely used to evaluate pollutional strengths of wastewater. But the need for several days' incubation time and low precision and reproducibility made the test totally inadequate for the present day-to-day plant operation. Many investigators have tried to find new methods (2)(3)(4)(5)(6) which can rapidly and accurately determine the pollutional strength of wastes. Most of these methods have found only limited acceptance because they are not rapid enough or they need special, expensive equipment.

Perhaps the conventional chemical oxygen demand (COD) test proposed by Standard Methods for the Examination of Water and Wastewater (7) and the rapid COD test developed by Jeris (8) are the two most practical methods for measuring total organic matter. Using the COD test, it may be possible to establish a relationship between COD and BOD for a specific waste. After determining the relationship, the BOD of a sample may be estimated by the COD:BOD ratio.

These two methods are based upon the fact that all organic compounds, with few exceptions, can be oxidized by the action of strong oxidizing agents under acid conditions. Some chemical compounds which are oxidized in the COD test are not oxidized in the BOD test, or are oxidized to only a small degree. Also, some inorganic compounds are

oxidized by COD, so there are decided limitations to use of the COD test in predicting the BOD value.

In 1960, Symons, McKinney and Hassis suggested an improved method to determine the biological treatability of wastewater (9). They stated that

> ...the change in soluble COD through an activated sludge pilot plant tells exactly what portion of organic matter in the industrial waste is being removed and discounting special cases, this removal is due to biological action only (page 849).

Hiser and Busch (10) have proposed a total biological oxygen demand (T_bOD) test. The T_bOD test clarifies the relationship of the COD and the BOD by showing that the net reduction in soluble COD of a biological mass culture-substrate system is the total biological oxygen demand (T_bOD) of the system. They concluded for the T_bOD test that

> ...it provides a rapid determination of the total biological oxygen demand of soluble organics with a precision of ± 5 to 10 percent. This test also contains an inherent safety factor for the oxygen requirements of a waste (page 515).

Gaudy and Gaudy (11) have also recommended this biological treatability analysis. They noted the amount of organic matter removed in the reactor is the difference between initial (influent) and terminal (effluent) COD value:

$$CPD_i - COD_e = COD \qquad (1)$$

They also defined the term "ΔCOD_t" as the amount of COD removed at any time. When the amount of organic matter cannot be further reduced biologically, then ΔCOD indicates the amount of organic matter in the wastewater which can be removed by microorganisms. Actually, ΔCOD is always greater than ultimate BOD in a waste sample unless "total

oxidation" occurs. The difference is due to the subsequent fate of the microorganisms which were produced from the organic substrate.

In 1963, Van Hall and Stenger (12) introduced a method for measuring the organic carbon present in water, the total organic carbon (TOC) test. This method is especially applicable to small concentrations of 100 mg/l or less of organic matter. The test is performed by injecting a known quantity of sample in a stream of oxygen on a contact catalyst bed. The organic carbon is oxidized to CO_2 and is swept by oxygen through a nondispersive infrared analyzer (sensitized to CO_2) which, in turn, relays a signal to a recorder. This test can be performed very rapidly and is very accurate. It is free of many of the variables inherent in the COD and BOD tests. The correlation between TOC and COD is very good for a specific waste or one for which the chemical components are known. The correlation between TOC and BOD is not so good as TOC and COD, especially when the wastewater contains some complex organic materials (13)(14). For using total carbon as a test parameter, Busch (15) suggested total biologically available carbon (T_bAC) as a term to indicate the biological treatability, which is the net reduction in total carbon of a mass culture system.

In 1966, Busch (15) stated that the biodegradable content of organics in aqueous solutions can be assessed in two ways, by measuring the change in organic content effected by bacterial metabolism, or by measuring the consumption of oxygen by bacteria in affecting the removal of organics. He presented a balance equation for measuring the oxygen requirement, that is, the difference in mixed liquor COD (ΔCOD_{ML}) from the zero time to the point of maximum solids, multiplied by a dilution factor:

$$O_2 \text{ uptake} = DF \times COD_{ML} \quad (2)$$

$$DF = \frac{\text{volume of mixed liquor}}{\text{volume of substrate}}$$

Gaudy and Gaudy (11) present a readily facilitated energy balance, in which all componets of the balance are expressed in terms of oxygen, i.e., as oxygen uptake and COD:

$$\Delta COD_{filtrate} = O_2 \text{ uptake} + \Delta COD_{biological\ solids} \quad (3)$$

or

$$O_2 \text{ uptake} = \Delta COD_{filtrate} - \Delta COD_{biological\ solids} \quad (4)$$

This balance represents the partitioning of the substrate between respiration and synthesis. The COD of biological solids can be determined either by a calculation or by direct measurement. The "theoretical COD" of the cells based on the empirical formula for sludge, $C_5H_7O_2N$, is 1.42 mg COD/mg cells (11), so the above equation can be written as

$$O_2 \text{ uptake} = \Delta COD_{filtrate} - 1.42\ \Delta \text{biological solids} \quad (5)$$

In another paper, Gaudy, et al. (16) presented four ways of approaching the calculation of the energy balance. They also found that the cell composition is greatly affected by operational conditions. Also, with cells of different cell age, the COD of biological solids is different. So, one COD value for all samples of cells may lead to a considerable error in calculation; thus, determination of cell COD by actual measurement is recommended.

In the bioenvironmental laboratories of Oklahoma State University, a series of investigations has been undertaken on determination of the O_2 uptake by monitoring the dissolved oxygen (DO) sag and integrating these data with reaeration rate of the system.

Jennelle and Gaudy (17) compared oxygen uptake in four systems--an open channel, an open stirred reactor, closed bottles, and stirred BOD bottles. In their studies, they found no increase in the rate of oxygen uptake in the stirred closed bottles over the quiescently inoculated BOD bottles. They were not particularly interested in agitation effects, but they did note and study in some detail the effect substrate concentration had in increasing the logarithmic rate of O_2 uptake.

Peil and Gaudy (18) investigated the use of open-stirred reactors for the prediction of oxygen utilization in a receiving stream. They also investigated the effects of reaeration rate (i.e., agitation or mixing) on oxygen uptake, and found that the increases in reaeration rate caused higher oxygen uptake values. The present studies offered an opportunity to assess oxygen utilization in a high energy mass culture system. The O_2 uptake was measured using DO sag and vessel reaeration data, and these results were compared with the oxygen uptake values which were calculated from balance equations of both Gaudy and Busch.

CHAPTER III

MATERIALS AND METHODS

Laboratory Apparatus

The aeration vessel used in these studies consisted of a 20-inch high, 5-inch diameter test tube with rounded bottom. The aeration volume was 3000 ml. A constant compressed air flow of 3000 cc/min was supplied. A Fisher and Porter Model 53 RB 2110 air flow meter was employed to control air flow rate. A plastic tube "tee" with a 3/16-inch diameter was used as a diffuser. This arrangement eliminated clogging by microorganisms, and negated concern over change in head loss during the experiments. In these experiments, it was desired to maintain the reaeration characteristics of the water as constant as possible during any given run. When carborundum diffusers were employed in preliminary experiments, some clogging problems were encountered. A cotton filter was placed in the air line to clean the compressed air. The experimental apparatus is shown in Figure 1.

Composition of Synthetic Waste

Glucose was selected as carbon and energy source in these studies. The daily synthetic wastewater fed to the batch unit was designed to have a chemical oxygen demand (COD) of 1000 milligrams per liter (mg/l). Other required nutrients contained in the wastewater are shown in Table I.

Figure 1. Batch Treatability Study Apparatus

(1) cotton filter

(2) air flow regulator

(3) batch aeration tube

(4) dissolved oxygen probe

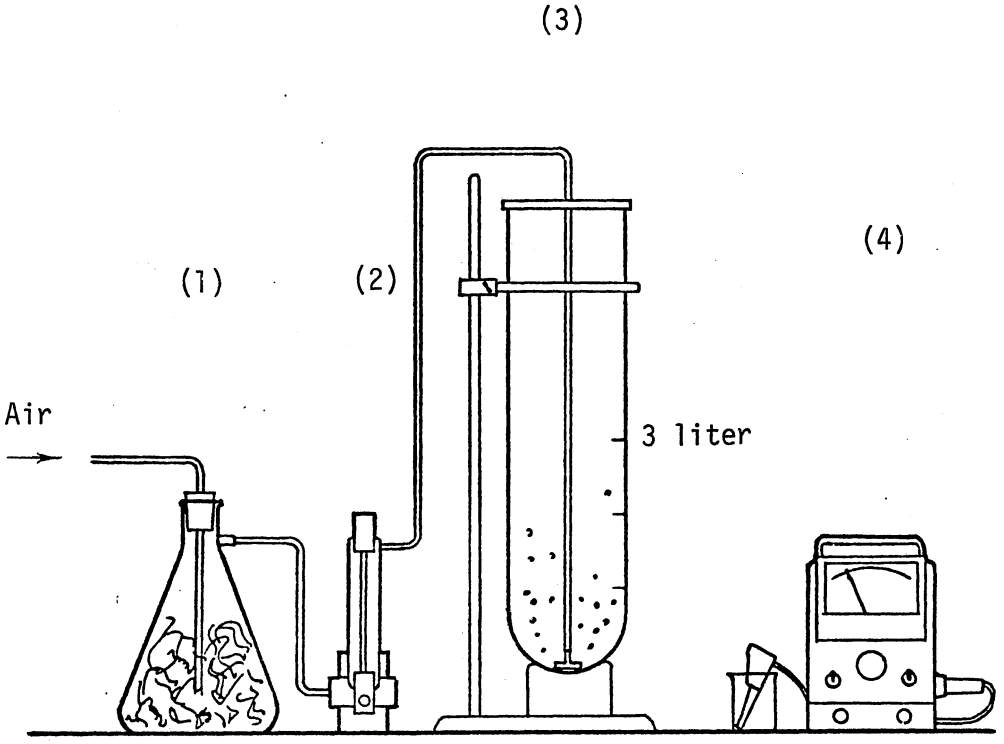

(3)
(1)
(2)
(4)
Air
3 liter

TABLE I

COMPOSITION OF THE WASTE

Constituents	Concentration
Glucose	1000 mg/l
$(NH_4)_2SO_4$	500 mg/l
$MgSO_4 \cdot 7H_2O$	100 mg/l
$FeCl3 \cdot 6H_2O$	0.5 mg/l
$MnSO_4 \cdot H_2O$	10.0 mg/l
$CaCl_2 \cdot 2H_2O$	7.5 mg/l
1.0 M phosphate buffer	100 ml/l
(KH_2PO_4 - 52.7 g/l K_2HPO_4 - 107 g/l)	
Tap water	100 ml/l
Distilled water	to volume

Source of Microbial Populations

The first microbial population employed was that taken over from Mr. Harry Little. This batch activated sludge system was started on January 12, 1974, and terminated on July 9, 1974.

The second population was developed in a batch tube with daily feeding of glucose and necessary nutrients (see Table I). The seeding material was supernatant from an extended aeration pilot plant being operated by Mr. Larry Roach. This population was started on June 10, and terminated on August 23, 1974.

The third batch activated sludge employed was started July 25, and operated through September 27, 1974. The seed was obtained from the primary clarifier of the Stillwater municipal waste treatment plant.

Experimental Procedures

Daily feeding was performed at the same time each day. One-third of the mixed liquor was wasted through a siphoning tube, then aeration was stopped. The cells were allowed to settle for 30 minutes; then another one-third was removed as supernatant. After synthetic waste feed was added, distilled water was added to volume, three liters, and the unit was again aerated.

The pH value of the mixed liquor was maintained at 7.0; pH was checked every day by use of a Beckman Expandomatic SS-2 pH meter. Alkaline solution (sodium hydroxide) was added to the reactor as needed to maintain pH at $7.0 \pm .2$. Every two days, samples were taken before and after feeding. The chemical oxygen demand (COD) and mixed liquor suspended solids (MLSS) were determined to assess the performance of the system. When terminal, i.e., 24-hour, COD value (COD_e) and biological solids concentration were shown to be approximately constant for several days, the system was adjudged to be in "solids balance," and batch studies to measure the rate of COD removal and solids growth were made.

Ten such runs were made during these studies. The food-to-microorganism ratio (F/M) of the experiments ranged from 0.5 to 29. Prior to each run, the MLSS concentration was diluted to yield the desired concentration. The experiment was started immediately after adding the feed. COD and MLSS samples were taken at half-, one-, or two-hour intervals. Dissolved oxygen (DO) readings were taken every one minute

to every 15 minutes, depending upon the rapidity of change of DO. Sampling was continued until the substrate was removed.

Analytical Procedures

Chemical Oxygen Demand

The COD procedure employed was that given in Standard Methods for the Examination of Water and Wastewater (7). Sample sizes were 5, 10, or 20 ml, depending upon estimation of the COD value.

Mixed Liquor Suspended Solids

The biological solids concentrations were determined by the membrane filter technique. A membrane filter (0.45 μ pore size, Millipore Filter Corp., Bedford, Mass.) was dried at 103°C for two hours, cooled to room temperature in a desiccator, and weighed on a Fisher Scientific Company Gram-Atic scale. After vacuum-assessed filtration of a known volume of sample, the filter papers were put back in the oven at 103°C for two hours, cooled to room temperature in a desiccator, and weighed. From the difference of weight before and after filtration, the biological solids concentration could be found.

Dissolved Oxygen

A Weston & Stack dissolved oxygen meter was employed for dissolved oxygen measurements. The meter was calibrated once every two days against the Winkler dissolved oxygen analysis. When taking a DO reading, slight agitation is necessary. When not agitated, the water sample forms a stagnant film of deoxygenated water and acts as an added

diffusion barrier for the dissolved oxygen. Proper agitation reduces this film to a constant minimum thickness (19). The DO was monitored throughout the deoxygenation and recovery periods. The accumulated oxygen uptake was calculated using the reaeration rate (K_2) of this system and the DO profile. The procedure for calculating oxygen uptake is described in the Appendix.

Total Organic Carbon

In the first three experiments, samples were taken for analysis of total organic carbon (TOC). After the COD sample was taken from the filtrate, the remaining filtrate was placed in a small sampling bottle, capped, and kept in a freezer for later TOC analysis. Dilution of the TOC samples was made according to Beckman Company Instructions 1706 (20). Distilled water was used for dilution; it had been stripped of CO_2 by passing Lamp Grade nitrogen through it for 30 minutes. It was then stored in a bottle with an ascarite-filled vent tube.

The TOC sample bottles were covered with parafilm and sent to the Oklahoma State University Zoology Department. Analysis was performed by Ms. Mary Ann Nichol. Her analysis procedure and accuracy in using the Zoology Department's Model 915 Beckman total organic carbon analyzer had been previously checked by the U. S. Environmental Protection Agency personnel at the Robert S. Kerr Laboratory at Ada, Oklahoma.

Mixed Liquor COD

In experiments 6 through 10, mixed liquor COD (COD_{ML}) samples were taken. At various time intervals, known volumes of mixed liquor were placed directly into the COD flasks. The reagents in the flasks were

the same as in the standard COD test; procedures of refluxing and titration were also the same. The sample sizes were 5-, 10-, or 20-ml, depending on the estimated COD_{ML} value.

