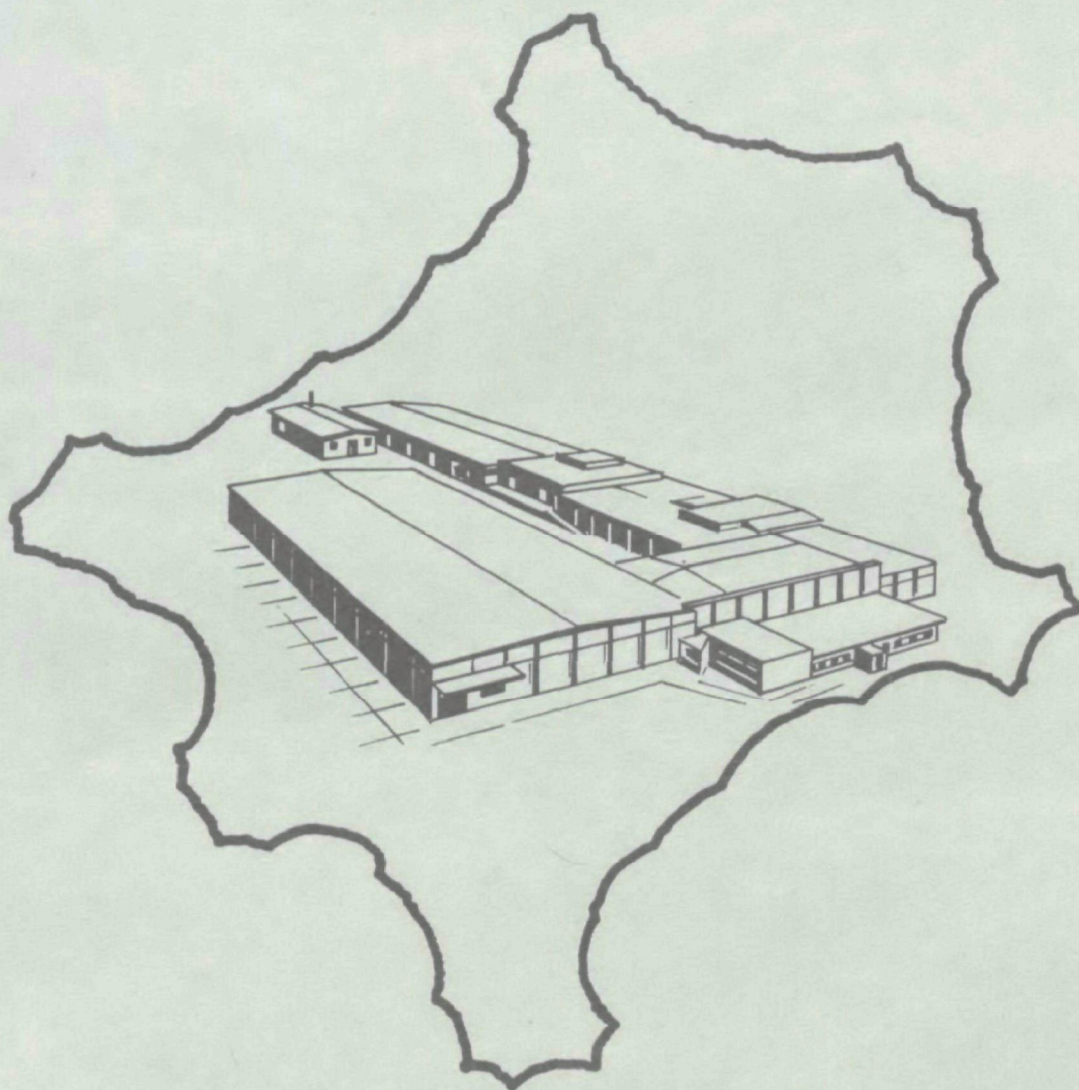




Anaerobic-Aerobic Lagoon Treatment for Vegetable Tanning Wastes



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ANAEROBIC-AEROBIC LAGOON TREATMENT FOR
VEGETABLE TANNING WASTES

by

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for the
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ABSTRACT

A field demonstration lagoon was operated at Virginia Oak Tannery, Inc., Luray, Virginia to evaluate the effectiveness of an anaerobic-aerobic lagoon in treating spent vegetable tannins blended with batepool and soak waste waters. The anaerobic-aerobic lagoon system was used to treat combined waste streams with a BOD₅ concentration of approximately 1000 mg/l. Aeration and volume of the lagoon were fixed and flow to the system was varied. The system load varied by increasing the flow so as to observe five operational phases. Operational phases were designed to cause the system to go from aerobic conditions to anaerobic-aerobic. After reaching anaerobic-aerobic conditions, doubling the BOD₅ load did not result in a significant decrease in BOD₅ removal efficiency. Efficiency, measured in terms of soluble BOD₅, at a BOD₅ load of 17.3 lbs/1000 ft³/day (anaerobic-aerobic condition) was 81 percent compared to a 92 percent efficiency for a BOD₅ load of 4.5 lbs/1000 ft³/day (aerobic conditions). The final load on the system under anaerobic-aerobic conditions was 1.73 lbs. of BOD₅/1000 ft³/day/B.hp. During this loading condition soluble BOD₅ and soluble COD removal efficiencies of 81 and 58 percent, respectively, were observed.

Although the lagoon system proved successful in removing degradable organics, color of the waste water was not reduced by this method of treatment. Color of spent vegetable tannins is a major problem and will dictate the most desirable approach to treating this waste water.

A completely mixed aeration unit was used in the laboratory to study the biological degradation of spent vegetable tannins. Concentrated and diluted tannins were studied by varying the detention time in the aeration unit. It was found that approximately 60 percent of the COD of spent vegetable tannins is not biological degradable and the generally accepted substrate-growth interaction relationship required modification to take into account the non-degradable fraction of COD. Yield coefficients, endogenous respiration rate, and specific growth were computed from the results of the laboratory study.

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Key Words: Spent tannins, tannery waste waters, anaerobic-aerobic lagoon, biological treatment, biological growth units.

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SECTION I

CONCLUSIONS

1. Spent vegetable tannins and spent vegetable tannins blended with soak and hairwasher waste water, and batepool waste water are biologically degradable. However, only about 40 percent of the COD of spent vegetable tannins can be removed by biological treatment. Biological treatment of waste water that contains spent vegetable tannins will not reduce color of the waste water.
2. A deep lagoon operated under anaerobic-aerobic conditions can be used to treat spent vegetable tannins that have been blended with batepool waste water. An anaerobic-aerobic lagoon 15 feet deep, aerated at the surface with mechanical aerators, can receive batepool waste water and spent vegetable tannins in a ratio of 8:1 and provide soluble BOD₅ removal of 81 percent and soluble COD removal of 58 percent when the load on the system is 1.73 lbs of BOD₅/1000 ft³/day/B.hp and 7.00 lbs of COD/1000 ft³/day/B.hp. No appreciable solid build up will occur in the lagoon system.
3. The most difficult problem that must be dealt with by a tannery in treating spent vegetable tannins is color removal; therefore, the most desirable method of treating spent vegetable tannins will depend upon the approach to color removal.
4. Spent vegetable tannins diluted to approximately 1000 mg/l of COD and fed into an aerobic system will result in an organism decay rate between 0.041 and 0.045 hours⁻¹, and yield coefficients of $0.62 \frac{\text{mg MLVSS}}{\text{mg COD}}$ and $0.78 \frac{\text{mg MLSS}}{\text{mg COD}}$. An organism decay rate of 0.061 hours⁻¹ and a yield coefficient of $0.91 \frac{\text{mg MLSS}}{\text{mg COD}}$ will result when concentrated vegetable tannins with COD concentrations between 11,860 mg/l and 32,800 mg/l are used as feed.
5. The Michaelis-Menten expression for substrate (or nutrient)-enzyme interaction will not describe dilute spent vegetable tannins when substrate is measured in terms of COD. The equation
$$\mu = \hat{\mu} \frac{S_1 - A}{S_1 + B}$$
 provides an adequate relationship between COD and growth for diluted spent vegetable tannins. For tannins diluted to 1000 mg/l of COD and fed into an aerobic system, $\hat{\mu} = 0.21 \text{ hours}^{-1}$, $A = 590 \text{ mg/l}$ of COD and $B = -491 \text{ mg/l}$ of COD.

SECTION II

RECOMMENDATIONS

Design of systems to treat spent vegetable tannins should be based on pilot studies of the waste at each tannery under consideration. These studies will be required to insure the adequacy of the system in meeting the needs of the particular tannery and water quality standards. The importance of color removal should be recognized in the design of both pilot and prototype. The approach to color removal will greatly influence design of the treatment process and operation of the constructed facility.

SECTION III

INTRODUCTION

The tannery industry recognized the need for sound technological developments in tannery waste treatment and in 1965 the Tanners' Council of America retained Dr. J. David Eye of the University of Cincinnati, a waste management consultant, to make a detailed field investigation of the tanning industry. Dr. Eye found that no tannery had a treatment procedure that was entirely satisfactory. Indications were that the design engineers lacked sufficient knowledge of the waste characteristics and its treatability to properly design effective treatment units. Apparently, the effect of tannery waste was not understood and conventional treatment methods had failed to provide adequate treatment. As a result, suitable treatment methods had not been employed and progress in this area lagged.

During the summer of 1966 a waste water study was made at Virginia Oak Tannery, Incorporated, Luray, Virginia. This project was sponsored by Virginia Oak Tannery, Incorporated, and was under the direction of Dr. Clinton E. Parker. Data from this waste study and bench scale pilot plant, and the results of a study at the University of Cincinnati by Lin (1) were the basis for this investigation.

The purpose of this study was to evaluate and derive data for biological treatment of spent vegetable tannins blended with other tannery waste streams, except lime and unhairing waste water. This work was to study in the field the characteristics of an anaerobic-aerobic system in treating these waste waters and to evaluate the effectiveness of the system in meeting the need of a low cost treatment system capable of producing an effluent that meets pollution abatement standards.