COD of Biological Solids

The COD of the biological solids was determined in experiments 6 through 10 as the difference in COD of the mixed liquor and of the filtrate. In two experiments the cell COD was also determined by another method. In experiments 9 and 10, instead of taking duplicate MLSS samples each time, one was taken for determining MLSS and the other was used for determining COD of the biological solids. After filtration, the solids on the filter paper was scraped off, put into a sample bottle, and frozen for later processing. After the experiment was finished, the bottle of frozen samples was removed from the freezer, thawed, diluted to 25 ml; five or ten ml of diluted sample were put into COD flasks. The reagents in the COD flasks were the same as in the standard COD test; procedures of refluxing and titration were also the same.

It was desirable to gain some data regarding the efficiency of the scraping procedure. This data was obtained in the following way: after scraping off the solids, the filters were put back in the oven and dried. The differences of weights before and after filtration and scraping were the weights of solids remaining on the filters. The net weight of solids used for measuring COD was the difference of the weight of the MLSS sample and the solids remaining on the filter paper; i.e., the difference of two filters.

Determination of Reaeration Constant

Various investigations (e.g., Eckenfelder, et al. [21], and Poon and Campbell [22]) have found that soluble chemicals and suspended solids in the water could affect the oxygen absorption rate constant. The waste components in the present studies were the same in all experiments, although the waste concentration changed during the course of every experiment. As the waste concentration decreased, the biological solids were utilizing the substrate and increasing in concentration. The increase of solids concentration was considerable during each experiment, and this change could affect the reaeration rate. Since the O_2 uptake values were computed from the DO profile and the reaeration rate data from the reactor (K_2 and C_s), the calculation of O_2 uptake might be improved by adjusting K_2 during each experiment as necessary. After every ΔCOD test, various reaeration tests were run. Some were run on various concentrations of mixed liquor (these were run after experiments 6 through 10), and some were run using distilled water. In addition, special reaeration tests were run at different solids concentrations and different concentrations of inorganic salts in order to obtain enough data to cover a wide variety of conditions of biological solids concentrations and inorganic salts. Since the air flow rate (except for one instance) was always 3000 cc/min, any change in K_2 could be attributed to suspended or dissolved solids added, and to changes in barometric pressure and temperature. The K_2 value from each reaeration test was corrected to 25^o by Streeter's equation (23)

$$K_2(T^oC) = K_2(20^oC) \left[1.0159^{t-20)}\right] \qquad (6)$$

After this correction, these data were plotted as K_2 versus suspended solids concentration and K_2 versus mineral salts concentration, and curves were developed on the plots. When O_2 uptake was calculated, the K_2 values at different suspended solids concentrations were then determined from the K_2 versus SS curve. The procedures for running the reaeration tests are given below.

For reaeration experiments using distilled water, or distilled water plus varying concentrations of inorganic salts, for the synthetic medium, the reactor was cleansed with dichromatic cleaning solution and rinsed with distilled water prior to each test. The DO meter was standardized and calibrated against the Winkler dissolved oxygen analysis. Then three liters of distilled water were put into the reactor. Sufficient sodium sulfite (2.94 mg/l per mg/l DO) along with 0.5 mg/l cobalt chloride catalyst was added to remove the dissolved oxygen. When dissolved oxygen was totally removed, desired salts, buffer, and nitrogen were added in amounts proportional to those indicated in Table I. In these experiments, glucose was not added. After aeration was started, the DO readings were recorded at 15 seconds to one minute intervals until a constant value was attained. Temperature and air flow rate were monitored during the test. By using the Table of Solubility of Oxygen in Water given in Standard Methods (7), the saturation dissolved oxygen (C_s) was estimated and adjusted for the temperature and atmospheric pressure during the reaeration run. The dissolved oxygen deficit was found by subtracting dissolved oxygen levels from saturation DO. These values were plotted versus time on semilogarithmic graph paper. Data on the graph paper were adjusted using the α Method (24) until correct saturation DO was found. A straight line through all the

points was plotted; the slope of this line was K_2, the reaeration rate constant.

Reaeration studies in the presence of biological solids were run in essentially the same way as those with distilled water and salts. However, these studies were run using spent synthetic medium, i.e., medium after the substrate had been removed by the microorganisms. Thus, inorganic salts (Table I) were not present. The concentration of biological solids was adjusted in each experiment so as to give a range of solids concentrations. Also, Clorox was added to the reactor to kill the microorganisms. Preliminary tests on the Warburg respirometer (by P. Reddy) indicated that a concentration of 2.4 mg/l of Clorox was ample for killing 100 mg/l of microorganisms. After adding Clorox, the unit was mixed well for 4-6 hours using a magnetic stirrer. Sufficient sodium sulfite (2.94 mg/l per one mg/l DO) along with 0.5 mg/l cobalt chloride catalyst was added to remove the dissolved oxygen, and the reaeration test was conducted as previously described.

CHAPTER IV

RESULTS

Daily values of COD and MLSS before and after feeding were measured to ascertain that the terminal COD (COD_e) had been nearly constant and an acclimated microbial population had been developed before a kinetic test of substrate removal and growth was begun. Data for several days before each experiment are shown in Figures 2 and 3. Values of COD_e ranged from 20-40 mg/l. The efficiency of COD removal based on filtrate COD varied from 96 to 98.2 percent. During operation of the batch pilot plant in preparation for experiments 1 through 5, a record of daily solids wasting was kept. Wastage was measured as the difference in suspended solids concentration before and after the daily feeding protocol. Solids wastage was 28 to 35 percent; daily solids production was 550 to 620 mg/l. The data shown in the figures indicate that a fairly constant COD_e and biological solids production was attained, i.e., the system had reached a balanced condition prior to using the cells in a ΔCOD test.

During the first three ΔCOD experiments, an attempt was made to find a correlation between COD and TOC, using glucose as the organic carbon source. The COD and TOC data were plotted versus aeration time. The theoretical COD, which was computed by multiplying the measured TOC value by 2.67 (calculated ratio of COD and TOC for glucose), was plotted on the graphs.

The results of experiment 1 are shown in Figure 4. The initial COD

Figure 2. Performance of the Batch Activated Sludge Unit From 5-11-74 to 7-22-74

Initial COD ○

Terminal COD ●

Initial MLSS △

Terminal MLSS ▲

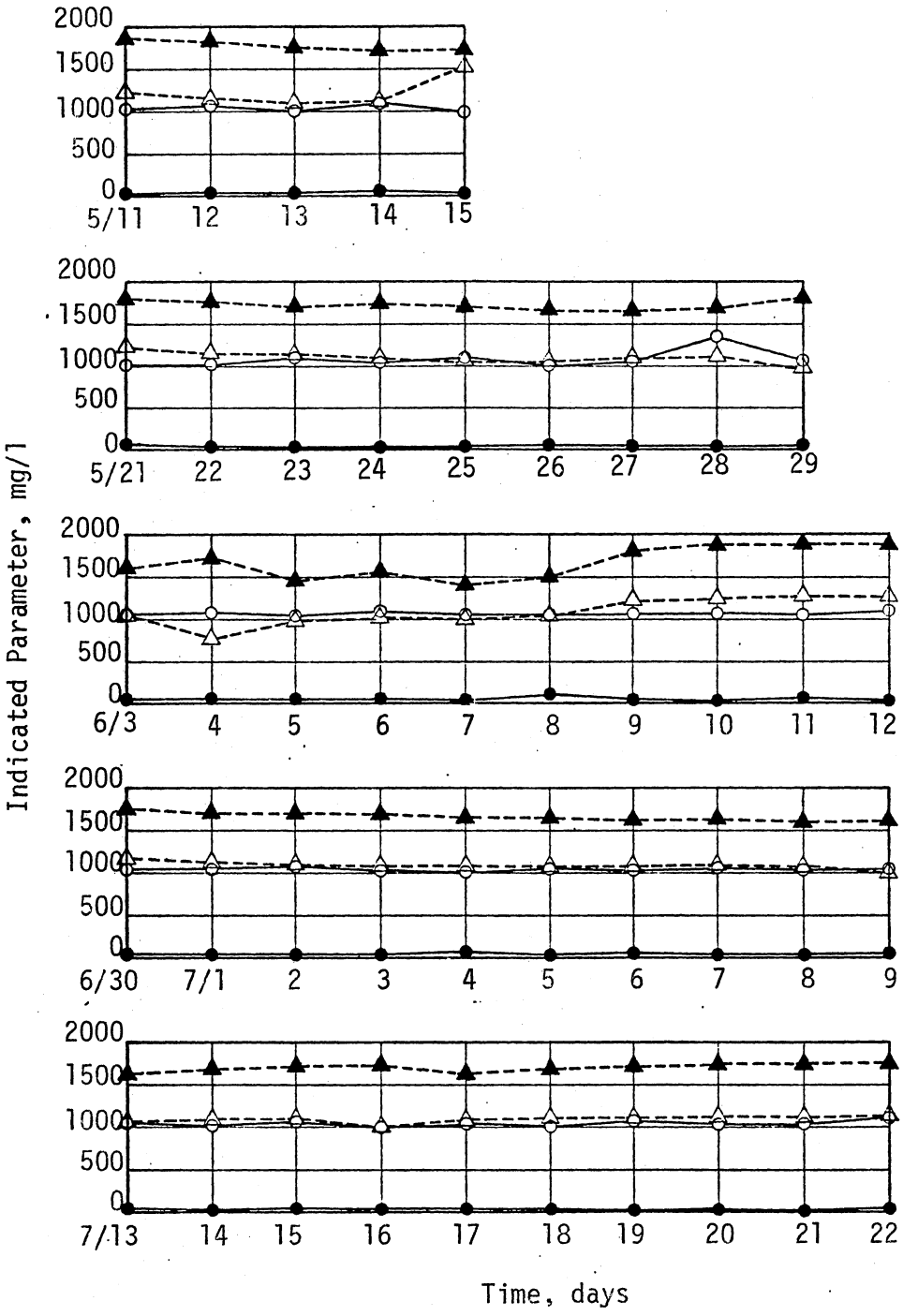

Indicated Parameter, mg/l
2000
1500
1000
500
0
5/11 12 13 14 15
5/21 22 23 24 25 26 27 28 29
6/3 4 5 6 7 8 9 10 11 12
6/30 7/1 2 3 4 5 6 7 8 9
7/13 14 15 16 17 18 19 20 21 22
Time, days

Figure 3. Performance of the Batch Activated Sludge Unit From 7-23-74 to 9-25-74

Initial COD ○

Terminal COD ●

Initial MLSS △

Terminal MLSS ▲

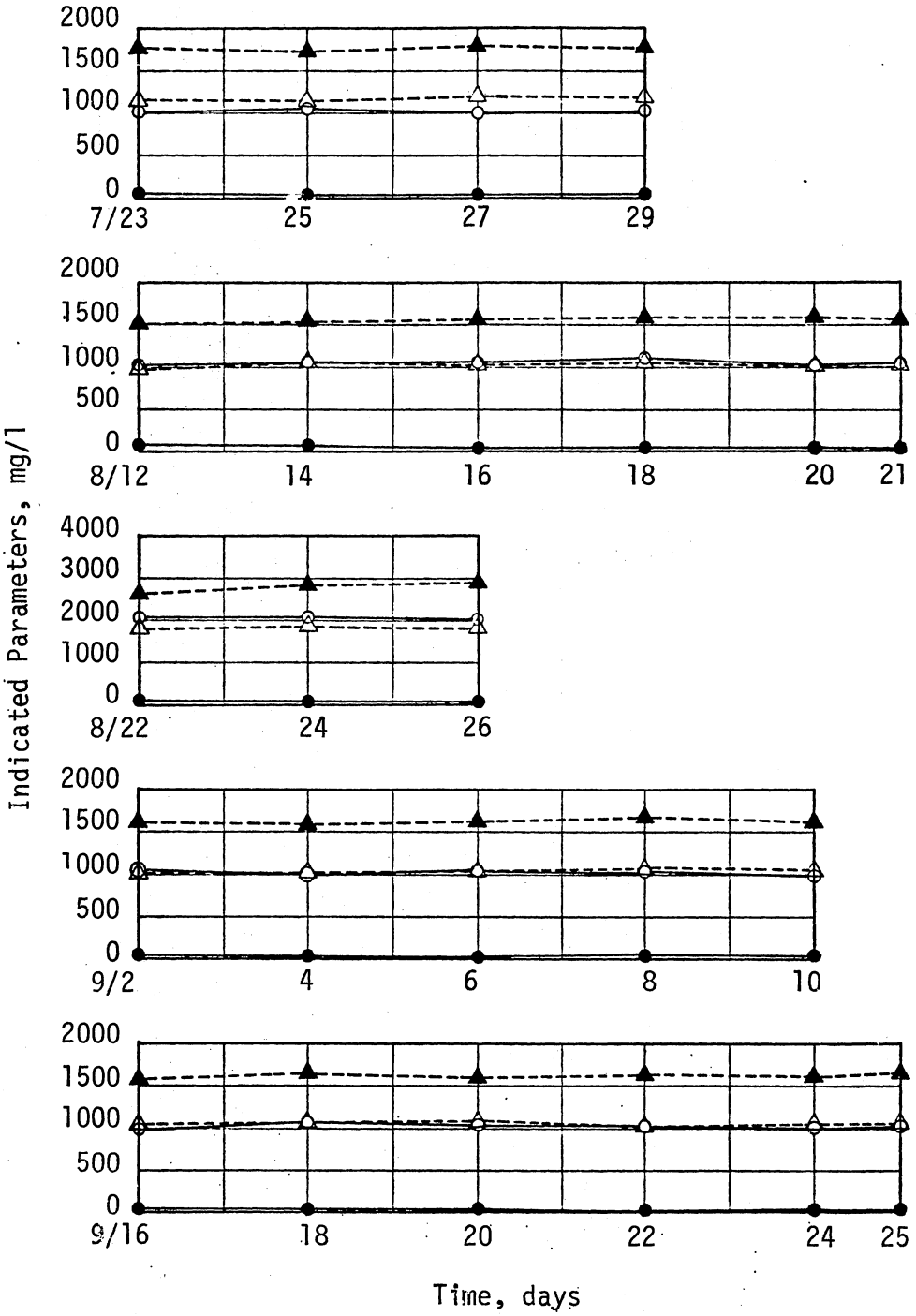

Indicated Parameters, mg/l
2000
1500
1000
500
0
7/23
25
27
29
2000
1500
1000
500
0
8/12
14
16
18
20
21
4000
3000
2000
1000
0
8/22
24
26
2000
1500
1000
500
0
9/2
4
6
8
10
2000
1500
1000
500
0
9/16
18
20
22
24
25
Time, days

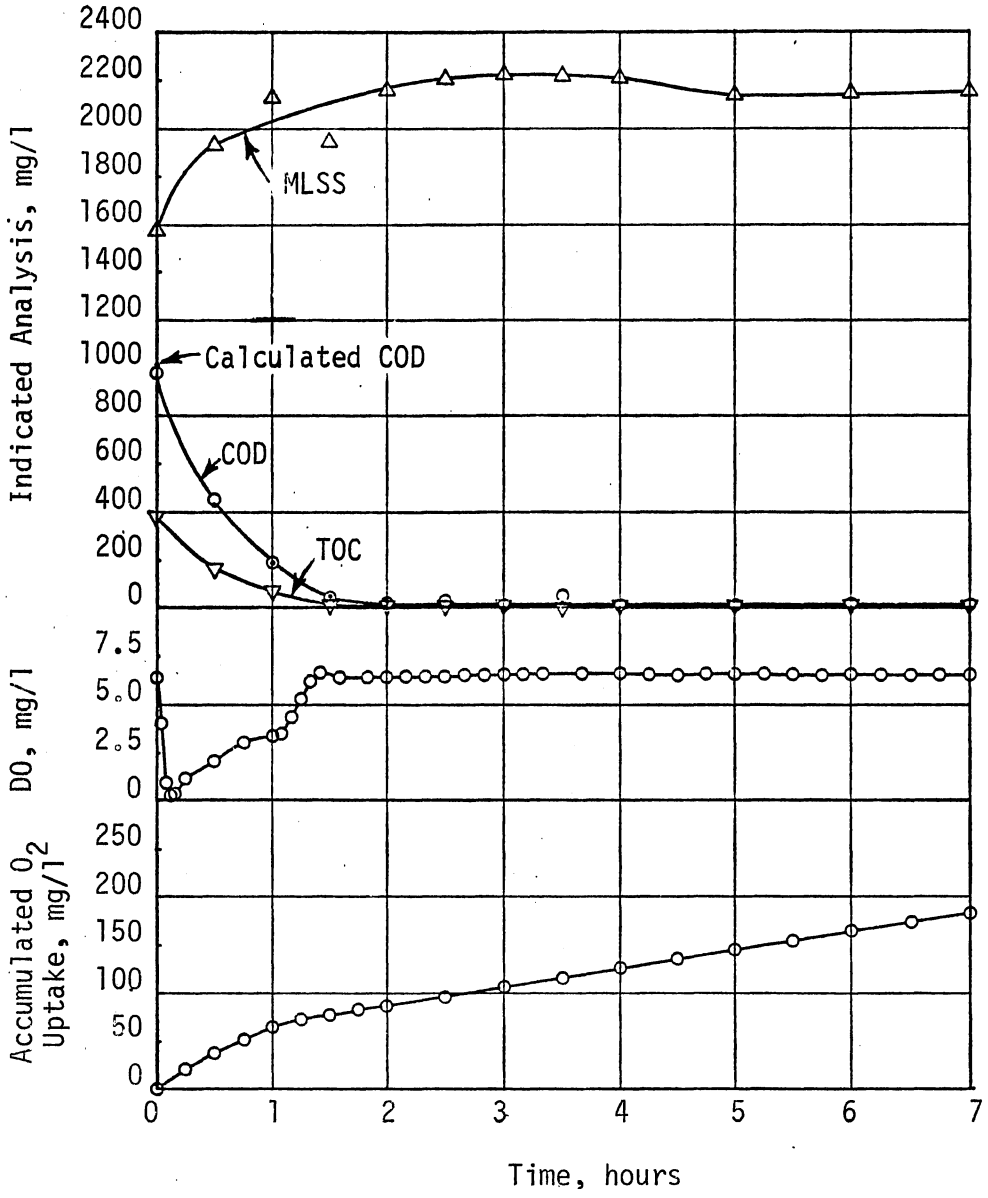
Figure 4. Dissolved Oxygen Profile, O_2 Uptake, COD, MLSS, and TOC vs Time for Experiment 1

Initial Conditions:

F/M = 0.6
COD = 980 mg/l
TOC = 377 mg/l
MLSS = 1564 mg/l

Reaeration Constants:

K_2 = 0.1320 min^{-1} from 0 hr 0 min to 0 hr 9 min
K_2 = 0.1680 min^{-1} from 0 hr 9 min to 0 hr 30 min
K_2 = 0.1654 min^{-1} from 0 hr 30 min to 7 hr 0 min


Indicated Analysis, mg/l
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
MLSS
Calculated COD
COD
TOC
DO, mg/l
7.5
5.0
2.5
0
Accumulated O_2 Uptake, mg/l
250
200
150
100
50
0
0
1
2
3
4
5
6
7
Time, hours

(COD_i) was 980 mg/l; the corresponding TOC_i was 377 mg/l. Thus, the COD/TOC ratio was 2.6 at the start. At the first hour, the average ratio was 2.68. By the second hour, the organic matter was essentially removed; the COD/TOC ratio was decreased to 2.22. After three hours, the ratio was 1.76 on average. The lower portion of the figure showing the DO profile and the calculated O_2 uptake will be commented upon later.

The results of experiment 2 are shown in Figure 5. The COD_i was 1023 mg/l; the TOC_i was 411 mg/l. The COD/TOC ratios were lower in this experiment than in the previous one; the average ratio in the first two hours was 2.44. After substrate removal, the average ratio decreased to 2.17. Theoretical (calculated) COD values were compiled by multiplying results of the TOC analyses by the theoretical COD/TOC ratio for glucose, 2.67. In general, the calculated COD was slightly higher than the measured COD.

The results of experiment 3 are shown in Figure 6. Although the TOC_i was the same as in experiment 2, the initial COD was higher (COD_i = 1077 mg/l). The average COD/TOC ratio during the first two hours was 2.61, i.e., these compared well with experiment 1, and these values are close to the theoretical values. As in the previous experiments, after the organic matter had been utilized, the ratio decreased (average = 1.22).

In addition to TOC analysis, COD and MLSS data were also taken on dissolved oxygen, from which the BOD curve was computed. O_2 uptake was also computed from the COD and MLSS data.

In experiments 1 through 5 (Figures 4 through 8), O_2 uptake was also computed, using the energy balance concept of Gaudy, et al. (11)

Figure 5. Dissolved Oxygen Profile, O_2 Uptake, COD, MLSS, and TOC vs Time for Experiment 2

Initial Conditions:

F/M = 1.0
COD = 1023 mg/l
TOC = 411 mg/l
MLSS = 986 mg/l

Reaeration Constants:

$K_2 = 0.1325\ min^{-1}$ from 0 hr 0 min
$K_2 = 0.1304\ min^{-1}$ from 0 hr 10 min to 7 hr 0 min

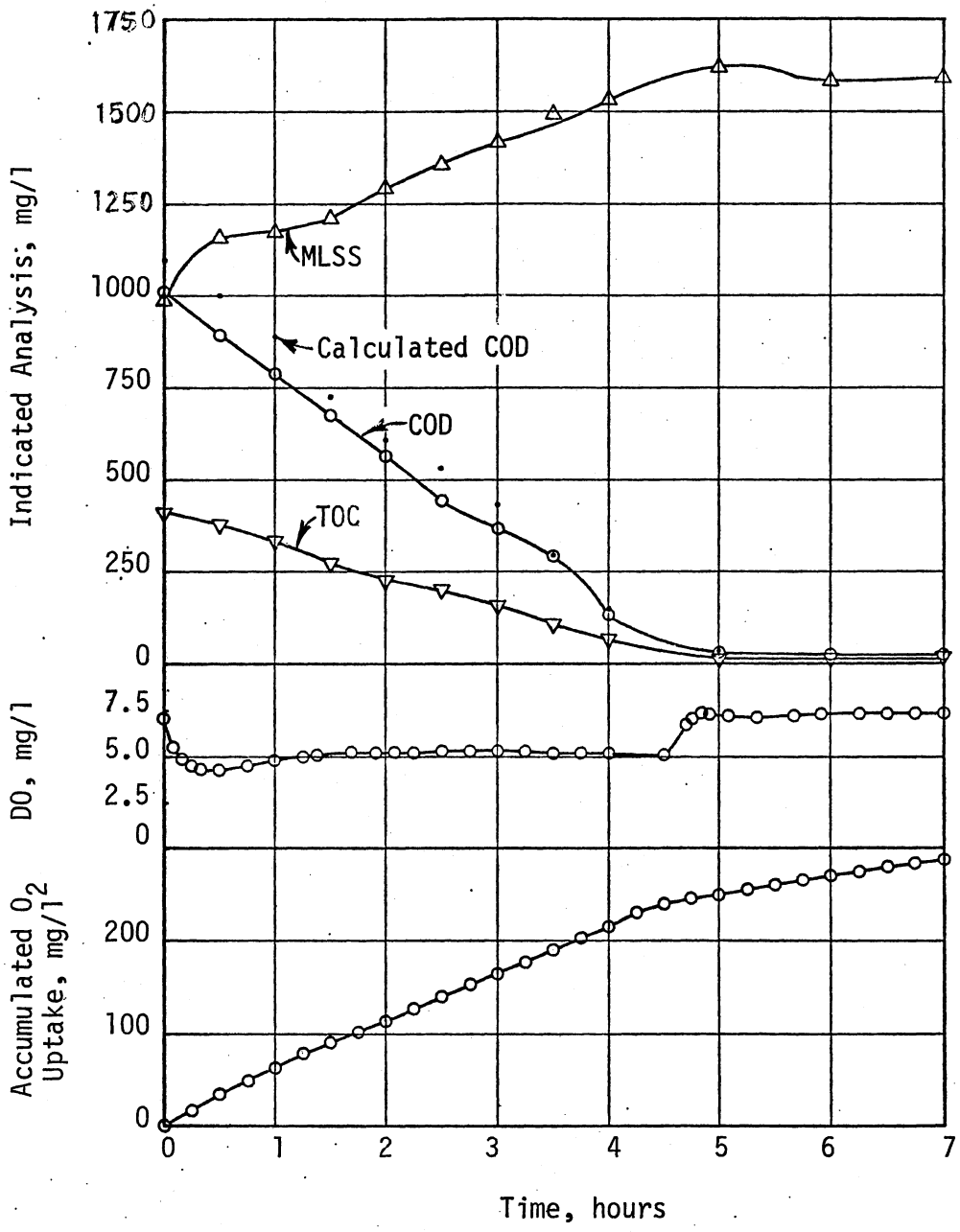

1750
1500
1250
1000
750
500
250
0
MLSS
Calculated COD
COD
TOC
Indicated Analysis, mg/l
7.5
5.0
2.5
0
DO, mg/l
200
100
0
Accumulated O_2 Uptake, mg/l
0
1
2
3
4
5
6
7
Time, hours

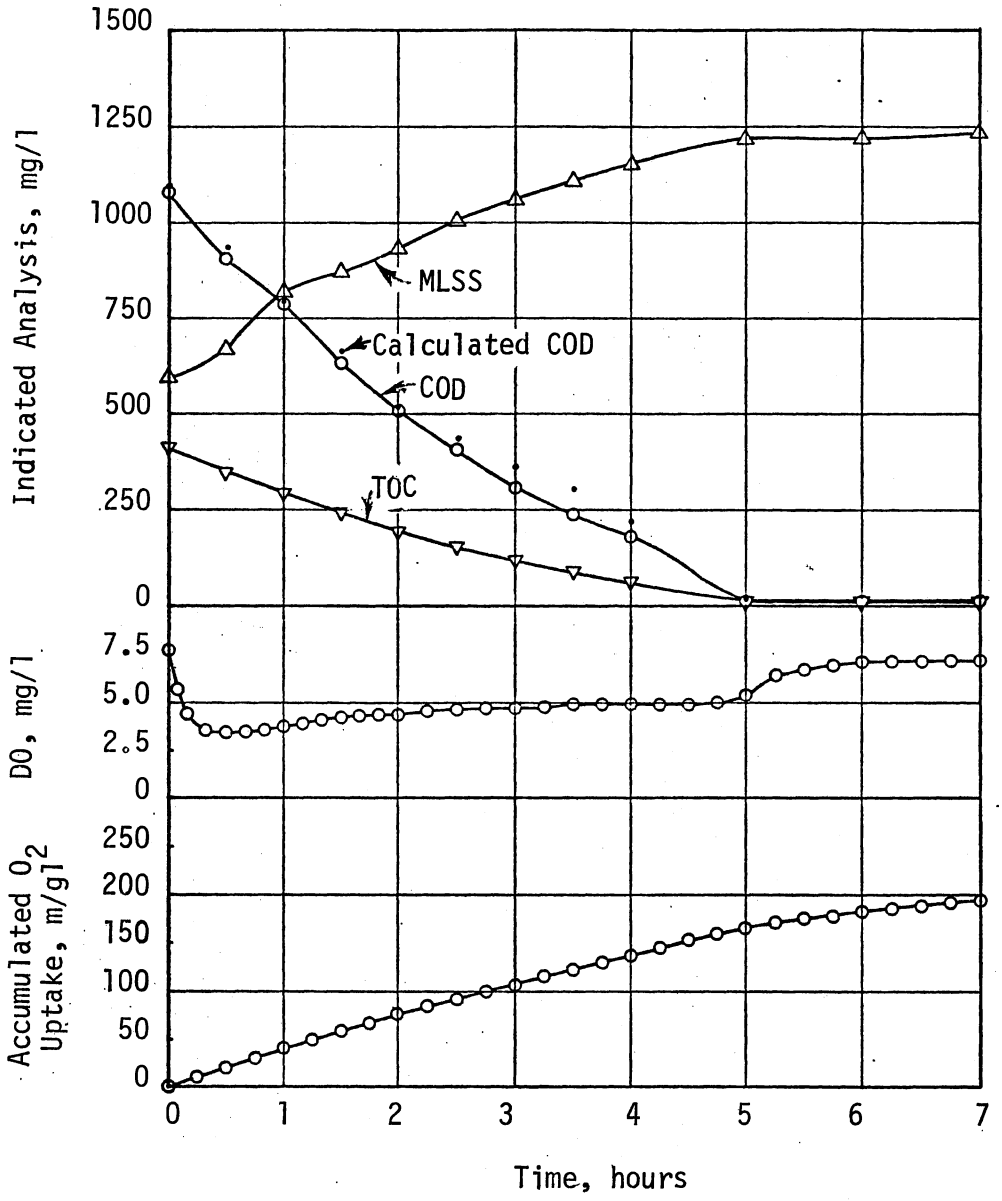
Figure 6. Dissolved Oxygen Profile, O_2 Uptake, COD, and MLSS vs Time for Experiment 3

Initial Conditions:

F/M = 1.8
COD = 1077 mg/l
TOC = 411 mg/l
MLSS = 592 mg/l

Reaeration Constant:

$K_2 = 0.1298\ min^{-1}$


1500
1250
1000
750
500
250
0
Indicated Analysis, mg/l
MLSS
Calculated COD
COD
TOC
7.5
5.0
2.5
0
DO, mg/l
250
200
150
100
50
0
Accumulated O_2 Uptake, m/gl
0
1
2
3
4
5
6
7
Time, hours

(see equation 3), but with a cell COD factor of 1.42 mg COD/mg cells. In the remaining experiments, the actual COD of the cells was measured, thus the O_2 uptake could also be assessed by this means.

In experiment 1 (Figure 4), the initial soluble organic substrate concentration was 980 mg/l COD. After a 2-hour period for substrate removal, 960 mg/l of COD had been utilized. Initial biological solids concentration was 1564 mg/l. The solids concentration reached a maximum after three hours; the net microbial growth (ΔX or ΔMLSS) was 661 mg/l. Oxygen uptake computed using equation 3 was equal to 114 mg/l at the end of the substrate removal period.