Tanning is the process of converting the fibers of the hide to leather. Vegetable tannin is the aqueous extract of certain forms of plant life such as barks, woods, leaves, twigs, fruit pods and roots. Spent vegetable tannins are highly colored and account for 5 to 10 percent of the total waste flow and 25 to 30 percent of the total BOD₅ from the tanning processes.

Soak waste waters result from the process of removing salt used to pack the hides during storage and shipment. This process also removes dirt, blood, manure, and non-fibrous proteins. The soak waste water is high in solids and is 10 to 15 percent of the total tannery waste water discharge and 15 to 20 percent of the BOD₅.

Bating is the term which applies to the process of preparing the hide for tanning after hair removal. The bate solution is usually made up of ammonia salts and a mixture of commercially prepared enzymes. This solution is used in basins which are referred to as batepools. Batepool waste water is usually about 40 percent of the total tannery waste water flow and 15 percent of the BOD₅.

Initially spent tannins (with bleach waste water) were blended with batepool and soak waste water and fed into the field lagoon. This was followed by observations of spent tannins blended with batepool waste water and fed into a lagoon system constructed at Virginia Oak Tannery, Inc., Luray, Virginia. Aeration was held constant and total flow was varied between 15 gpm and 127 gpm. Analyses were made of the influent and effluent waste waters.

A laboratory aeration unit was used to study biological treatment of spent vegetable tannins. Studies were carried out using concentrated and diluted tannins. Results from these studies were used to describe organism growth parameters when the only substrate available was the spent tannins.

SECTION IV

TANNERY WASTE WATERS

General

Tanning is as much of an "art" as a science. For a complete understanding of the composition and chemistry of tanning waste one must learn why the tanner uses the processes he does, the role of the chemicals used and the waste contribution that can be attributed to hide substance. Basic flow diagrams of tanneries using the same method of tanning are similar, but unit processes and unit operations vary and reflect the experience of the particular tannery.

The conversion of animal hides, primarily cattle, into leather is generally comprised to ten separate physiochemical or biological processes [2], [3]. The tanning step is the actual conversion of the fibers in the hide to leather. In present practice two primary methods of tanning are vegetable tanning and chrome tanning. For vegetable tanning an aqueous extraction from certain forms of plant life is used as the tan solution. The hides are immersed in a weak extract and move through an increase in concentration, ranging from 0.3 to 6.0 percent tanning extract. Preliminary tanning is in rocker vats and takes about three weeks. This is followed by tanning in layer vats with a 6.0 percent tanning extract for another 3 weeks. Although tan solution is reused as much as the "art" will allow and is small in volume, the spent vegetable tannins are quite strong.

Tanning and Bating Processes

Virginia Oak Tannery, Inc. (VOTAN) processes cattle hides and employs both vegetable tanning and chrome tanning, however, between 70 and 80 percent of its production is by vegetable tanning. Although there is some variation, the processes employed at VOTAN are similar to those of other tanneries. The animal skins are received "cured" (packed in salt with a reduced moisture content). Tanning is accomplished by separate batch physiochemical or biological processes that are adequately described by others [2], [3]. The flow diagram in Figure 1 indicates the steps in the vegetable tanning process.

During this study VOTAN processed branded and native steer hides with an average green prefleshed weight of 54 pounds each. The average hides processed were 1100 per day with 75 percent of the hide being vegetable tanned (excludes bellies). Vegetable tanned leather yield was 87 percent of the green prefleshed weight. The finished product contained 35 percent tannin extract on a dry weight basis or 32 percent tannin extract on a moist basis. Vegetable tanned leather yield was 38,800 pounds per day, equivalent of 825 hides/day. Dry tannins were dissolved and blended on the premises and no leaching or evaporation was employed. The tannin extract blend was 55 percent quebracho, 20 percent wattle, 15 percent chestnut and 10 percent myrtan. The extract contained 67.2

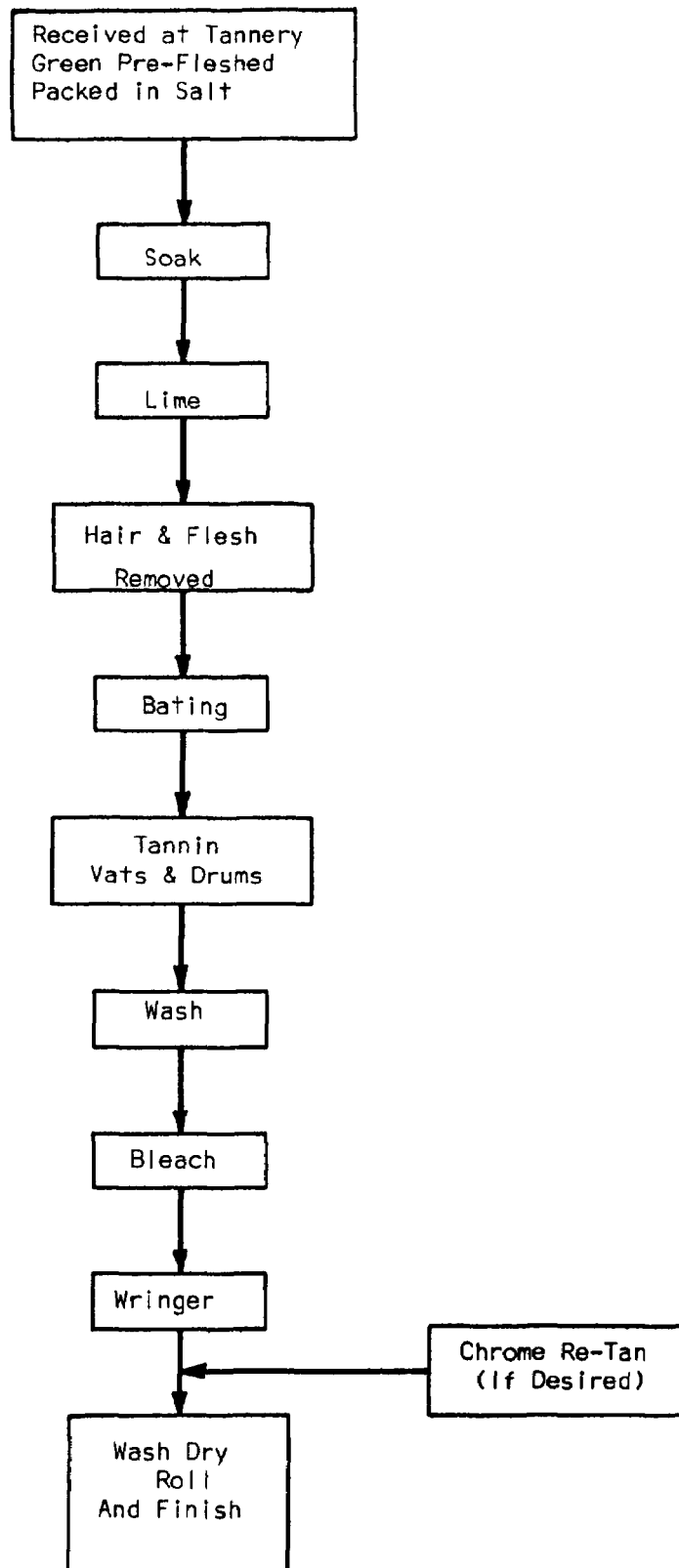


FIGURE 1 SCHEMATIC OF VEGETABLE TANNING PROCESS

percent tannins and the tannery used 118,511 pounds of the extract blend per week. The source of tannin waste water was the tannin yard, rinse liquor from sole leather and speciality leathers. All 1100 hides per day were soaked and washed, limed, and bated and delimed. Oropan XXS2 (product of Rohm Haas Co.) was used in the bating operation. Thirty-five hundred pounds of Oropan was used per week. Batepool waste water consisted of water from the bating and deliming process.

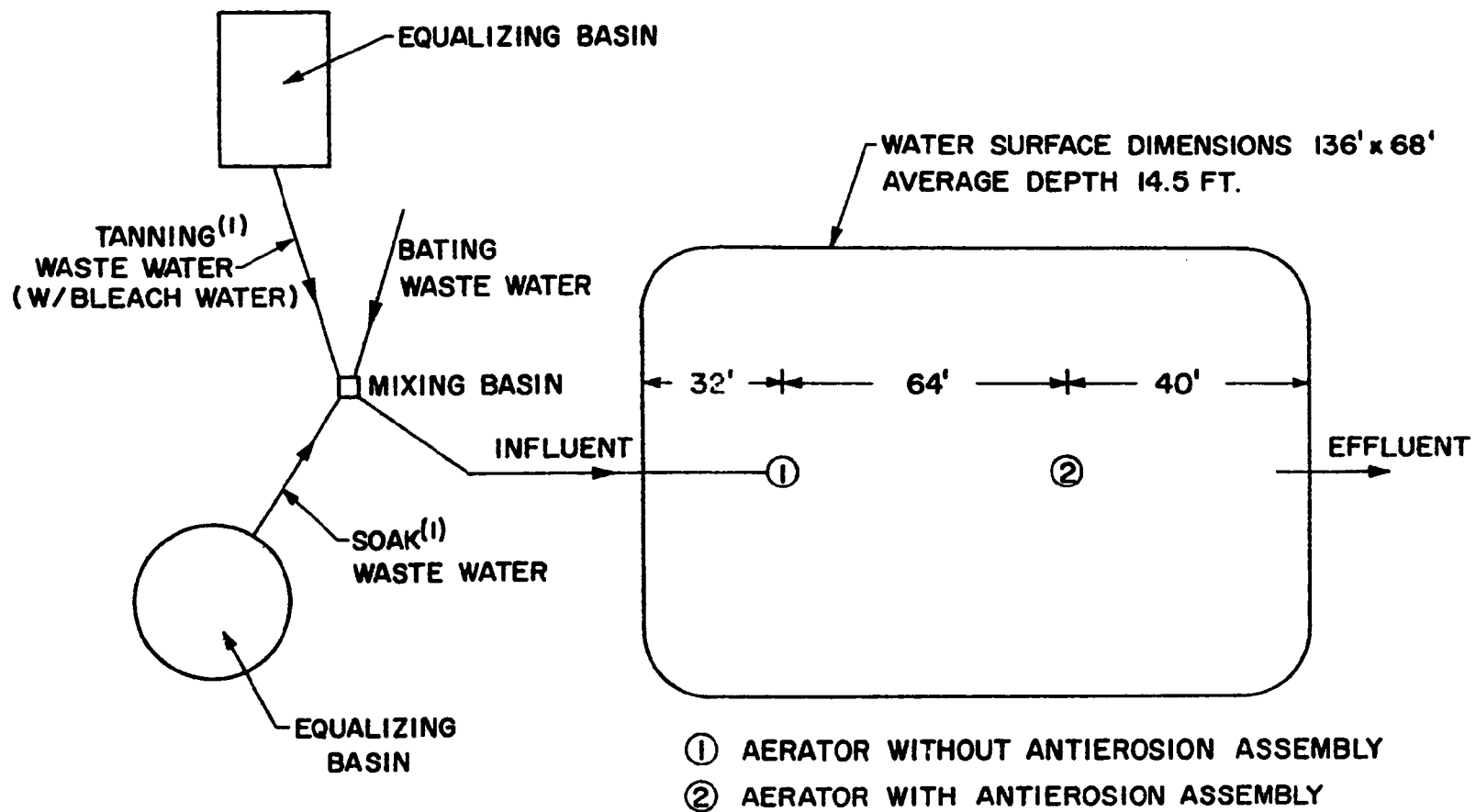
Total flow from the tannery during this study was 640,000 gpd of which 260,000 gpd was batepool waste water and 32,000 gpd was concentrated spent vegetable tannins.