In Figure 4 it can be seen that the DO profile exhibited a very sharp deoxygenation phase. Thus, at the ninth minute, the air flow rate was increased from 3000 cc/min to 4000 cc/min to stop the rapid decrease in dissolved oxygen. Between the 65th minute and the 85th minute, the dissolved oxygen recovered rapidly and then it came to a constant value. It is seen that the resulting O_2 uptake curve did not follow a first order increasing rate during the substrate removal phase. The O_2 uptake curve followed first order-like kinetics with a slowly decreasing rate until the 65th minute; following this, the rate was of zero order. The O_2 uptake value shown on the curve is 87 mg/l at the second hour, i.e., at the time of substrate removal.

In experiment 2, Figure 5, the COD_i was 1023 mg/l, and the initial MLSS (X_i) was 986 mg/l. After 4.5 hours, 975 mg/l of COD was utilized by the microbial population, and 632 mg/l of microorganisms had grown. The dissolved oxygen decreased rapidly at the start. The maximum sag occurred from the 11th minute through the 15th minute at a deficit of 4.32 mg/l (DO = 4.3 mg/l). The DO recovered slowly until the 100th

minute, and then remained at 5.2 mg/l. After the substrate was removed, the DO increased sharply within 26 minutes, and remained constant thereafter. At the end of the substrate removal period, the O_2 uptake was 121 mg/l, and the O_2 uptake measured using the materials balance principle was 124 mg/l. For the experimental results shown in Figure 6 (experiment 3), the COD_i was 1077 mg/l after the 5-hour substrate utilization period; 1065 mg/l of COD had been removed. Initial MLSS was 592 mg/l, the biological solids increased during the substrate removal phase, and at the time of substrate removal, a level of 1212 mg/l was attained (ΔX = 650 mg/l). Computed O_2 uptake (mass balance) was 142 mg/l at the fifth hour.

After starting the experiment, the DO dropped to the minimum value (DO = 3.45 mg/l) in 30 minutes, and then began a long sag, lasting almost five hours. The O_2 uptake curve is similar to that shown in Figure 5. The O_2 uptake at five hours was 166 mg/l.

Experiment 4 (shown in Figure 7) was conducted at a higher F/M ratio (10) than the previous experiments. Initial COD was 1038 mg/l and initial MLSS was only 108 mg/l. The rates of microbial growth and substrate utilization were rather slow. It took 17 hours to attain substrate removal, and a biomass yield (0.41) was computed. A small DO sag is shown on the DO profile. The maximum deficit was only 2.8 mg/l (DO = 5.4 mg/l). The O_2 utilization increased at a slow rate commensurate with slowness of the increase in biomass and decrease of COD. Between the 14th and 16th hours, there was a short-lived, relatively rapid increase in biomass concentration, which was reflected in the DO profile and thus in the O_2 uptake curve. The O_2 uptake was 238 mg/l at the end of the substrate removal period. Computed by equation 3, the

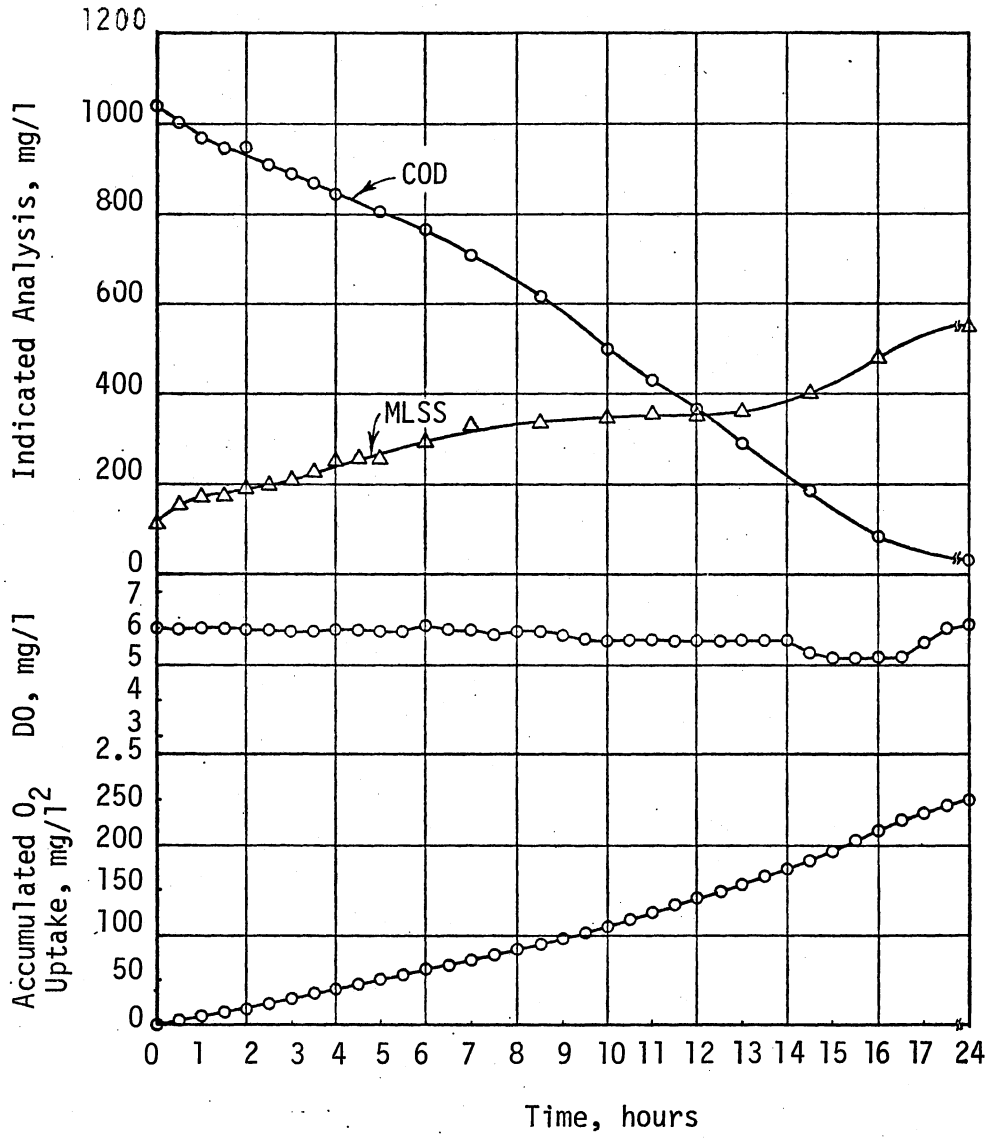
Figure 7. Dissolved Oxygen Profile, O_2 Uptake, COD, and MLSS vs Time for Experiment 4

Initial Conditions:

F/M = 9.6
COD = 1038 mg/l
MLSS = 108 mg/l

Reaeration Constants:

$K_2 = 0.1468\ min^{-1}$ from 0 hr 0 min to 2 hr 0 min
$K_2 = 0.1424\ min^{-1}$ from 2 hr 0 min to 4 hr 0 min
$K_2 = 0.1382\ min^{-1}$ from 4 hr 0 min to 18 hr 0 min


1200
1000
800
600
400
200
0
COD
MLSS
Indicated Analysis, mg/l
7
6
5
4
3
2.5
DO, mg/l
250
200
150
100
50
0
Accumulated O_2 Uptake, mg/l
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 24
Time, hours

O_2 uptake was 429 mg/l.

The results of experiment 5 are shown in Figure 8; the F/M ratio, 10.9, was slightly higher than in the preceding experiment. Initial COD was 1116 mg/l, and initial MLSS was 102 mg/l. Time for substrate removal was four hours less than in the previous experiment. The value of ΔCOD was 1089 mg/l, and that for ΔMLSS was 591 mg/l. Dissolved oxygen in the system increased slightly during the first two hours; later, there was a long deoxygenation phase lasting slightly longer than eight hours. As soon as the DO reached its minimum (DO = 4.35 mg/l) at the eleventh hour, it recovered rapidly to 5.5 mg/l. The O_2 uptake formed a concave upward curve, suggestive of first order increasing rate kinetics during the O_2 deoxygenation portion of the DO profile. After the 13 hours of substrate removal period, the biomass had utilized 255 mg/l of oxygen. By way of comparison, the values computed from mean balance technique using the calculable COD of the biomass, was 250 mg/l.

In experiments 6 through 10, the COD of the biological solids was determined experimentally, as recommended by Gaudy, et al. (16). The COD of the biomass ($COD_{biomass}$) is easily obtained as the difference between the mixed liquor COD (COD_{ML}) and the filtrate COD (COD_f). The oxygen or energy equivalent of the biomass is

$$(COD_{ML} - COD_f) \div MLSS$$

The O_2 uptake may also be obtained as ΔCOD_{ML}, as suggested by Busch (10).

In experiments 9 and 10, the membrane filter scraping technique was also performed for the determination of biomass COD. Thus, O_2 uptake was obtained by various means.

The results of experiment 6 are shown in Figure 9. The reactor

Figure 8. Dissolved Oxygen Profile, O_2 Uptake, COD, and MLSS vs Time for Experiment 5

Initial Conditions:

F/M = 109
COD = 1116 mg/l
MLSS = 102 mg/l

Reaeration Constants:

$K_2 = 0.1491\ min^{-1}$ from 0 hr 0 min to 6 hr 0 min
$K_2 = 0.1449\ min^{-1}$ from 6 hr 0 min to 25 hr 0 min

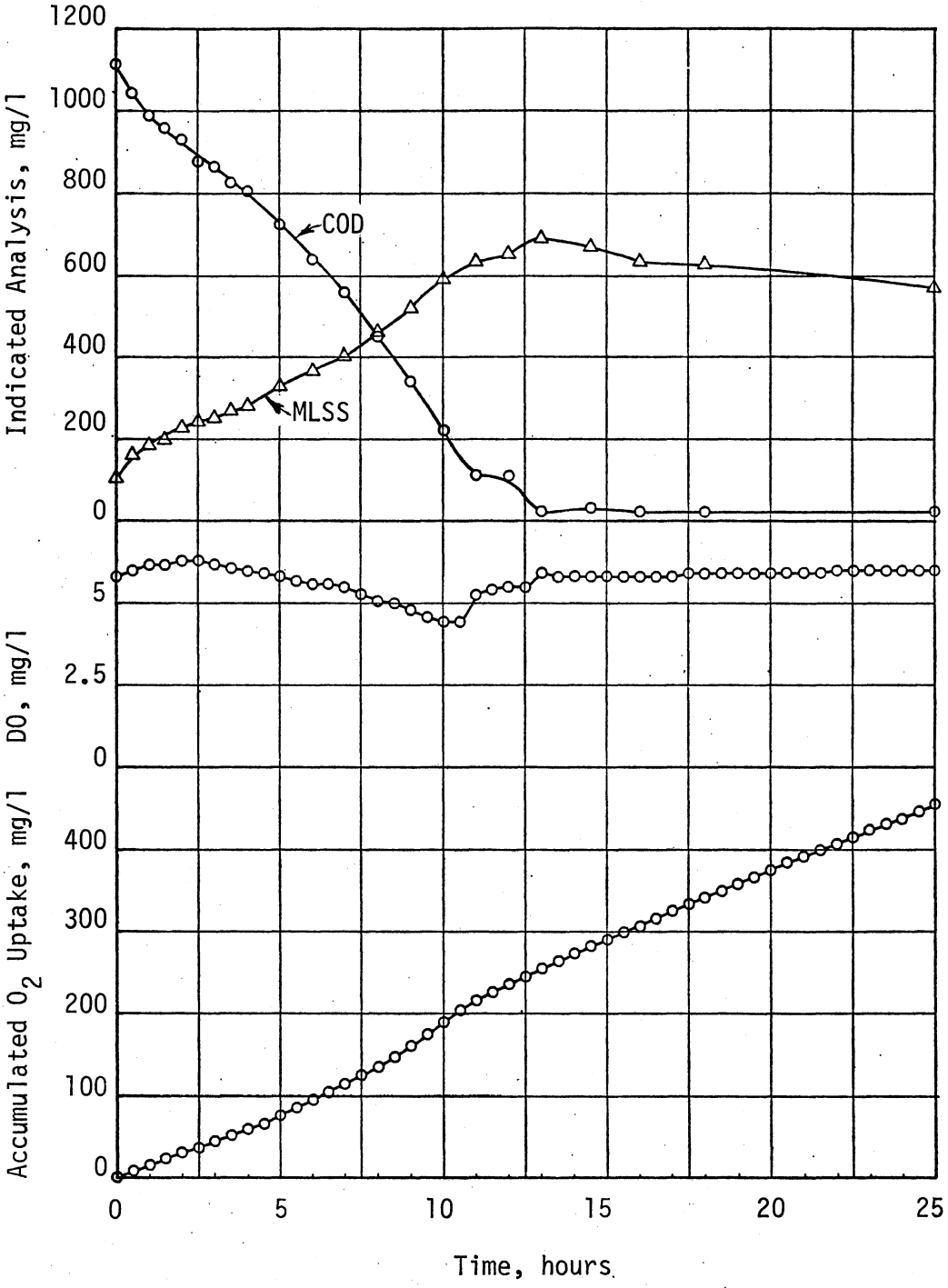

1200
1000
800
600
400
200
0
Indicated Analysis, mg/l
COD
MLSS
5
2.5
0
DO, mg/l
400
300
200
100
0
Accumulated O_2 Uptake, mg/l
0
5
10
15
20
25
Time, hours