SECTION V

LAGOON AND FLOW SYSTEM

Figure 2 shows the actual constructed site plan of the lagoon system and the positioning of the aerators. Water surface dimensions were 136 feet by 68 feet and the average depth was 14.5 feet. The inside bank slope was 2 to 1 for the first four feet and then 1 to 1 to the lagoon bottom. Water volume of the lagoon was 770,000 gallons. The influent pipe extended 32 feet into the lagoon and was positioned 6.0 feet from the lagoon bottom. Construction of the facilities and installation of pumps, pipes, tanks, and aeration equipment was completed in April 1968. The aeration equipment consists of two 5-horsepower aerators (model FLTM-5), Welles Products Corporation). The oxygen transfer rate given by the manufacturer was 3.2 lbs of O_2 per nameplate horsepower per hour at standard conditions (water with zero dissolved solids, $20^\circ C$ and at one atmosphere). An anti-erosion assembly was used on the aerator nearest the effluent but was not placed on the aerator nearest the influent. Advantage was taken of the aerator draft depth at the influent by positioning the aerator over the end of the influent pipe to immediately mix fresh waste entering the lagoon. Positioning the aerator directly over the influent was an attempt to minimize any shock load that may have occurred.

Flow to the lagoon system was proportioned to correspond with actual 24-hour plant waste water flow. (In-plant changes from time to time caused some variation in both waste water characteristics and flows). Initially the flow scheme was as shown in Figure 2, however, after starting up and experiencing some difficulty with pump clogging the soak hair and bleach water were diverted to another system. Since flow from the plant required pumping, flow measurements were made at the effluent with a V-notch weir and a Stevens recorder. Evaporation and seepage losses from the lagoon were estimated by observing lagoon water surface elevation change with zero influent. These losses were obscured by the accuracy of the flow measurements, estimated to be ± 10 percent. In addition to flow from the lagoon system, flow measurements were made of the spent tannins, batepool and total plant waste water discharge.



(1) Bleach water and soak waste water were diverted to another facility after experiencing pump difficulties.

FIGURE 2 SITE PLAN

SECTION VI

PROCEDURES AND ANALYSES

The following laboratory analyses were made on the waste waters (see Section XIII for notations):

Biochemical Oxygen Demand	Suspended Solids
Chemical Oxygen Demand	Fixed Suspended Solids
Organic Nitrogen	Volatile Suspended Solids
Ammonia Nitrogen	Settleable Solids
Total Kjeldahl Nitrogen	Hydrogen Ion Concentration
Total Solids	Total Sulfides
Total Fixed Solids	Total Phosphorus
Total Volatile Solids	Color

All laboratory analyses were made in accordance with Standard Methods for the Examination of Water and Waste Water [4] with the exception of total phosphorus. Total phosphorus was determined in accordance with a wet oxidation procedure in Official Methods of Analysis of the Association of Official Agricultural Chemists [5] and the method of Pons and Guthrie [6]. Phosphorus recovery by this method was 99 percent. The modified method for determining total phosphorus is presented in the Appendix. All BOD determinations (except effluent) were made with dilution water seeded with lagoon effluent. Both ultimate BOD and BOD₅ were made at 20°C.

In addition to laboratory analyses, field analyses of dissolved oxygen (DO), pH, and temperature were made. A model 54 RC YSI DO meter was used for field oxygen measurements and model 30 pH recorder (Analytical Measurements, Inc.) was used for continuous pH measurement.

SECTION VII

LAGOON OPERATIONAL RESULTS

General

The lagoon system became operative in April 1968 and flow to the system was increased systematically during the period of study from 15 April 1968 through 18 September 1969. Operation of the system was divided into five phases which were designed to go from an aerobic condition to an anaerobic condition. The following dates delineate the operative phases:

I. 15 April 1968 - 15 August 1968 -- During this period the lagoon was filled and allowed to reach a steady-state condition. The influent consisted of batepool, soak waste water and tannins (with bleach waste water) proportioned at a ratio of 6 to 2 to 1, respectively. Operations diminished beginning the last week of June and returned to normal the first week in July because of a vacation period observed by the tannery. This resulted in 10 days of zero flow. The flow rate into the lagoon during this phase was 15 gpm.

II. 15 August 1968 - 11 December 1968 -- An attempt was made to increase the flow to the system, however, the pumping system required modification before this could be accomplished. Therefore, since it was desirable to extend the data at low flow to include filtered effluent samples, a low flow of 20 gpm was observed. This period provided additional data on soluble and insoluble effluent fractions at an extremely low flow. The waste streams and flow ratios remained the same as in the above operational phase.

III. 11 December 1968 - 19 March 1969 -- Flow to the lagoon system was increased to an average flow of 33 gpm. Because of problems with freezing, hair clogging pumps, and in-plant changes, after 8 January 1969 soak and bleach waste waters were not pumped into the system. From 8 January 1969 to the end of the study only batepool and tannin waste waters were proportioned during the 5-day work week at a batepool to tannins ratio of 8:1 and pumped into the lagoon. In addition, batepool waste water was allowed to enter the lagoon on a 7-day basis. Examination of the weekend batepool flow revealed that it was essentially potable water and did not contribute to the waste load. This weekend flow was necessary to prevent pipes and pumps from freezing.

IV. 19 March 1969 - 26 June 1969 -- Flow to the lagoon averaged 69 gpm and consisted of a batepool to tannins ratio of 8:1. Beginning the end of April and through part of May in-plant

changes were made which required frequent diversion of the tannins. From the end of May through 26 June the flows were normal.

V. 26 June 1969 - 18 September 1969 -- Average flow into the lagoon was 127 gpm. The last week in June and the first week in July were affected by the tannery closing for vacation. During this operational phase the flows remained in the same proportion as the previous phase (batepool to tannins of 8:1).

Influent Characteristics

In addition to routine analyses, ultimate BOD and oxygen transfer measurements were made in the laboratory. Figure 3 shows the arrangement used to measure oxygen transfer to water and waste water. The DO probe position, stirrer speed, aeration vessel size, aeration bubble size and air flow rate were the same for all measurements. Data from these analyses are given in Table A-1 of the Appendix and results from the plot of

$$\log \left(\frac{C_s - C_t}{C_s - C_o} \right) = -K_L t$$

are shown in Figure 4. The data indicate an alpha value of 0.72 for the influent waste water which consisted of a batepool to tannins ratio of 8:1. It should be noted that these data were obtained by a comparison of the waste water with distilled water. Dissolved oxygen of distilled water was depleted by using enough sodium sulfite catalyzed with cobalt to lower the dissolved oxygen. Since the dissolved oxygen of the waste water was low enough to measure oxygen transfer, sodium sulfite and cobalt were not added to the waste water to reduce the dissolved oxygen.

Long term BOD data was obtained on different samples at 20°C. Figure 5 and Figure 6 show the results of both observed and theoretical values for different samples with different ultimate BODs. These data indicate a velocity constant (log to the base 10) of 0.22 day⁻¹. Calculated BOD values shown on the figures were obtained by using the indicated first stage ultimate BOD values and the first stage velocity constant. Data from which these figures were obtained are included in Table A-2 of the Appendix.

During the first phase of operation flow recording equipment was not available, therefore measurements were made periodically to determine the flow. At low flow problems were frequently encountered with pumping because of hair, therefore, the low flow of 15 gallons per minute is a best estimate during this period.

Influent flow arrangements were such that it was impossible to obtain an accurate influent flow rate, hence effluent flows were measured throughout the study. To obtain an accurate estimate of influent flow the evaporation and seepage rates were measured. This was accomplished by shutting off flow to the lagoon, measuring the effluent flow, and

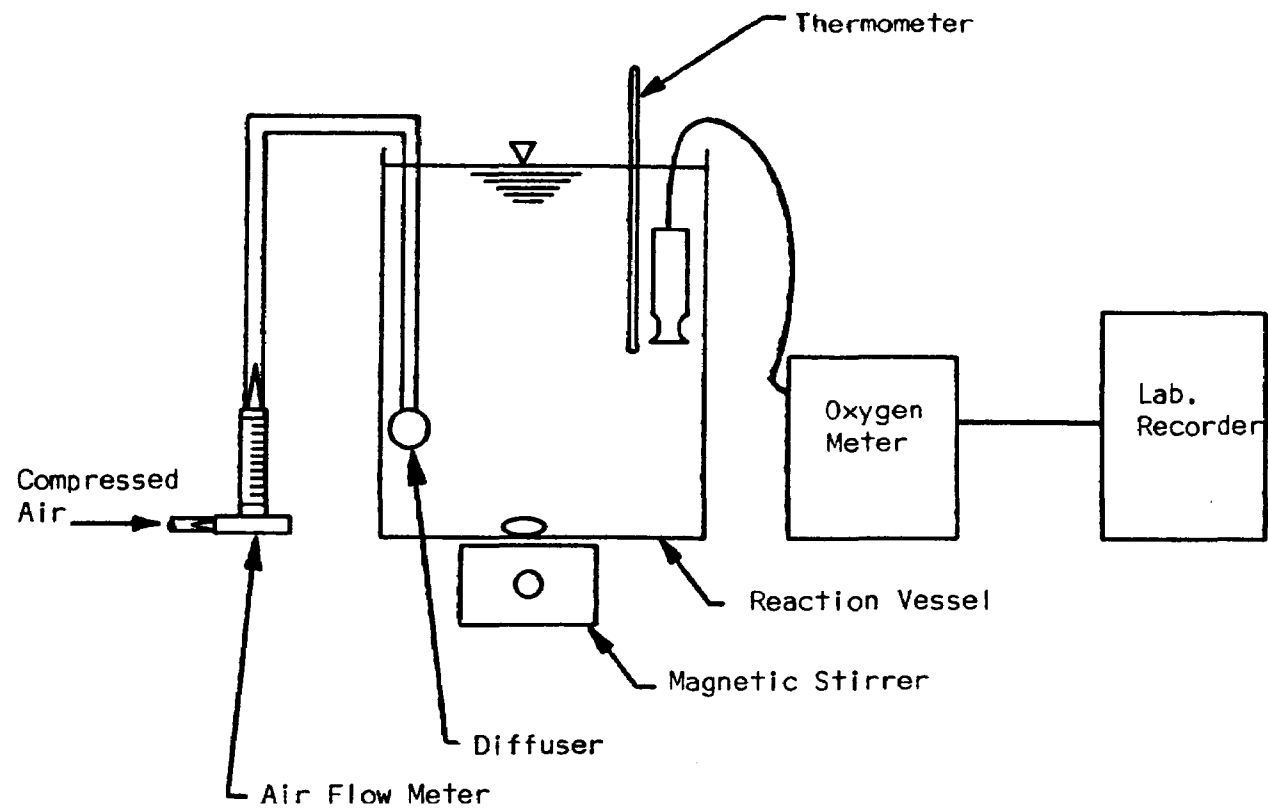


FIGURE 3 SCHEMATIC OF LABORATORY APPARATUS FOR MEASURING OXYGEN TRANSFER

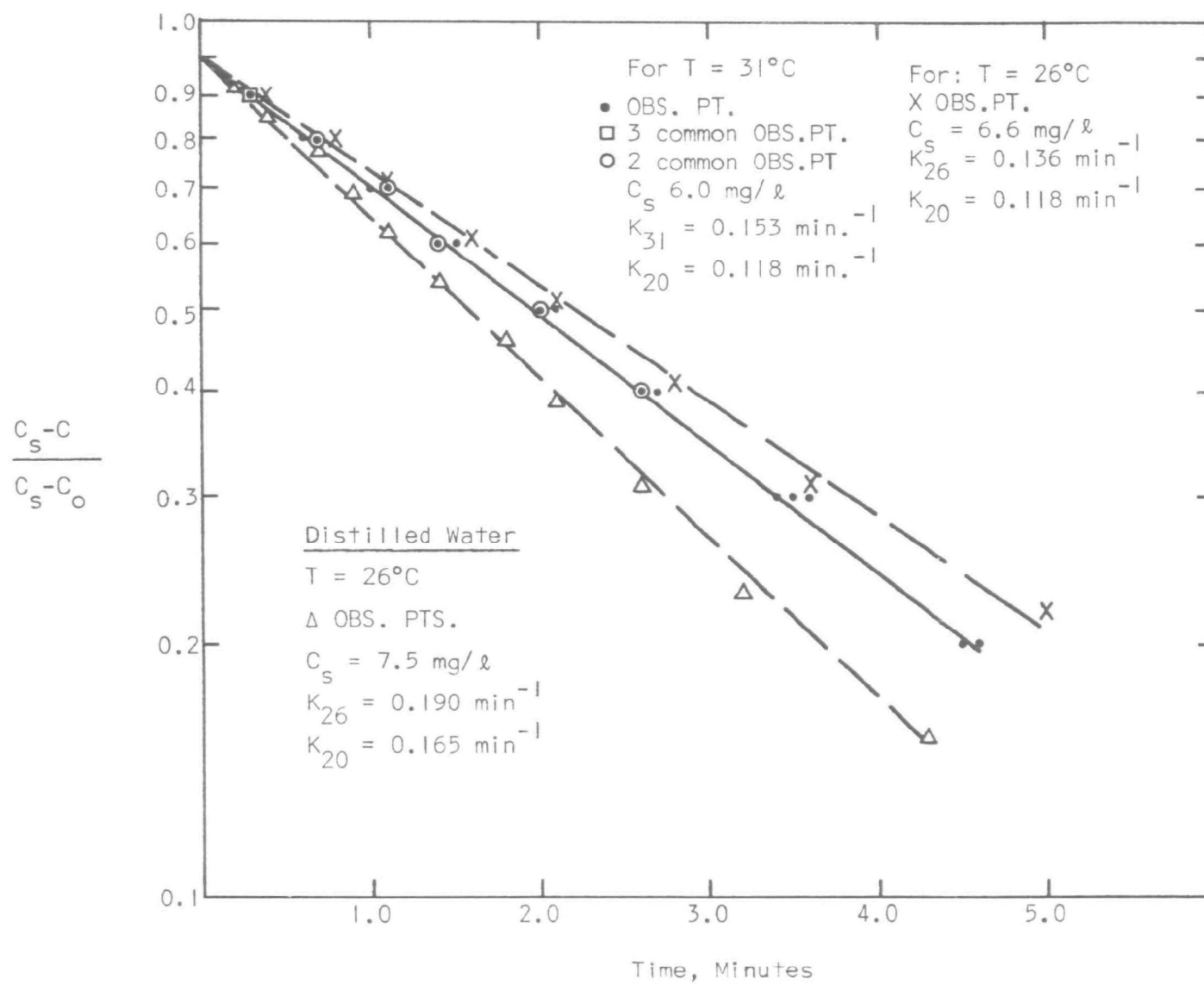


FIGURE 4 OXYGEN TRANSFER: LAGOON INFLUENT

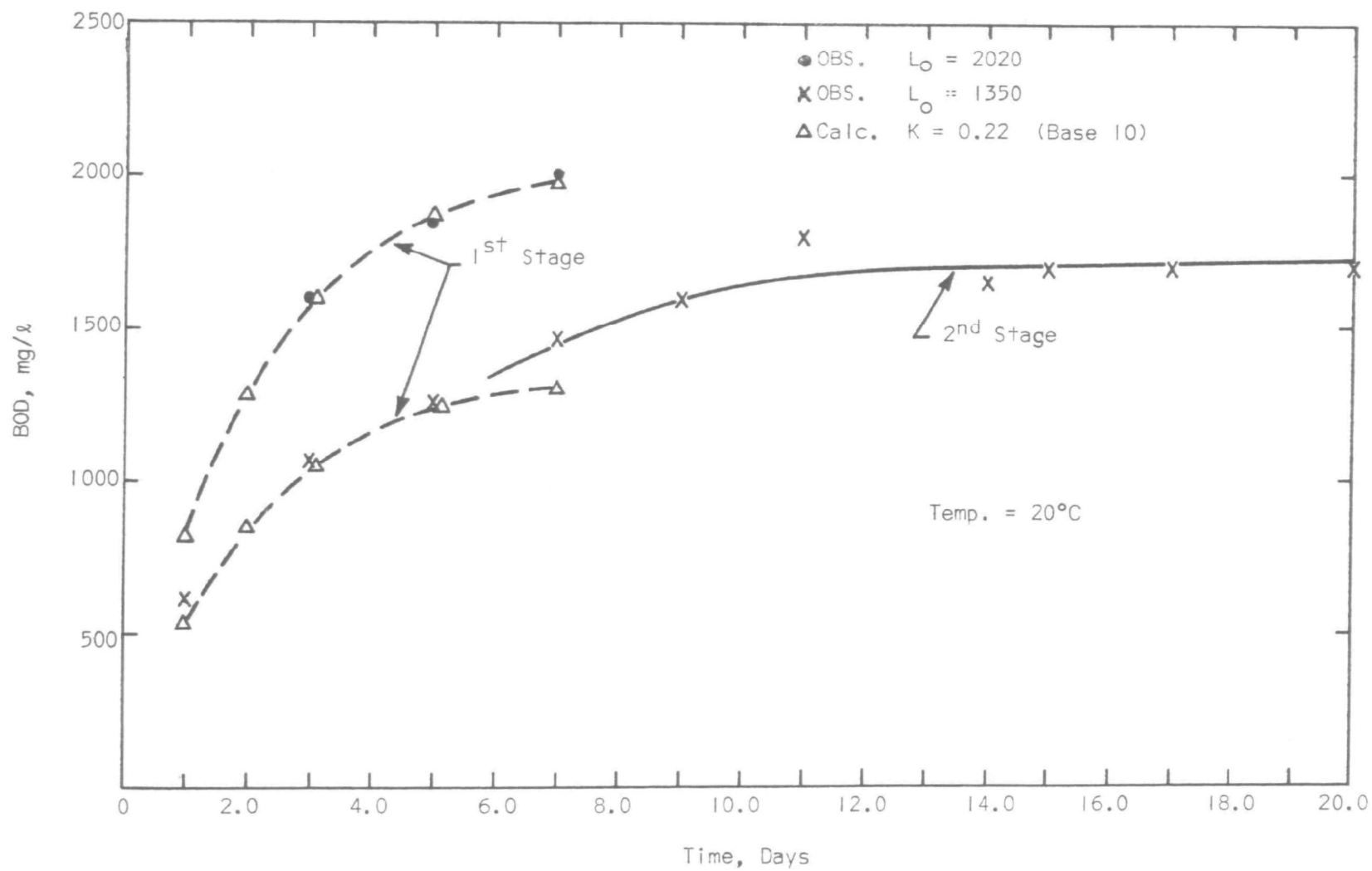


FIGURE 5 1. ULTIMATE BOD: LAGOON INFLUENT

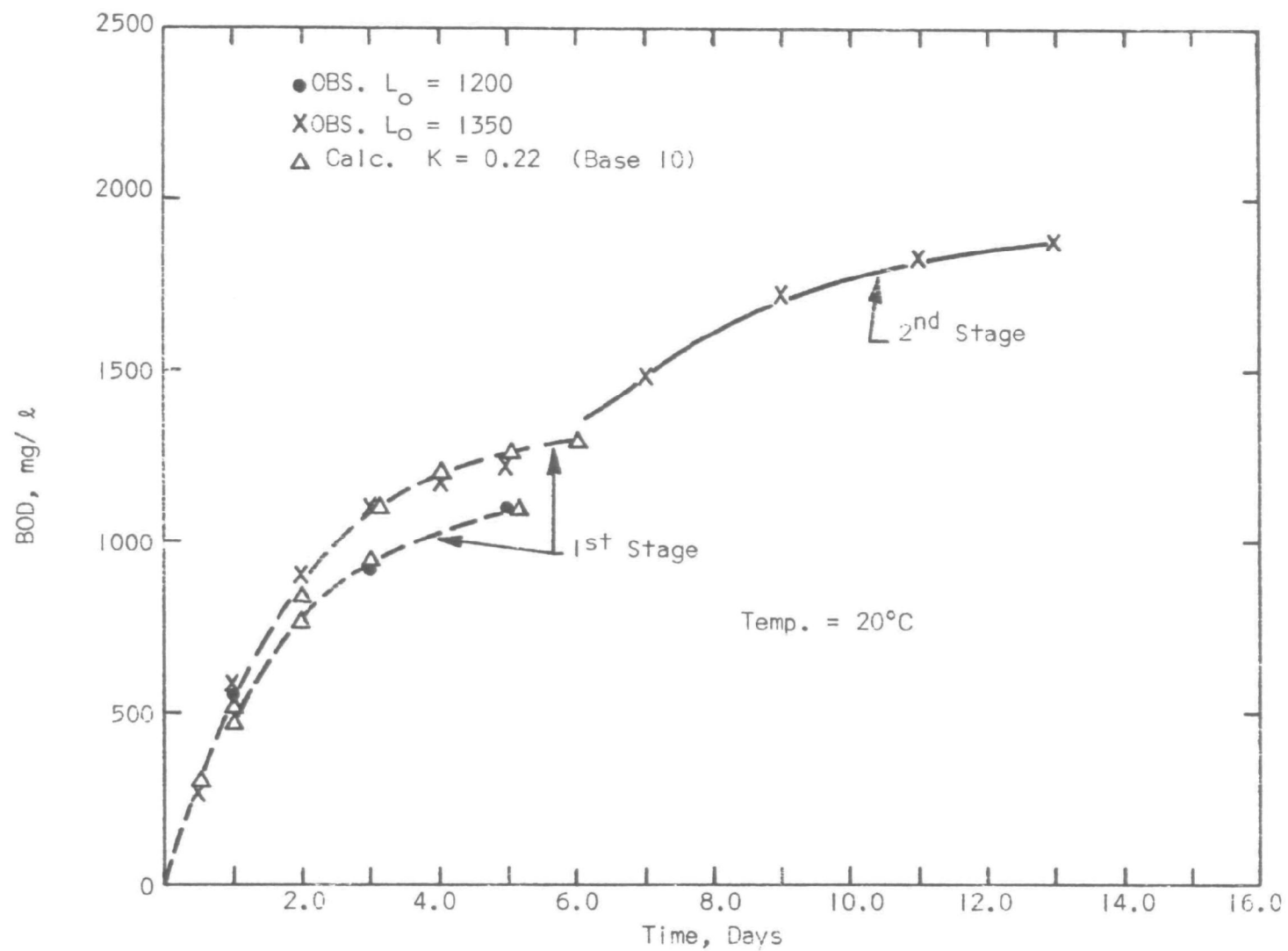


FIGURE 6 II. ULTIMATE BOD: LAGOON INFLUENT

recording the change in lagoon surface elevation. From these measurements a water balance was struck. The losses were not detectable with the flow recorder, therefore, the effluent flow was a reasonable measurement of the influent flow.

Results of flow measurements during the periods in which accurate measurements were made is shown in Figure 7. These data show weekly average flows and the average flow for the individual phases III, IV and V. The change from a five day flow arrangement to a seven day flow arrangement is noted. It should be understood that the switch to flow during the weekends resulted in an essentially clear water flowing into the lagoon for two days - i.e., BOD_5 during weekends was 3 mg/l. The weekly average flow values are also given in Table A-3 of the Appendix.

During the period of study the influent flow consisted of two different combinations of in-plant waste stream flows. The first combination of batepool, soak, and tanning (with bleach water) waste waters is presented in Table A-4 of the Appendix and summarized in Table 1. Table 2 is a summary of the influent data presented in Table A-5 of the Appendix. This last set of data is for the lagoon influent when it consisted of batepool and tanning. It should be noted that the most significant difference between these two flow arrangements was the solids content.