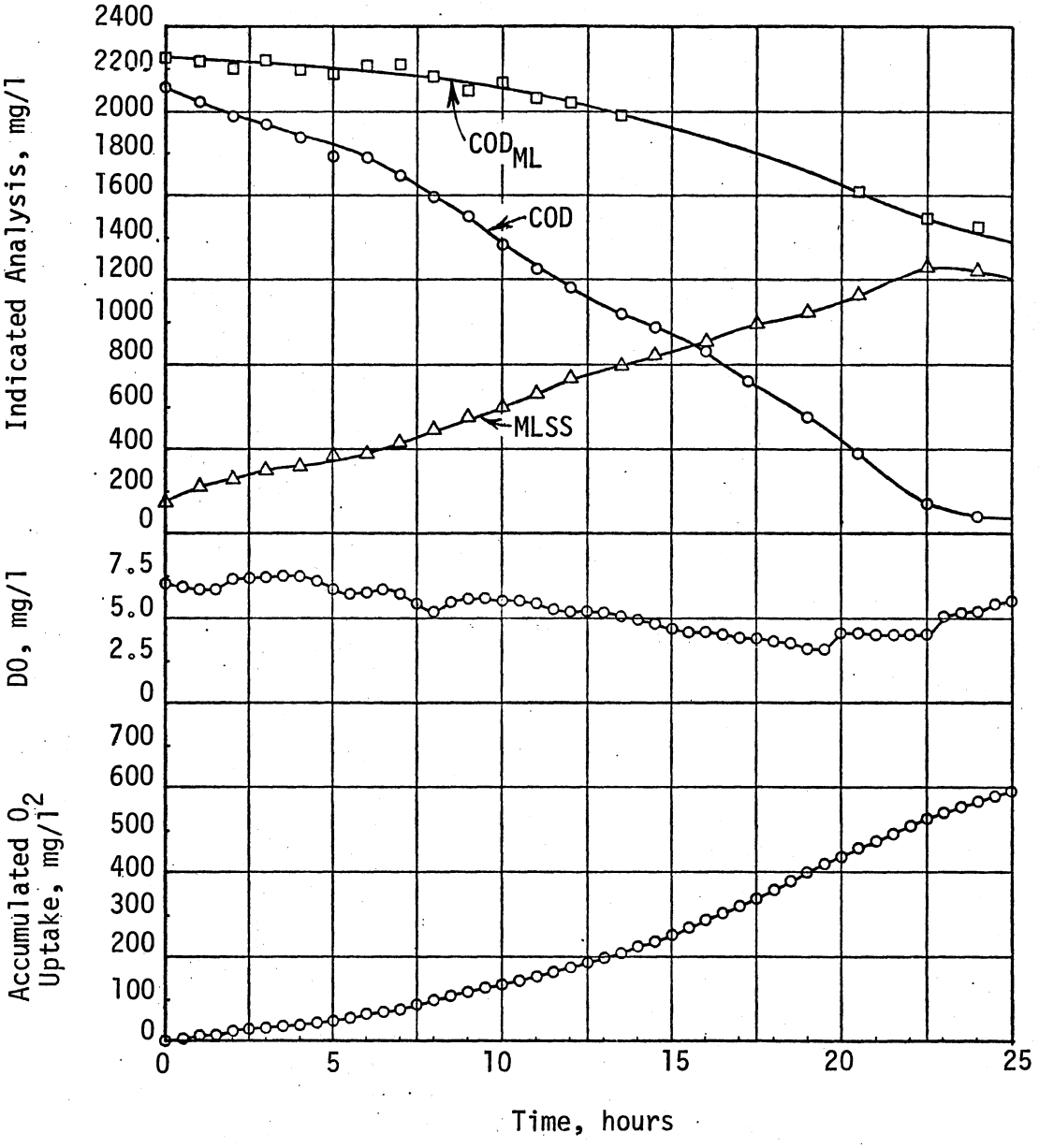
Figure 9. Dissolved Oxygen Profile, O_2 Uptake, COD, MLSS, and COD_{ML} vs Time for Experiment 6

Initial Conditions:

F/M = 13.4
COD = 2116 mg/l
MLSS = 158 mg/l
COD_{ML} = 2243 mg/l

Reaeration Constants:

$K_2 = 0.1358\ min^{-1}$ from 0 hr 0 min to 5 hr 0 min
$K_2 = 0.1329\ min^{-1}$ from 5 hr 0 min to 10 hr 0 min
$K_2 = 0.1319\ min^{-1}$ from 10 hr 0 min to 15 hr 0 min
$K_2 = 0.134\ min^{-1}$ from 15 hr 0 min to 25 hr 0 min


Indicated Analysis, mg/l
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
COD_ML
COD
MLSS
DO, mg/l
7.5
5.0
2.5
0
Accumulated O2 Uptake, mg/l
700
600
500
400
300
200
100
0
0
5
10
15
20
25
Time, hours

initially contained 2116 mg/l of soluble organic material (COD_i) and 158 mg/l of biological solids. After 22.5 hours of aeration, 1975 mg/l of COD were utilized and 1100 mg/l of microbial mass were produced. The initial COD_{ML} was 2243 mg/l; in 22.5 hours, 753 mg/l were converted to CO_2. There are several small sags during the deoxygenation phase of the DO profile, yielding a slightly increasing rate of oxygen utilization during the deoxygenation portion of the sag curve. There are also several stages of O_2 recovery, yielding the decreasing rate of O_2 utilization in the recovery portion of the DO profile. The O_2 uptake curve showed an O_2 utilization of 525 mg/l during the substrate removal rate phase. The O_2 uptake computed by Gaudy's mass balance equation with actual measurement of cell COD was 743 mg/l. Using Busch's equation (ΔCOD_{ML}), 753 mg/l was obtained.

A very high F/M ratio (F/M = 29) was employed for experiment 7. Initial COD was 3178 mg/l, and initial MLSS was 108 mg/l. Results are shown in Figure 10. An autocatalytic curve was obtained for both COD and MLSS. Like most of the experiments, the end of substrate removal coincided with the maximum point of MLSS. The ΔCOD was 3020 mg/l, and net microbial growth was 1664 mg/l. During the 20-hour substrate removal period, mixed liquor COD decreased from 3333 mg/l to 2252 mg/l. The DO decreased with a first order-like increasing rate until shortly before the 14th hour, when the dissolved oxygen approached zero. It remained low until the organic matter was gone. The corresponding O_2 uptake curve indicated 755 mg/l had been used by the time of substrate removal. By use of Gaudy's equation 3, O_2 uptake was computed to be 1118 mg/l. The mixed liquor COD curve shows a ΔCOD_{ML} of 1081 mg/l after 20 hours.

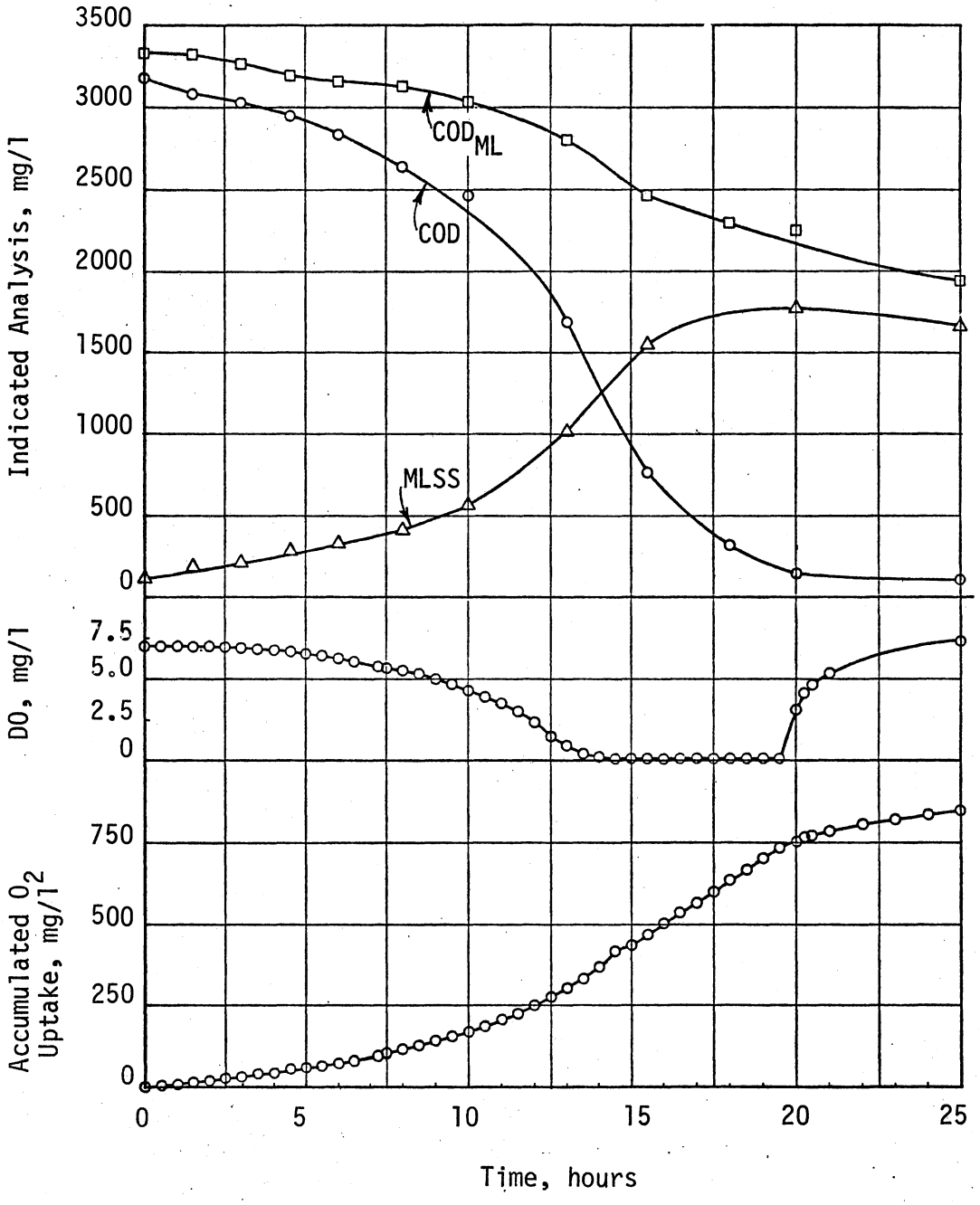
Figure 10. Dissolved Oxygen Profile, O_2 Uptake, COD, MLSS, and COD_{ML} vs Time for Experiment 7

Initial Conditions:

F/M = 29.4
COD = 3178 mg/l
MLSS = 108 mg/l
COD_{ML} = 3333 mg/l

Reaeration Constants:

$K_2 = 0.1412\ min^{-1}$ from 0 hr 0 min to 5 hr 0 min
$K_2 = 0.1382\ min^{-1}$ from 5 hr 0 min to 10 hr 0 min
$K_2 = 0.1351\ min^{-1}$ from 10 hr 0 min to 25 hr 0 min


3500
3000
2500
2000
1500
1000
500
0
Indicated Analysis, mg/l
COD_ML
COD
MLSS
7.5
5.0
2.5
0
DO, mg/l
750
500
250
0
Accumulated O2 Uptake, mg/l
0
5
10
15
20
25
Time, hours

Experiment 8 was conducted at a very low F/M ratio. The system initially contained 2212 mg/l of MLSS and 993 mg/l of COD; the results are shown in Figure 11. The organic carbon was utilized rapidly--within two hours. The ΔMLSS was 728 mg/l, and ΔCOD was 954 mg/l. There was very little reduction in mixed liquor COD within the 2-hour substrate removal period; the ΔCOD_{ML} was only 37 mg/l. The DO dropped to zero within four minutes after starting the experiment, and remained low for two hours. Because of the essentially zero DO, the O_2 uptake curve was a straight line during this portion of the DO profile. Later, it followed a slightly increasing rate curve. The O_2 utilization was 132 mg/l during the 2-hour substrate removal period. Computed by the mass balance equation, the O_2 uptake was 102 mg/l.

The results of experiment 9 are shown in Figure 12. Initial COD was 1049 mg/l. Initial biological solids concentration was 1200 mg/l. During the two hours required for substrate removal, 1029 mg/l of COD was utilized. Solids production was estimated at 648 mg/l (see biological solids curve). O_2 uptake assessed as the difference between initial mixed liquor COD and mixed liquor COD at the end of the substrate removal period was 213 mg/l. The DO remained at zero for 1.7 hours before recovering. The O_2 uptake curve had a shape similar to those shown in Figure 11. At the time of substrate removal, 127 mg/l of O_2 were utilized by calculation of O_2 uptake using the sag curve data. The COD/biomass calculated as:

$$(COD_{ML} - COD_f) \div MLSS$$

Using the mass balance equation, O_2 uptake was 259 mg/l. Using membrane filter scraping technique, a lower COD/biomass ratio was computed.

Figure 11. Dissolved Oxygen Profile, O_2 Uptake. COD, MLSS, and COD_{ML} vs Time for Experiment 8

Initial Conditions:

F/M = 0.5
COD = 993 mg/l
MLSS = 2212 mg/l
COD_{ML} = 3512 mg/l

Reaeration Constant:

$K_2 = 0.1270\ min^{-1}$

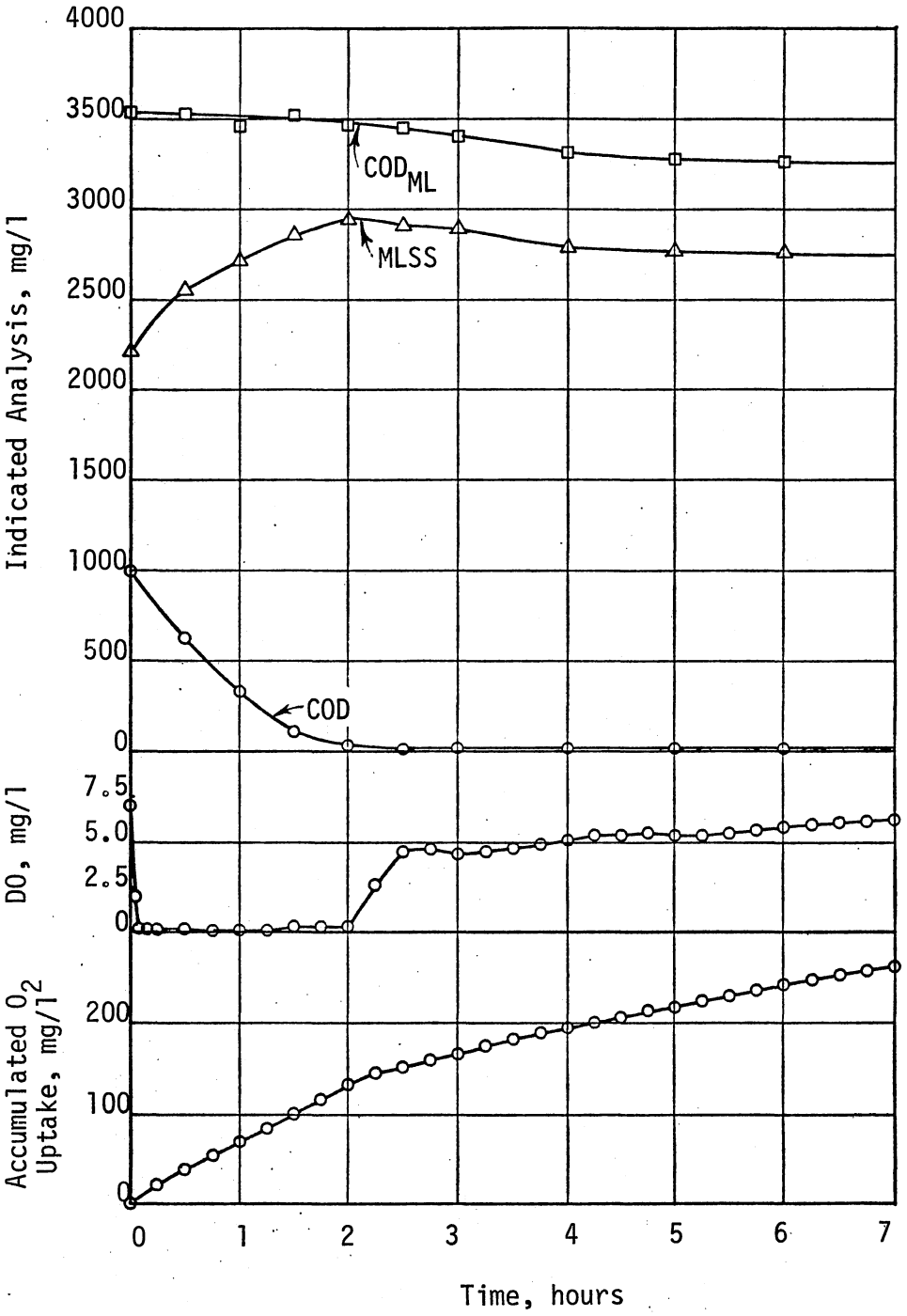

4000
3500
3000
2500
2000
1500
1000
500
0
COD_ML
MLSS
COD
Indicated Analysis, mg/l
7.5
5.0
2.5
0
DO, mg/l
200
100
0
Accumulated O2 Uptake, mg/l
0
1
2
3
4
5
6
7
Time, hours