Since the tanning process is a batch process pH can be expected to vary during the day. Figure 8 illustrates the variation in the influent pH that was observed.

Color in the waste took on an orange-red hue as is indicated in Table 3. Although these data were collected in accordance with Standard Methods [4], they do not indicate the severity of the color problem. Color of the waste water on the platinum-cobalt scale was estimated by diluting with distilled water. This method of measurement indicated that the color was about 5000 units.

Effluent Characteristics

Results from lagoon effluent analyses are presented in a form compatible with the five phases previously described. These data are presented in Table A-6, Table A-7, Table A-8, Table A-9, and Table A-10 of the Appendix. Table 4 summarizes the average effluent data for the five operational phases. The BOD_5 and COD for each phase are shown graphically. Figure 9 is a plot of the BOD_5 and COD values for the first phase, showing the progression to steady-state. This figure shows the change in total BOD_5 and total COD through August 15, 1968. Total BOD_5 and total COD, and soluble BOD_5 and soluble COD for the other four phases are shown separately. Results from flows of 20 gpm, 33 gpm, 69 gpm, and 127 gpm are shown in Figure 10, Figure 11, Figure 12, and Figure 13, respectively. It should be noted that Figure 12 reflects in-plants changes that resulted in the diversion of tannings from the end of April through part of May. In addition, the variation of the effluent in August shown in Figure 13 should be noted. The reason for this variation is uncertain, but it is believed to have resulted from in-plant changes also.