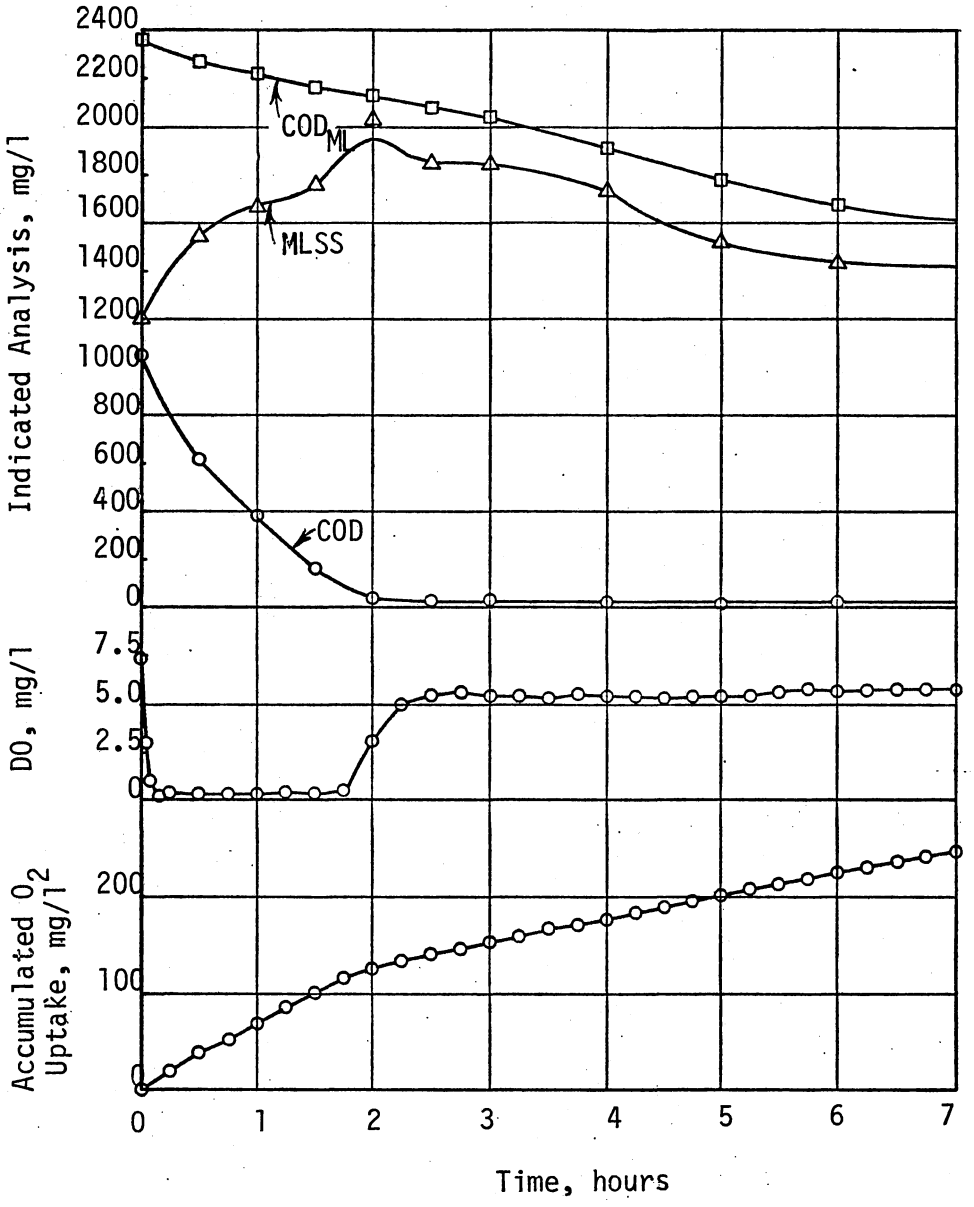
Figure 12. Dissolved Oxygen Profile, O_2 Uptake, COD, MLSS, and COD_{ML} vs Time for Experiment 9

Initial Conditions:

F/M = 0.9
COD = 1049 mg/l
MLSS = 1200 mg/l
COD_{ML} = 2355 mg/l

Reaeration Constant:

$K_2 = 0.1289\ min^{-1}$


Indicated Analysis, mg/l
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
COD
ML
MLSS
COD
DO, mg/l
7.5
5.0
2.5
0
Accumulated O_2 Uptake, mg/l
200
100
0
0
1
2
3
4
5
6
7
Time, hours

This caused a higher calculated O_2 uptake value (312 mg/l).

In Experiment 10, the reactor contained a very low initial MLSS--46 mg/l; the COD_i was 1044 mg/l. Results are shown in Figure 13. The substrate was removed within 17 hours. ΔCOD was 1013; ΔMLSS was 594 mg/l. Mixed liquor COD decreased by 328 mg/l. The DO profile shows a long and slow deoxygenation phase. It recovered rapidly after the substrate had been removed. An S-shaped O_2 uptake curve typical of a growth system was obtained. The O_2 uptake at the 17th hour was 313 mg/l. By subtracting COD_f from COD_{ML}, the COD/biomass ratio was computed to be 1.18. Calculated O_2 uptake was then equal to 312 mg/l. Using the COD/biomass ratio measured by membrane filter scraping technique, the calculated O_2 uptake was 365 mg/l.

Pertinent data from the ten experiments are summarized in Table II. The values given in column 18 for O_2 uptake are the values of accumulated O_2 uptake at the time of substrate removal calculated from the DO sag aeration data. The percent recovery shown in column 18 represents the sum of the O_2 uptake shown in column 19, and the ΔX of column 16 multiplied by 1.15 ÷ the ΔCOD value shown in column 14. The factor 1.15 represents the average experimental values for COD of the biomass (mg COD/mg cells) calculated from the measurements made in experiments 6 through 10.

Determining the correct value for reaeration rate, K_2, is important in computing O_2 uptake using the oxygen sag reaeration method. In these studies, the K_2 values employed for calculation were corrected (or adjusted) to account for the effect of the biological solids concentration, water, and temperature. Consideration of other correction factors such as inorganic salts concentration was also made. All data

Figure 13. Dissolved Oxygen Profile, O_2 Uptake, COD, MLSS, and COD_{ML} vs Time for Experiment 10

Initial Conditions:

F/M = 22.7
COD = 1044 mg/l
MLSS = 46 mg/l
COD_{ML} = 1080 mg/l

Reaeration Constants:

K_2 = 0.1430 min^{-1} from 0 hr^{-0} min to 10 hr^{-0} min
K_2 = 0.1320 min^{-1} from 10 hr^{-0} min to 25 hr^{-0} min

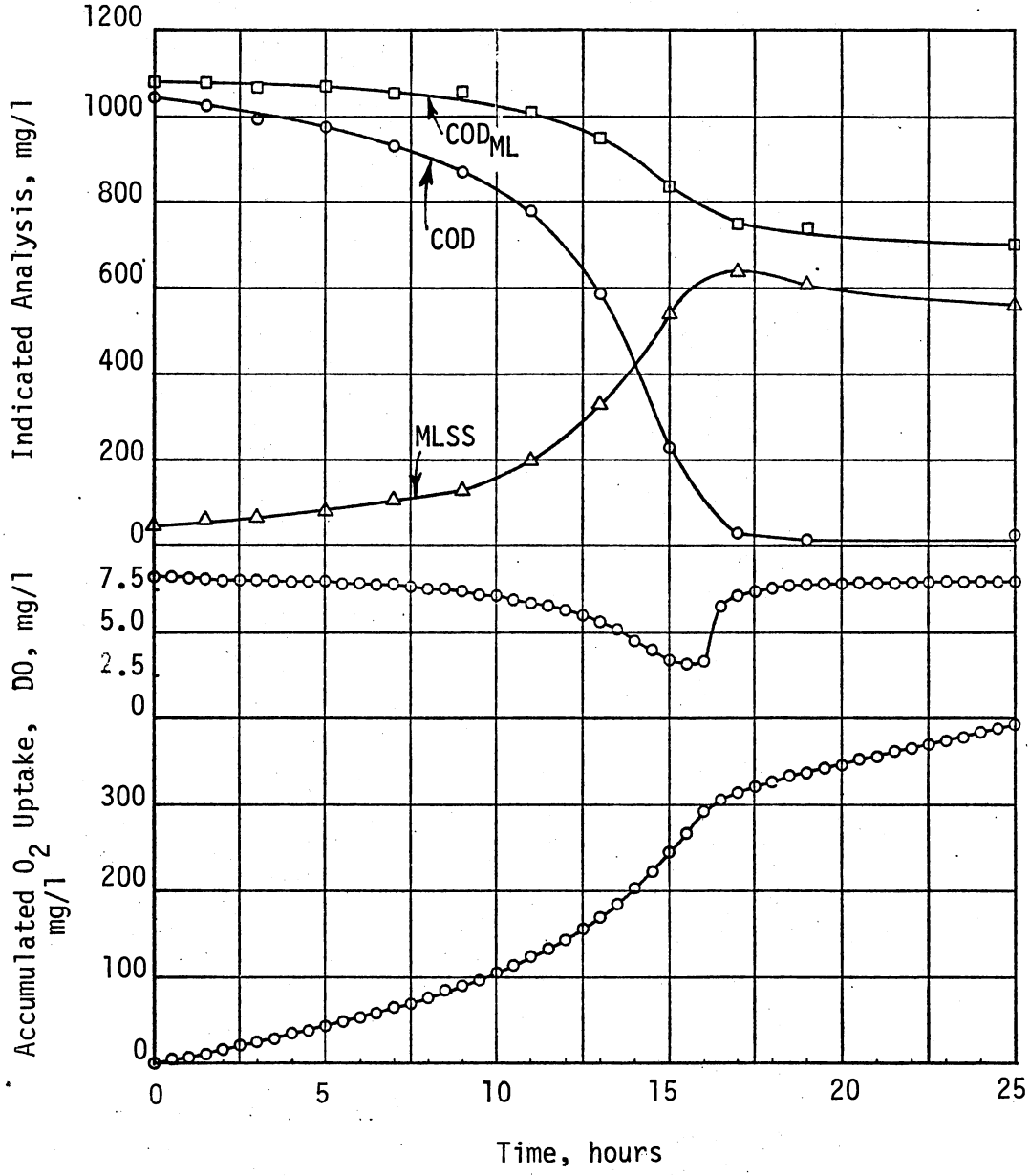

1200
1000
800
600
400
200
0
COD_ML
COD
MLSS
Indicated Analysis, mg/l
7.5
5.0
2.5
0
DO, mg/l
300
200
100
0
Accumulated O2 Uptake, mg/l
0
5
10
15
20
25
Time, hours

TABLE II

SUMMARY OF EXPERIMENTAL DATA

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	
Exp.	Date (1974)	Temp. (^{o}C)	Barometic Pressure (in. Hg.)	Airflow Rate (cc/min)	K_2 (min^{-1})	C_s (mg/l)	COD_i (mg/l)	X_i (mg/l)	(F/M)	COD_f (mg/l)	X_f (mg/l)	Time for Substrate Removal (hr)	ΔCOD (mg/l)	$\Delta COD/COD_i$	ΔX (mg/l)	Yield	O_2 Uptake (mg/l)	Recovery (%)	Remarks*
1	5-15	25	29.7	3000 →4000	0.1320	8.34	980	1564	0.6	15	2154	2	965	0.985	656	0.68	87	0.87	TOC = 377 mg/l
2	5-29	25	29.7	3000	0.1325	8.34	1023	986	1.0	20	1596	4.5	1003	0.981	632	0.63	121	0.85	TOC = 411 mg/l
3	6-12	23	30.1	3000	0.1298	8.73	1077	592	1.8	12	1224	5	1065	0.989	620	0.58	166	0.83	TOC = 411 mg/l
4	7- 9	27.5	29.95	3000	0.1468	8.00	1038	108	9.6	20	510	17	1018	0.981	412	0.41	237	0.70	
5	7-22	29	30.0	3000	0.1491	7.80	1116	102	10.9	23	570	13	1093	0.979	613	0.56	255	0.88	
6	7-30	26	30.05	3000	0.1358	8.26	2116	158	13.4	47	1200	22.5	2030	0.969	1100	0.54	525	0.88	COD_{ML} = 2243 mg/l
7	8-21	26	30.0	3000	0.1412	8.24	3178	108	29.4	106	1668	20	3012	0.948	1664	0.55	755	0.89	COD_{ML} = 3333 mg/l
8	8-27	24	29.9	3000	0.1270	8.52	993	2212	0.5	20	2720	2	793	0.980	728	0.75	132	1.00	COD_{ML} = 3512 mg/l
9	9-12	23.5	30.0	3000	0.1289	8.6	1049	1200	0.9	24	1440	2	1025	0.977	670	0.65	127	0.88	COD_{ML} = 2355 mg/l
10	9-25	21	30.0	3000	0.1430	9.01	1044	46	22.7	20	560	17	1020	0.977	594	0.58	313	0.98	COD_{ML} = 1080 mg/l

*The TOC and COD_{ML} values shown are initial TOC and initial COD_{ML}

obtained from reaeration tests converted to K_2's at 25^o are shown in Figures 14 and 15.

In Figure 14, it is seen that the K_2 of pure water at 25^oC varied from 0.198 min^{-1} to 0.210 min^{-1} at the 3000 cc/min air flow rate. However, in the presence of a solids content at 100 mg/l, the K_2 value decreased to 70 percent of the value for pure water. When the solids content was increased to 500 mg/l, the K_2 was decreased to 65 percent of the pure water value. However, further increase in suspended solids concentration did not change the K_2 significantly.

The inorganic nutrients (nitrogen, salts, and buffer) needed for microbial growth were also found to exert some effect on K_2. Necessary nutrients for 1000 mg/l of glucose (25 ml/l) was found to decrease K_2 by five percent. Doubling the strength of nutrients decreased K_2 by eight percent; so the nutrients in the mass culture are not expected to exert much effect on K_2. The data are plotted in Figure 15. The inorganic salts concentration on the abscissa are the relative total salts concentration, in accordance with Table I. The number "1" indicates inorganic salts concentration equal to that added when S_i is equal to 1000 mg/l. The number "2" indicates double strength in organic salts; "3" indicates triple-fold strength, etc.

Figure 14. Effect of Biological Solids Concentration on Reaeration Rate

Air flow rate = 3000 cc/min
Clorox dosage = 2.4 ml/l per 100 mg/l biological solids
Cells suspended in distilled water, i.e., no mineral salts and glucose in the system

All K_2 values were adjusted to $25^{o}C$

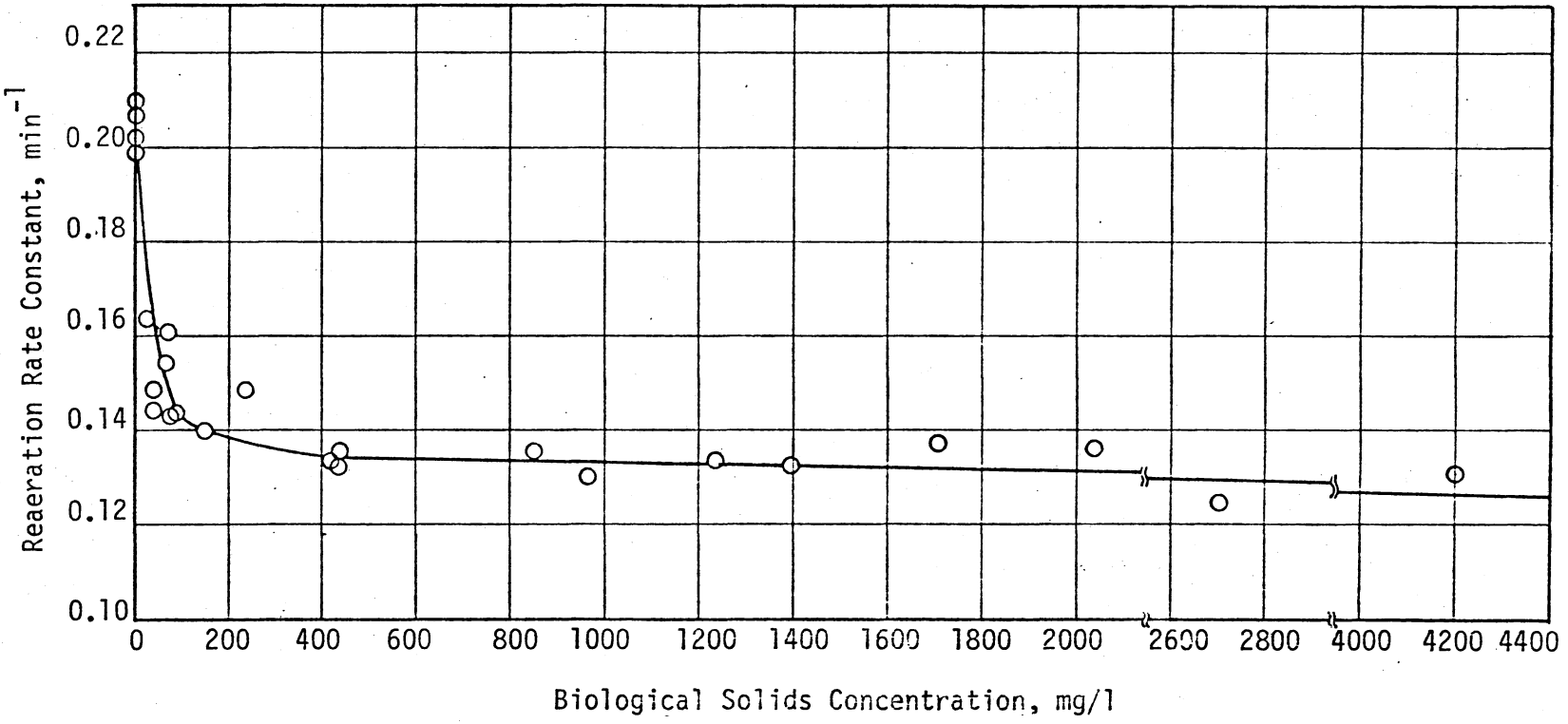
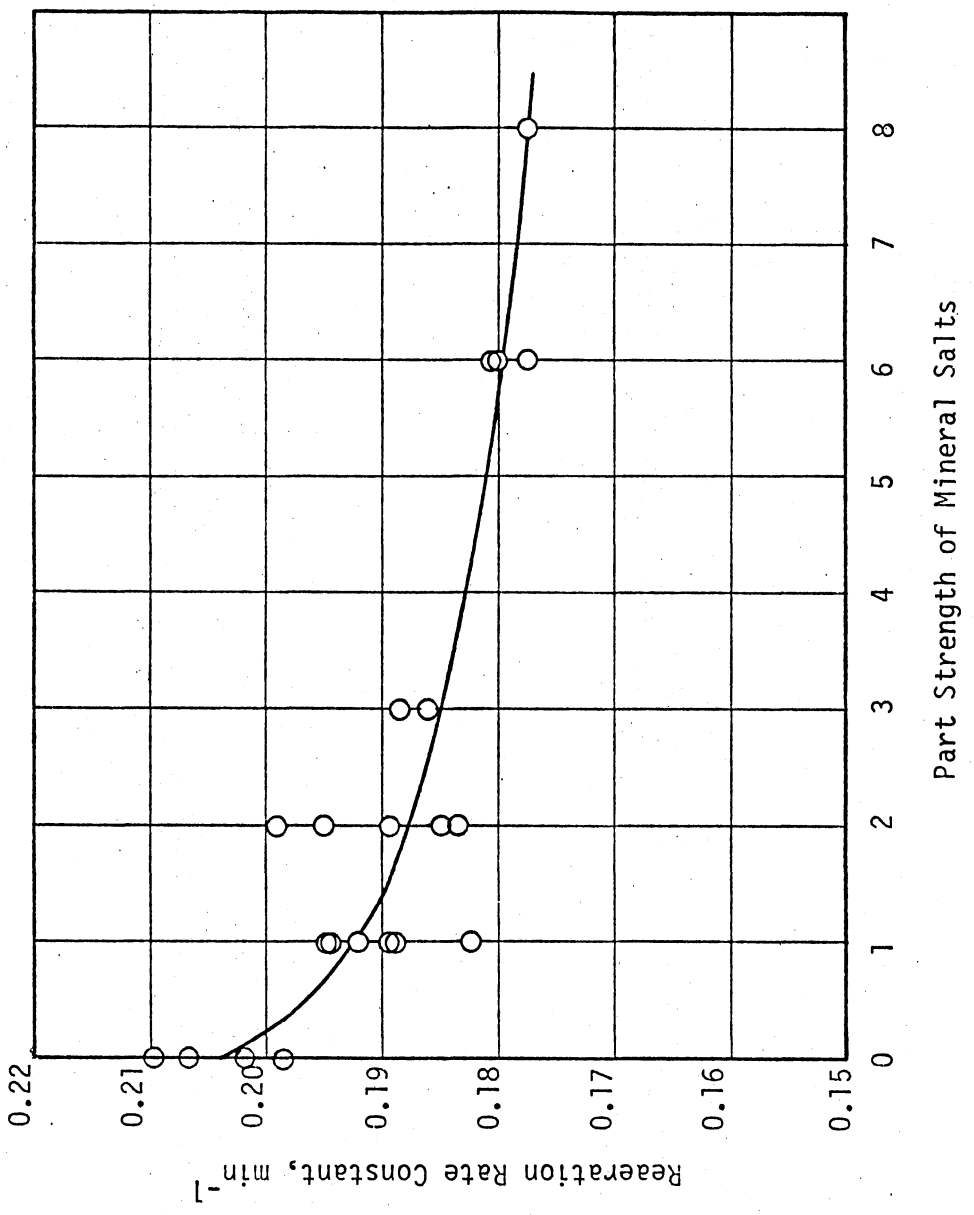

Reaeration Rate Constant, min^{-1}
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0
200
400
600
800
1000
1200
1400
1600
1800
2000
2600
2800
4000
4200
4400
Biological Solids Concentration, mg/l

Figure 15. Effect of Mineral Salts (Salts, Nitrogen, and Buffer) on Reaeration Rate

Air flow rate = 3000 cc/min

No biological Solids in the system

All K_2 values were adjusted to $25^{o}C$


Reaeration Rate Constant, min-1
0.22
0.21
0.20
0.19
0.18
0.17
0.16
0.15
0
1
2
3
4
5
6
7
8
Part Strength of Mineral Salts

CHAPTER V

DISCUSSION

Studies on the Correlation of COD and TOC

It has been found that the COD/TOC ratio decreases during purification, i.e., the COD/TOC ratio for the raw waste is higher than for the treated effluent. The data shown in Table III follows this general trend, although in experiment 2 the decreasing trend in COD/TOC ratio is not really in evidence. Various reasons for such a trend have been suggested by Eckenfelder (25). His suggestions pertained largely to situations not really applicable to the present case wherein all of the COD was due to a known carbohydrate which is readily metabolized. It is believed that there is a fundamental reason why the chemical oxygen demand should be proportionally lower than the carbon content after treatment in an aerobic system. It is recalled that in the three systems under study, the residual COD was very low. Also, it is readily appreciated that in the process of aerobic metabolism, the overriding drive or pressure is to oxidize the substrate. Any reduced carbon is contained within the cells (synthesis). Any carbon in solution after the exogenous substrate has been removed would be expected to be oxidized products or carbon leaked from the intact cells. Thus, it is believed that the reason for the decreasing trend in COD/TOC ratio in comparing raw and treated effluents is an expectable one on the basis

TABLE III

CORRELATION OF COD AND TOC VALUES

	Experiment 1			Experiment 2			Experiment 3		
Time	COD mg/l	TOC mg/l	COD/TOC	COD mg/l	TOC mg/l	COD/TOC	COD mg/l	TOC mg/l	COD/TOC
0	980	377	2.60	1023	411	2.49	1077	411	2.62
0.5	447	161	2.77	894	375	2.38	904	349	2.59
1	187	70	2.66	784	332	2.36	786	296	2.65
1.5	41	17	241	674	271	2.48	629	241	2.60
2	20	9	2.22	564	227	2.48	508	195	2.61
2.5	24	6		447	200	2.24	411	165	2.49
3	8	6	1.33	365	162	2.25	311	138	2.25
3.5	49	2		290	111	2.61	241	115	2.10
4	4	6	0.67	129	65	1.99	179	85	2.11
5	8	6	1.33	31	14	2.21	12	10	1.2
6	16	6	2.67	24	14	1.71	14	11	1.27
7	12	7	1.71	24	11	2.18	12	10	1.2
23	24	5		31	13	2.39	12	10	1.2

of metabolic considerations.

Table IV shows the treatable fraction of the synthetic waste as measured by COD (see $\Delta COD/COD_i$) and as measured by TOC (see $\Delta TOC/TOC_i$). It can be seen that either the COD or TOC test could be used with equal facility to gain insight into wastewater treatability.

TABLE IV

SUMMARY OF THE EFFICIENCY OF COD AND TOC REMOVAL

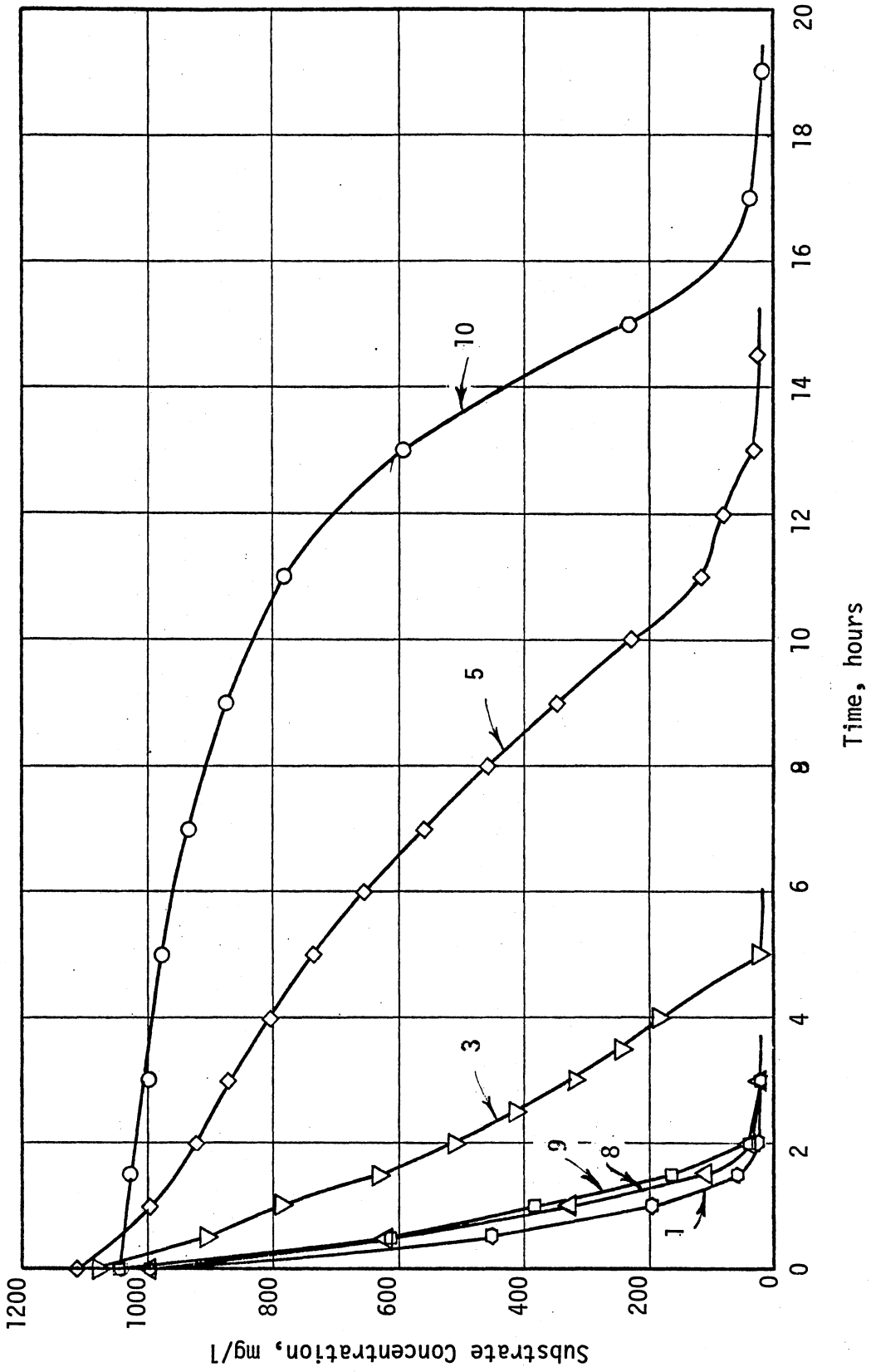
	Experiment 1	Experiment 2	Experiment 3
COD_i, mg/l	980	1023	1077
ΔCOD, mg/l	965	1002	1065
$\Delta COD/COD_i$	0.985	0.981	0.989
TOC_i, mg/l	377	411	411
ΔTOC, mg/l	371	398	401
$\Delta TOC/TOC_i$	0.984	0.968	0.976

Studies on the Effects of Initial Biological Solids Concentration on the Rate of Substrate Utilization and on the Oxygen Sag Curve

The effect of initial biological solids concentration on the rate of substrate utilization is shown in Figure 16. In all of the studies shown, the initial available organic carbon source concentration was

Figure 16. Effect of Initial MLSS on the Substrate Utilization Rate

Exp. No.	X_1 (mg/l)	F/M
VIII	2212	0.5
I	1564	0.6
IX	1200	0.9
III	592	1.8
V	102	10.9
X	46	22.7


Substrate Concentration, mg/l
1200
1000
800
600
400
200
0
0
2
4
6
8
10
12
14
16
18
20
Time, hours
1
3
5
8
9
10

constant, $\pm$ 1000 mg/l. It is seen that the higher the initial solids concentration, the higher the substrate utilization rate. Also, increasing the initial biological solids concentration (i.e., decreasing the F/M) changes the type of kinetics for substrate removal--going from kinetics approaching the first order increasing rate mode at high F/M ratios to kinetics approaching the first order decreasing rate mode at low F/M ratios.