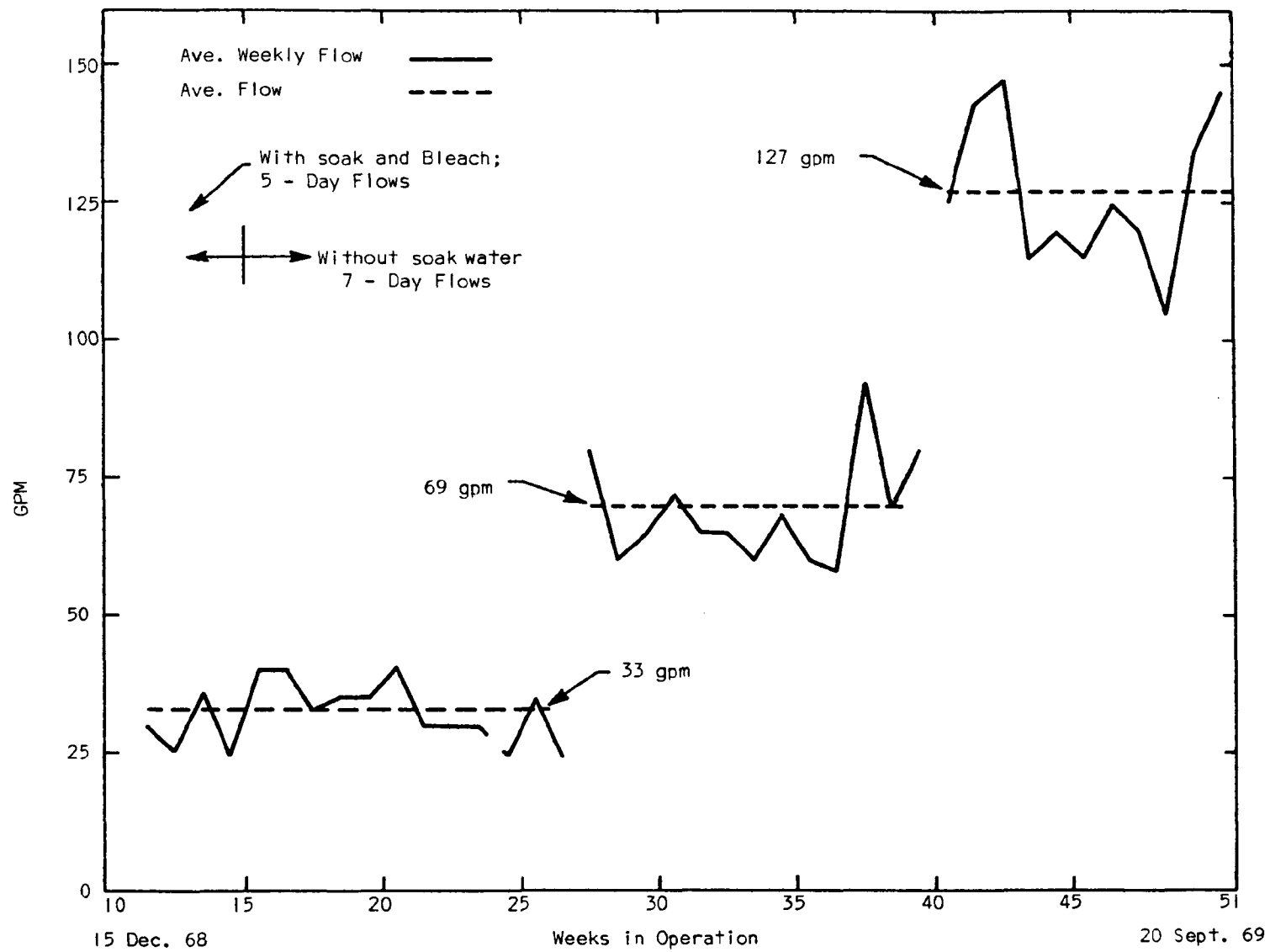


FIGURE 7 AVERAGE WEEKLY FLOW

TABLE I SUMMARY DATA FOR BLENDED BATEPOOL, TANNINS (WITH BLEACH WATER) AND SOAK WATER INFLUENT^{(1),(2)}

<u>Analysis</u>	<u>Maximum</u>	<u>Minimum</u>	<u>Average</u>
BOD ₅	1850	725	1043
COD	6616	1937	4470
ORG-N	48.3	28.3	40.6
NH ₃ -N	66.3	23.8	47.1
TKN	102.4	62.6	87.8
TS	15,845	5051	9190
TFS	13,675	3435	6500
TVS	4427	1143	2710
SS	975	350	539
FSS	182	0	48
VSS	975	350	582
Set. S	122	0.1	15.1
pH	8.6	3.2	6.0
T. Sulf.	1.8	1.0	1.5
TP	8.37	4.46	6.83

(1) Results in mg/l except pH and SS. SS in ml/l

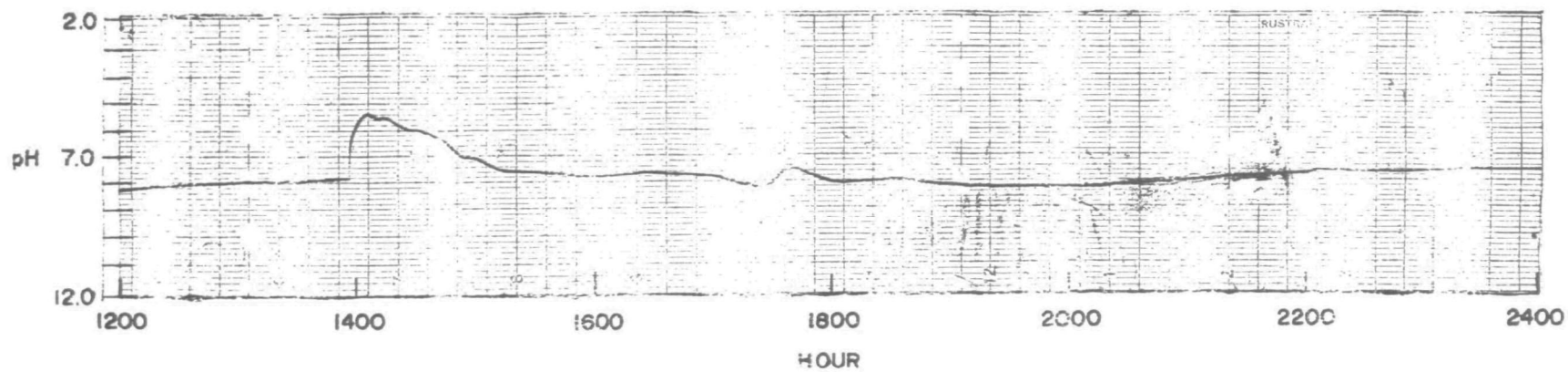
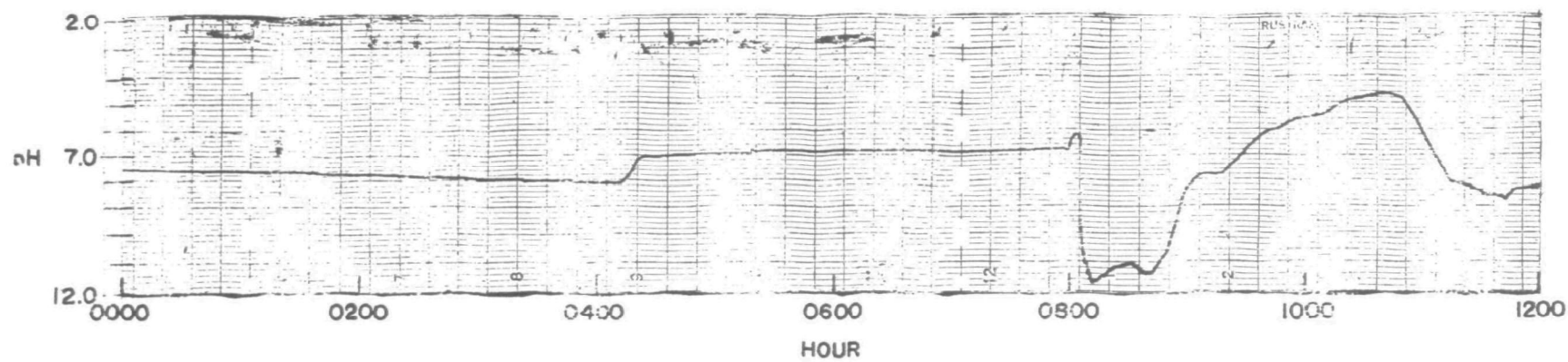
(2) Based on composite samples with the exception of total sulfides. Total sulfides based on grab samples.

TABLE 2 SUMMARY DATA FOR BLENDED BATEPOOL AND TANNIN INFLUENT^{(1),(2)}

<u>Analysis</u>	<u>Maximum</u>	<u>Minimum</u>	<u>Average</u>
BOD ₅	2050	725	1170
COD	7340	2349	4730
ORG-N	109.4	26.8	47.2
NH ₃ -N	99.6	33.1	59.3
TKN	209.0	63.0	106.5
TS	7579	2556	4392
TFS	3410	660	1850
TVS	4169	1384	2542
Set. S	> 40	0.5	-
pH	9.6	5.8	6.8
T.Sulf	1.2	0.4	0.7
TP	8.80	5.61	7.33

(1) Results in mg/l except pH and SS. SS in ml/l

(2) Based on composite samples with the exception of total sulfides.
Total sulfides based on grab samples



(24-HR. pH, APRIL 24, 1968)

FIGURE 8 TYPICAL INFLUENT pH

TABLE 3 LAGOON INFLUENT AND EFFLUENT COLOR⁽¹⁾⁽²⁾

	DATE				
	8/13/68	8/20/68	3/5/69	3/20/69	6/17/69
<u>(pH Adjusted to 7.6)</u>					
<u>Influent:</u>					
dominant wavelength, mμ	592	583	590	588	590
hue ⁽³⁾	0	Y-0	0	0	0
luminance, %	25	48	26	26	26
purity, %	74	55	68	70	76
<u>Effluent:</u>					
dominant wavelength, mμ	586	583	594	604	598
hue ⁽²⁾	Y-0	Y-0	0	0-R	0-R
luminance, %	30	48	13	15	10
purity, %	71	55	92	96	96

(1) Using dilutions, all results compare with about 5000 platinum-cobalt units.

(2) Spectronic 20; 10 ordinates; and spectral band width 20 mμ.

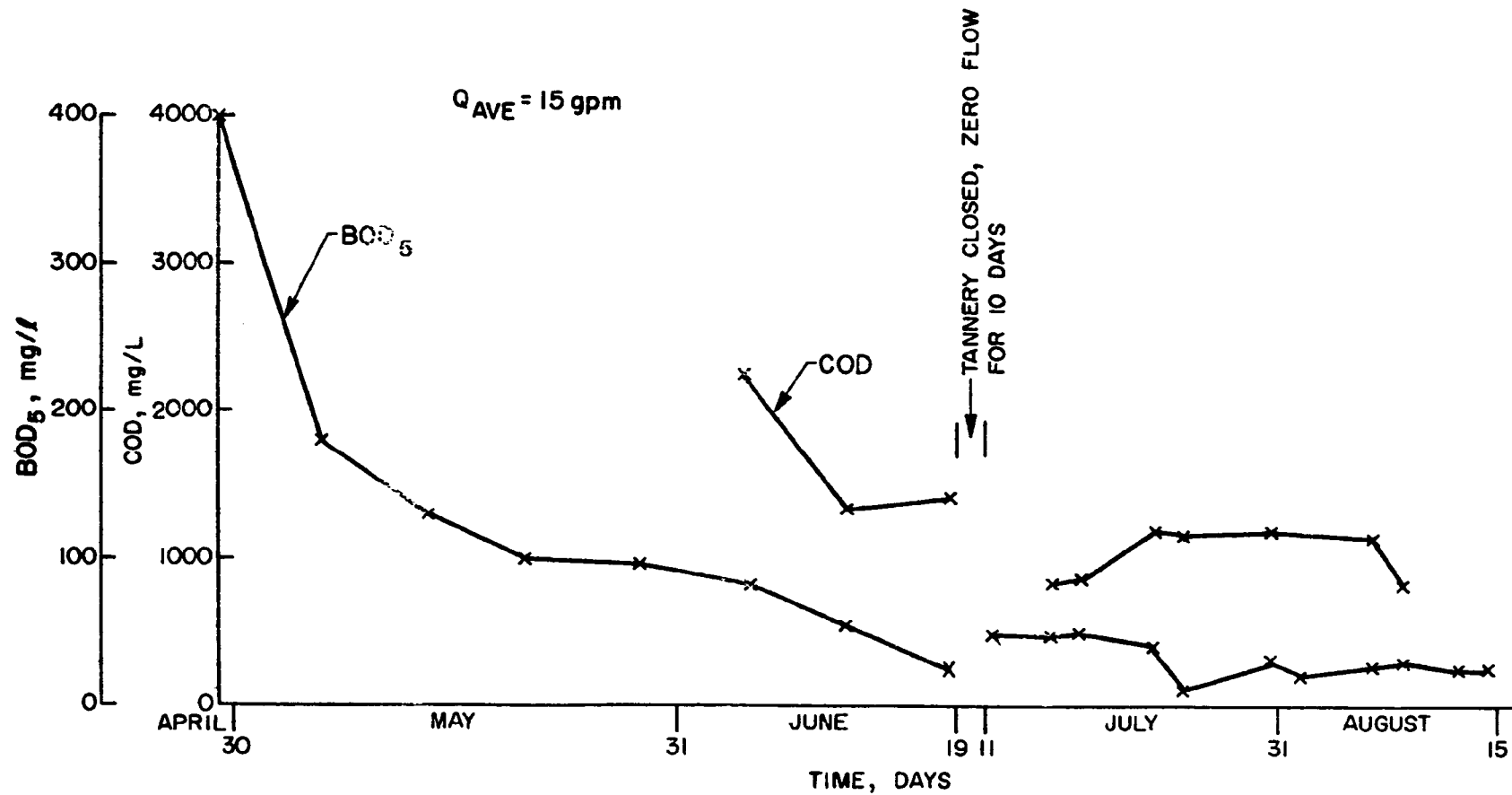
(3) 0 = orange; Y-0 = yellow-orange; R = red and 0-R = orange-red.

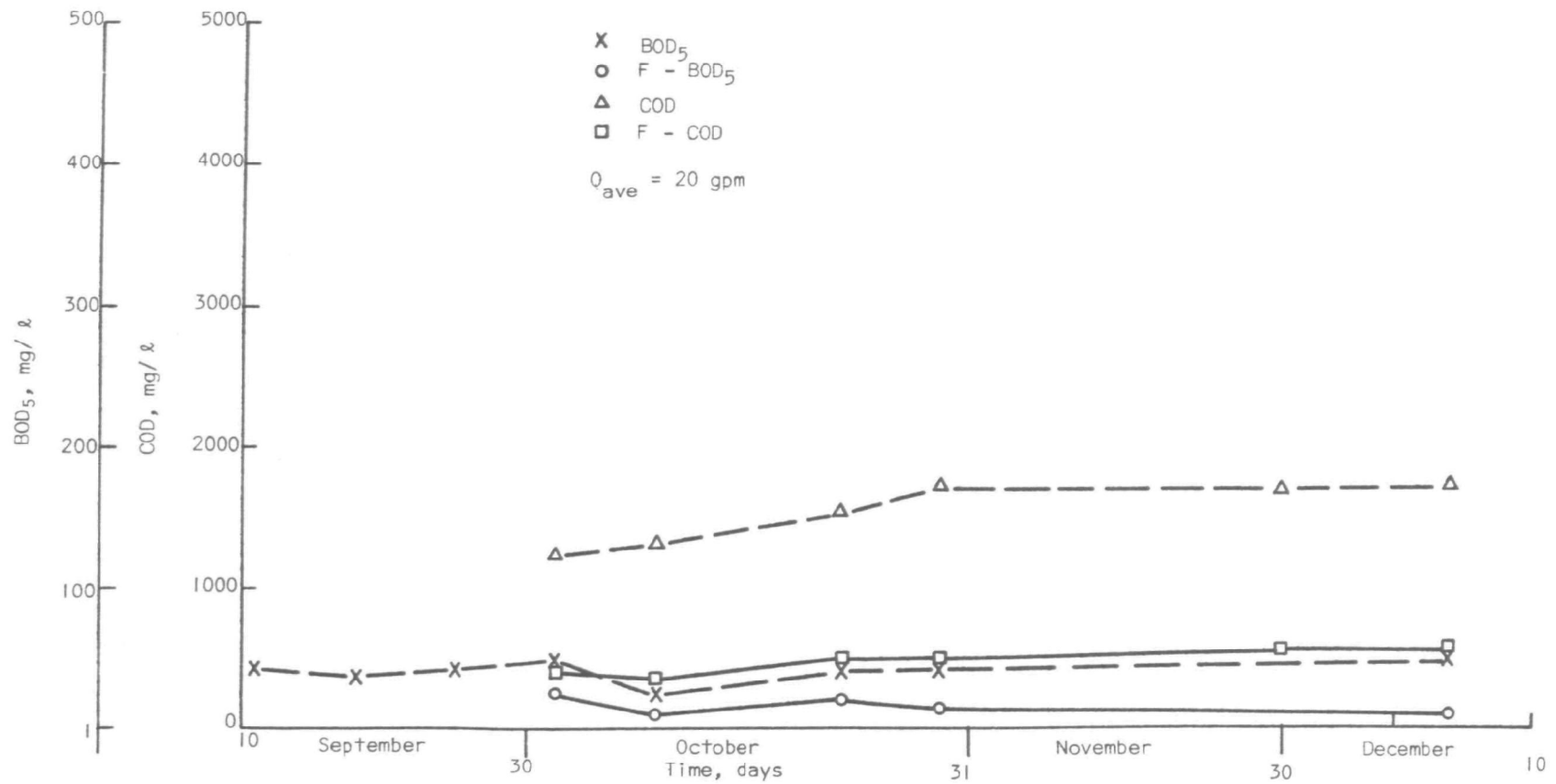
TABLE 4 EFFLUENT SUMMARY DATA: PHASE I-V⁽¹⁾⁽²⁾

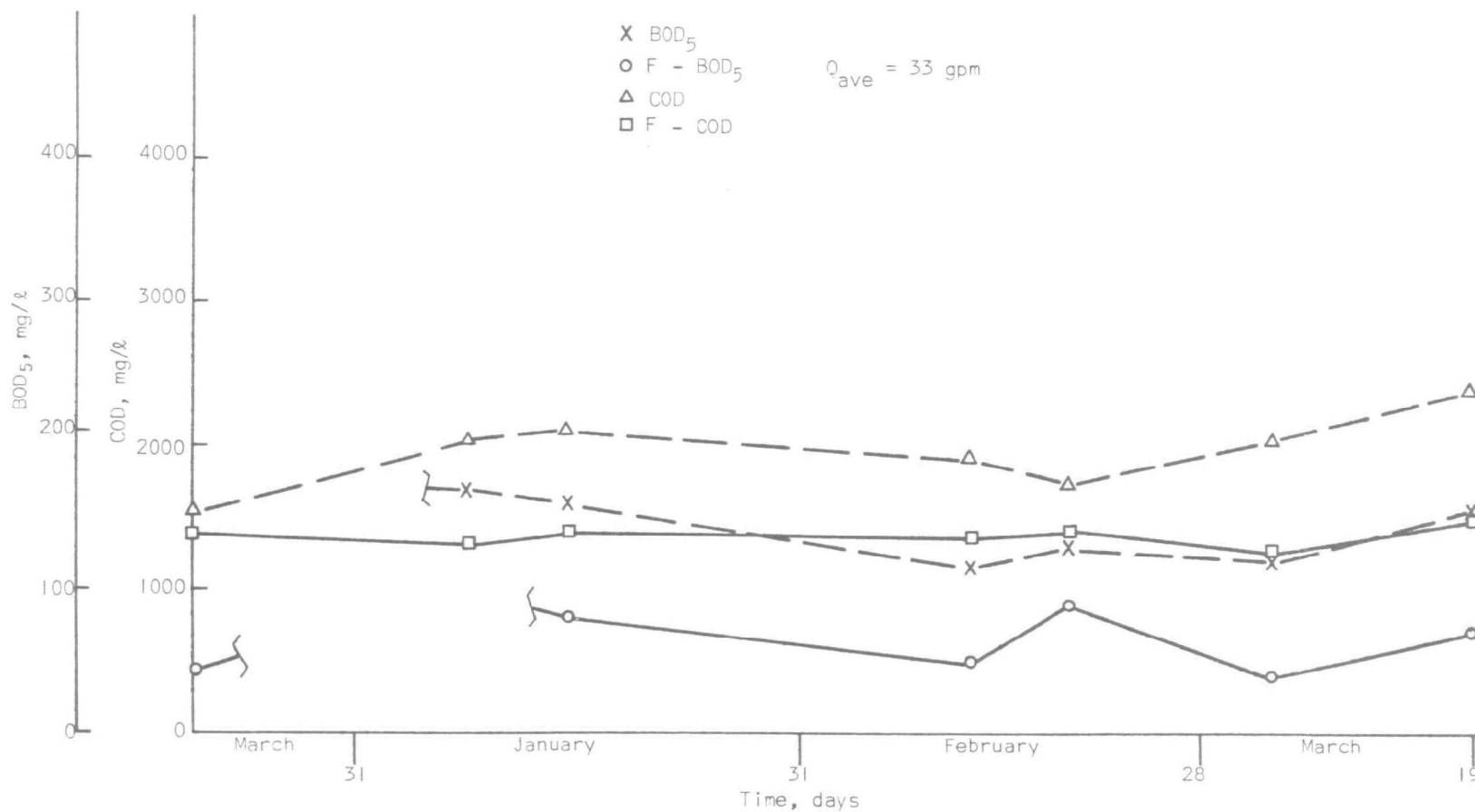
Analysis	AVERAGE				
	Q=15 gpm	Q=20 gpm	Q=33 gpm	Q=69 gpm	Q=127 gpm
BOD ₅	25	45	132	274	315
F-BOD ₅	-	17	64	145	159
COD	1083	1549	1960	2113	2114
F-COD	-	462	1362	1328	1431
ORG-N	17.5	31.6	27.7	16.7	23.9
F-ORG-N	-	6.2	6.7	5.5	11.3
NH ₃ -N	26.2	29.0	24.8	17.8	41.5
F-NH ₃ -N	-	27.7	23.7	16.8	35.2
TKN	43.7	60.6	52.5	34.5	65.4
F-TKN	-	33.9	30.4	223	46.5
TS	6130	7380	2330	2532	2255
TFS	5270	6300	1383	992	1038
TVS	850	1080	947	1540	1217
SS	495	890	435	503	459
FSS	117	250	150	100	98
VSS	378	747	283	402	362
Set. S.	25	32	2	1	2
pH	7.1	6.9	7.4	7.1	6.9
T. Sulf.	0.0	0.0	0.0	0.0	0.3
TP	2.36	7.67	5.6	5.8	3.6