Also, it is noted that the general shape of the oxygen sag curve is controlled by the substrate utilization curve and the growth curve. When the system has a high initial biological solids concentration, the dissolved oxygen will decrease rapidly in either linear or first order decreasing manner, as seen in Figures 4, 11, and 12. Under these conditions, the corresponding O_2 uptake curve can be expected to show a decreasing rate. When the system contains low initial solids concentration (high F/M), the rates of substrate and oxygen utilization will be slow at the start and then increase in keeping with increasing rate of biomass accumulation, as shown in Figures 9, 10, and 13. The corresponding O_2 uptake will show an increasing rate during the deoxygenation phase of the DO sag, in accordance with the findings of Jennelle and Gaudy (17). It is also interesting to note that at the time of substrate removal, somewhat less O_2 was used in systems operated at low F/M ratios (experiments 8 $\longrightarrow$ 1 $\longrightarrow$ 9 $\longrightarrow$ 2 $\longrightarrow$ 3) than for those at higher F/M ratios (experiments 4 $\longrightarrow$ 5 $\longrightarrow$ 10). The experiments cited above were all run at S_i = 1000 mg/l glucose; thus the lower F/M ratios were provided by higher initial cell concentrations. It is believed that in these systems the substrate was removed in large measure for production of storage products, e.g., polysaccharide.

These materials require less energy expenditure than does the synthesis of nucleic acid, protein, and lipids. Thus, O_2, during the substrate removal period, might be expected to be lower at higher F/M ratios. In these experiments, cell composition was not run. However, the results obtained are consistent with those of others who have run sludge composition analyses along with substrate removal, solids accumulation, and O_2 uptake (11)(28)(29). The slightly decreasing trend in cell yield as F/M is increased is also consistent with the above analyses.

Comparison of O_2 Uptake Value by Three Different Methods

Busch (10) has stated that mixed liquor COD decreases with time because part of the organic matter is converted to carbon dioxide. When all of the organics have been utilized, the mixed liquor COD continues to decrease because of the endogenous respiration and predator activity. So the difference of mixed liquor COD (ΔCOD_{ML}) represents the organic carbon which has been converted to CO_2. One can therefore reason that the decrease in mixed liquor COD is a measure of O_2 uptake, i.e., BOD exerted. Measurement of O_2 uptake by this approach has been compared to O_2 uptake using a Warburg respirometer in studies made previously by Carl Goldstein and Paul Perkins (see MS thesis by Perkins [30]).

In Gaudy's energy balance equation (equation 3), the difference in soluble COD (ΔCOD) represents the carbon utilized for synthesis and respiration. The difference in biomass COD ($\Delta COD_{biomass}$) represents the carbon source which has been converted to biomass. So the difference of these two parameters ($\Delta COD - \Delta COD_{biomass}$) represents the carbon

source, expressed in terms of O_2, which was used for respiration by the microorganisms. O_2 uptake value computed by either Gaudy's or Busch's method should be the same as the result computed by the "oxygen sag" method.

A summary of O_2 uptake results at the time of substrate removal is given in Table V. The column headings are self-explanatory although columns 6, 7, and 8 may need some explanatory comments. In column 6, the balance is based upon the theoretical COD of cells with empirical formula $C_5H_7O_2N$, i.e., 1.42 mg COD/mg cells. In column 7, the COD of the cells was determined by actual measurement of $COD_{ML} - COD_f$, and in column 8, the COD of the cells was measured directly, i.e., by removing the biomass from the filter and determining its COD. The method employed in column 7 is the one to be recommended, since it is the easiest to run and is less subject to experimental error than the method employed in column 8.

Comparing O_2 uptake values in columns 5, 7, and 9, it is seen that only in experiment 10 were the values very close to each other. The four remaining experiments for which a comparison is possible--6, 7, and 9--show reasonably good comparison with either COD method; however, the O_2 uptake by the sag method is lower. In experiments 7 and 9, the DO went to zero for some time, and the sag method is best employed when the K_2 is such that the DO does not go to zero or, in any event, stay there for long (18). However, this possible reason for the difference is not possible to cite for experiment 6. In experiment 8, this trend is reversed; the DO sag method yielded the highest O_2 uptake, and there is an apparent error in the mixed liquor COD measurement since there was a differnce of only 37 mg/l COD dissipated in the two hours required

TABLE V

SUMMARY OF THE RESULTS OF OXYGEN UPTAKE

1	2	3	4	5	6	7	8	9
					O_2 Uptake by Gaudy's Materials Balance Equation			
Exp.	Date	F/M	Time for Substrate Removal (hr)	O_2 Uptake by Oxygen Sag Method (mg/l)	Theoretical $COD_{biomass}$	Measured $COD_{biomass}$ by COD_M-COD_f	Measured $COD_{biomass}$ by Scraping Technique	O_2 Uptake by Busch's Method
1	5-15	0.6	2	87	114			
2	5-29	1.0	4.5	121	124			
3	6-12	1.8	5	166	142			
4	7- 9	9.6	17	237	435			
5	7-22	10.9	13	255	250			
6	7-30	13.4	22.5	525	413	743 (1.12)		753
7	8-21	29.4	20	755	669	1118 (1.15)		1081
8	8-27	0.5	2	132	79.8	102 (1.17)		37
9	9-12	0.9	2	127	114	259 (1.12)	312 (1.04)	213
10	9-25	22.7	17	313	40	312 (1.18)	365 (1.09)	328

*Values in ( ) are measured COD/biomass Ratio

to remove all of the substrate.

At this stage of investigation it must be said that more data are required before passing judgement on whether the DO sag method or the balance method or the mixed liquor COD method provides the best and most convenient procedure for estimating the O_2 uptake during treatability studies. The only two experiments where it can be said that valid comparison might be made are experiments 6 and 10. In experiment 10, all methods yielded essentially the same result, whereas in experiment 6, the DO sag method gave an O_2 uptake approximately 75 percent that of the two COD methods. Clearly, more work is indicated. Work is especially needed on the estimation of K_2 and C_s for the experimental system; some information is available and is discussed in the next section.

Effect of Suspended Solids and Soluble Chemicals on Oxygen Solubility and Reaeration Rate

Various workers (e.g., see Eckenfelder, et al. 29) have reported that soluble or insoluble solids will influence oxygen saturation. Since the biological solids concentrations were high in most of these tests, consideration of the saturation value was necessary. The α Method for calculating K_2 and C_s presented by Isaacs and Gaudy (24) can be usefully employed for the correction of solubility data for the particular liquid employed. Accordingly, the solubility data used in determination of the reaeration rates for this research were not those which appear in Standard Methods for the Examination of Water and Wastewater, but were those calculated in accordance with reaeration data using the α Method technique. As shown in Figures 14 and 15, increasing the solids concentration or increasing the nutrients

concentration reduced the K_2 value at the rather high mixing rate (air flow rate) employed. In a mass culture system, as the substrate and nutrients were decreased, the biological solids increased; so the determination of a "true" K_2 is rather complicated. Clorox was used in this research to kill the microorganisms; in preliminary experiments it was found to reduce K_2 by as much as 10 percent. Also, anti-foaming agents have been reported to reduce the K_2 by 35 percent (21). In present experiments, anti-foam agents were not employed except during two of the reaeration studies at high biological solids concentrations (see values at 2700 and 4200 mg/l, Figure 14), and the agent employed (Anti-foam A Spray, Dow Corning Corp.) did not cause any apparent effect, since it did not alter the trend of the data. In these two experiments, the agent was used very sparingly. All of these factors need consideration when estimating the system K_2.

The results of this investigation indicate that for high energy systems, the oxygen sag reaeration technique for determination of O_2 uptake in wastewater is not a technique that can be applied indiscriminately. First, it is necessary to adjust the air flow rate to the waste strength so that a reasonably well defined DO sag develops, yet the DO cannot be allowed to reach or in any event remain at zero for any length of time. Secondly, the reaction liquor constituents (cells, substrate, soluble or insoluble matter) can exert an effect on the K_2. The effect of the constituents of the system are more pronounced in whole waste high energy systems than in low strength systems such as secondary effluent in receiving streams. Thus, information for such systems cannot readily be transferred to the system studied here. It is apparent that more work will be needed in order to recommend the DO

sag procedure for measurement of O_2 uptake in treatability studies. The materials balance procedure or the COD_{ML} approach would appear to provide a convenient and useful means of obtaining the O_2 uptake at the time of substrate removal or at other selected points along the substrate removal and growth curves. However, such a procedure requires obtaining much COD and/or solids data.

CHAPTER VI

CONCLUSIONS

1. Regardless of the F/M ratio, the COD expressed as a fraction of COD_i (i.e., $\Delta COD/COD_i$) remains essentially constant, thus providing greater assurance that the ΔCOD of a waste sample can be determined under a variety of batch growth conditions.

2. In an aerobic system, the COD/TOC ratio of treated effluent can be expected to be lower than the COD/TOC ratio of the raw waste. Reasons for this have been presented in the discussion of results sector.

3. At high agitation or mixing rates, the reaeration rate decreases with an increase in biological solids concentrations; increasing concentration of dissolved inorganic solids (salts, etc.) also reduces the K_2, but at a lesser degree.

4. Definite conclusions regarding the suitability of the sag method for calculating O_2 uptake in a high energy-high mixing rate system such as exists for a batch treatability study cannot be made based on the results herein presented.

CHAPTER VII

SUGGESTIONS FOR FUTURE WORK

1. Continued experimental work is warranted on the effects of high concentration of biological solids and soluble chemicals on the reaeration rate. Analytical work is also warranted concerning ways of using the reaeration data to determine oxygen solubility and reaeration rate.

2. Treatability studies should be undertaken at different air flow rates using the 3-liter reactor to determine relationship between air flow rate and organic loading which would permit making the ΔCOD run without having the DO go to zero.

3. More work should be done for the purpose of comparing the oxygen uptake values computed by the three methods herein employed.

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APPENDIX A

A CALCULATION OF O_2 UPTAKE FROM AERATION REACTORS (TABLE VI)

TABLE VI

CALCULATION OF OXYGEN UPTAKE FROM DO PROFILE AND REAERATION RATE

1	2	3	4	5	6	7	8	9	10
Time hr-min	DO mg/l	D mg/l	K_2D mg/l-min	Δt min	$K_2D\Delta t$ mg/l	ΔDO mg/l	$K_2D\Delta t - \Delta DO$ mg/l	O_2 Uptake mg/l	Remarks
0- 0	7.50	0.74	0.11					0	K_2 = 0 1412 min^{-1}
				15	2.03	-0.40	2.43		
0-15	7.10	1.14	0.16					2.43	
				45	7.65	-0.10	7.75		
1- 0	7.00	1.24	0.18					10.18	
				60	10.80	0	10.80		
2- 0	7.00	1.24	0.18					20.98	
				60	11.10	-0.10	11.20		
3- 0	6.90	1.34	0.19					32.18	
				60	12.00	-0.15	12.15		
4- 0	6.75	1.49	0.21					44.33	
				60	13.50	-0.25	13.75		
5- 0	6.50	1.74	0.24					58.08	K_2 = 0.1382 min^{-1}
				60	15.60	-0.25	15.85		
6- 0	6.25	1.99	0.28					73.93	
				75	23.25	-0.45	23.75		
7-15	5.80	2.44	0.34					97.68	
				45	16.20	-0.30	16.50		
8- 0	5.50	2.74	0.38					114.18	
				60	24.90	-0.50	25.40		
9- 0	5.00	3.24	0.45					139.58	
				60	26.40	-0.70	27.10		
10-0	4.30	3.94	0.53					166.68	K_2 = 0.1351 min^{-1}
				60	35.10	-0.80	35.90		
11-0	3.50	4.74	0.64					202.58	
				60	43.20	-1.20	44.40		
12- 0	2.30	5.94	0.80					246.98	
				60	53.70	-1.40	55.10		
13- 0	0.90	7.34	0.99					302.08	
				60	62.40	-0.70	63.10		
14- 0	0.20	8.04	1.09					365.18	
				60	66.00	-0.15	66.15		
15- 0	0.05	8.19	1.11					431.33	
				120	133.20	0	133.20		
17- 0	0.05	8.19	1.11					564.53	
				120	133.20	0	133.20		
19- 0	0.05	8.19	1.11					697.73	
				30	31.50	0.85	30.65		
19-30	0.90	7.34	0.99					728.38	
				30	25.20	2.20	23.00		
20- 0	3.10	5.14	0.69					751.38	
				30	17.55	1.60	16.95		
20-30	4.70	3.54	0.08					768.33	
				30	13.20	0.60	12.60		
21- 0	5.30	2.94	0.40					780.93	
				240	63.60	2.00	61.60		
25- 0	7.30	0.94	0.13					842.53	

C_s = 8.80 mg/l

The reaeration rate constant is an important factor in calculating O_2 uptake. The procedure of determining the K_2 of an aeration system was described in the Materials and Methods section.

From the dissolved oxygen values recorded (column 2) during the experiment, the deficit (column 3) at each time may be found by subtracting the DO from the saturation value for the water temperature. The deficit produced in the jars is then multiplied by the reaeration rate existing in the vessels (column 4). Column 5 lists the time interval between DO determinations.

The amount of DO entering the system during a specific time interval is determined by multiplying K_2, deficit, and the length of the interval (column 6). The change in DO during each interval is the difference in DO recorded in column 7. The integral O_2 uptake caused by O_2 utilization by the microbes for a specific time period can be measured by subtracting column 7 from column 6 (column 8). Column 9 shows the summation of the O_2 uptake. This uptake curve is shown in Figure 10.

APPENDIX B

LIST OF SYMBOLS

C_s - Oxygen saturation constant, mg/l

$COD_{biomass}$ - Biomass COD, mg/l

COD_e - Terminal chemical oxygen demand, mg/l

COD_f - Filtrate chemical oxygen demand, mg/l

COD_i - Initial chemical oxygen demand, mg/l

COD_{ML} - Mixed liquor chemical oxygen demand, mg/l

D - Oxygen deficit from saturation at any specified time, mg/l

DO - Dissolved oxygen, mg/l

F/M - Food to microorganism ratio

K_2 - Reaeration rate constant, min^{-1}

MLSS - Mixed liquor suspended solids, mg/l

TOC - Total organic carbon, mg/l

Y - Microorganisms constant yield coefficient, mg/mg

X_e - Terminal cell concentration, mg/l

X_i - Initial cell concentration, mg/l

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