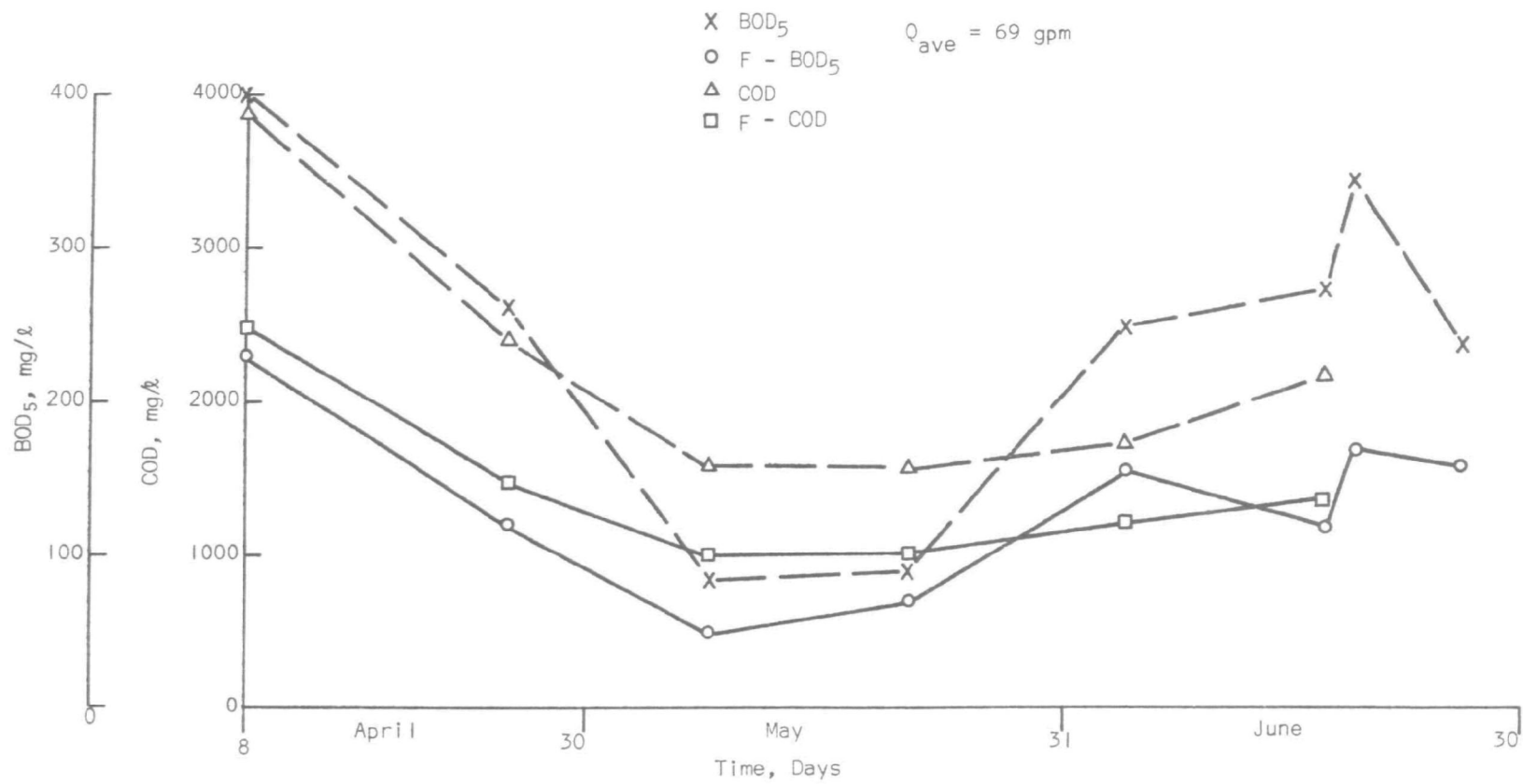
(1) Results in mg/l except pH and SS. SS in ml/l

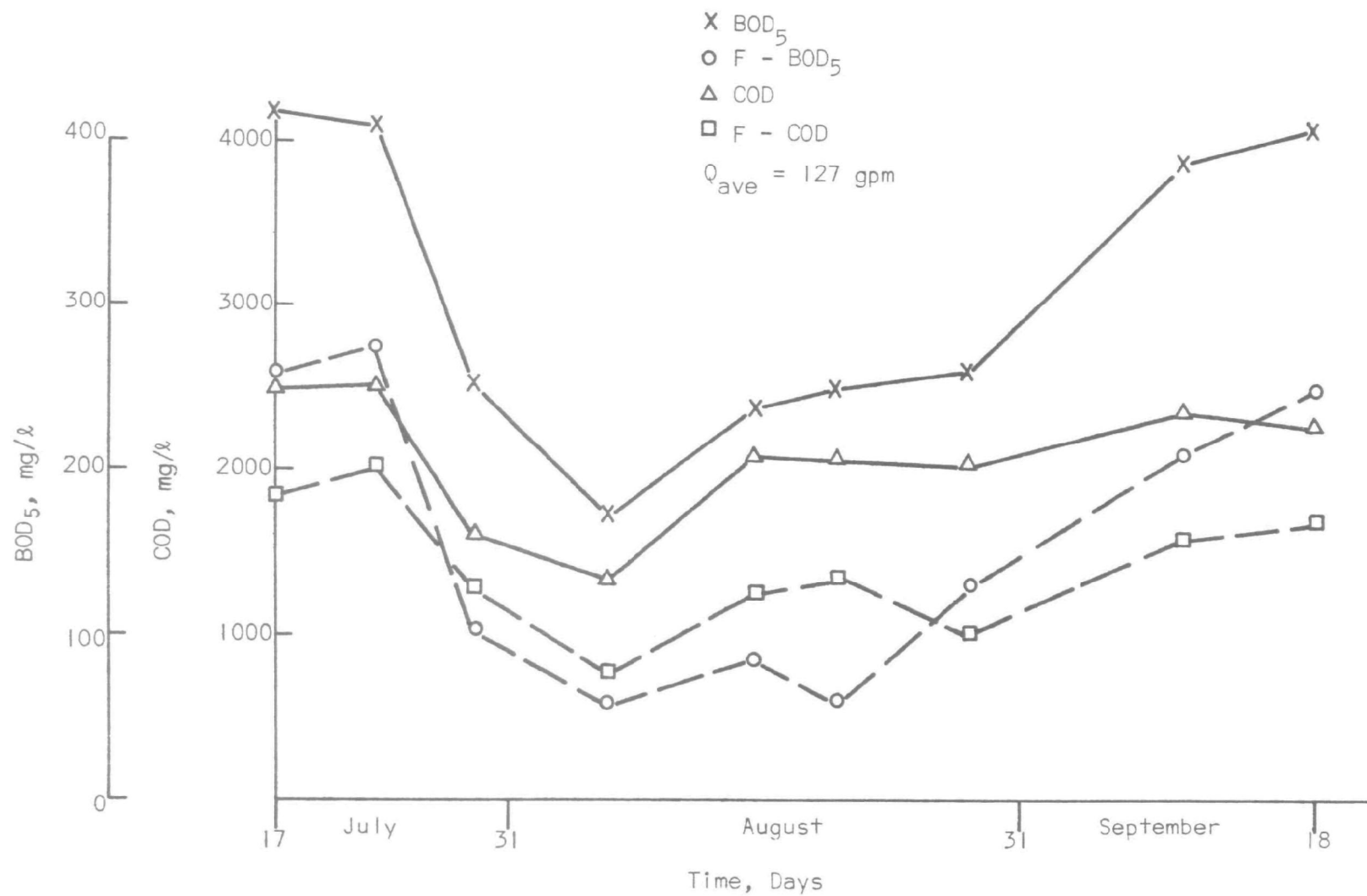
(2) Only for data after steady state

FIGURE 9 EFFLUENT BOD_5 AND COD: PHASE I

FIGURE 10 EFFLUENT BOD₅ AND COD: PHASE II

FIGURE 11 EFFLUENT BOD₅ AND COD: PHASE III

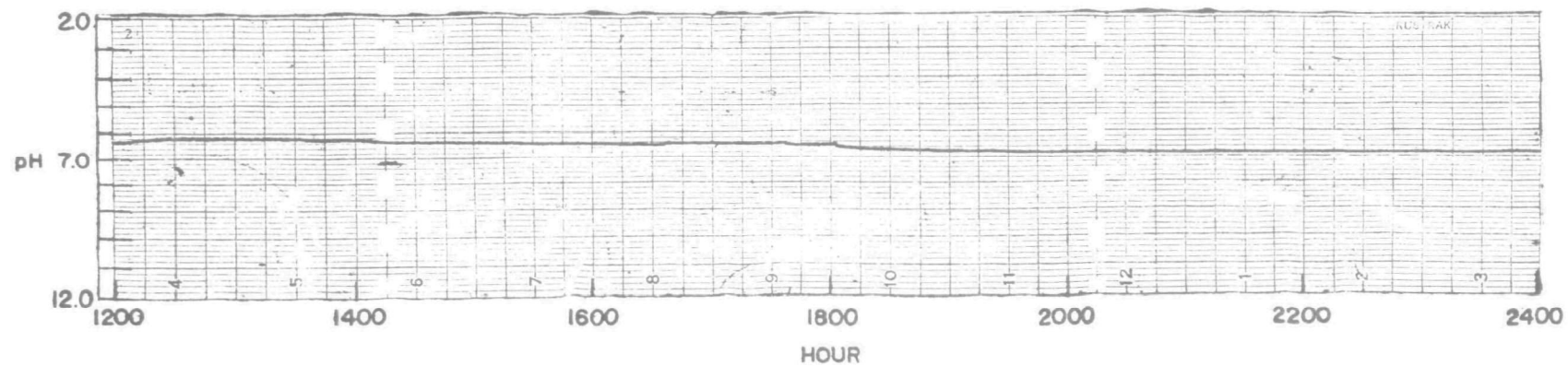
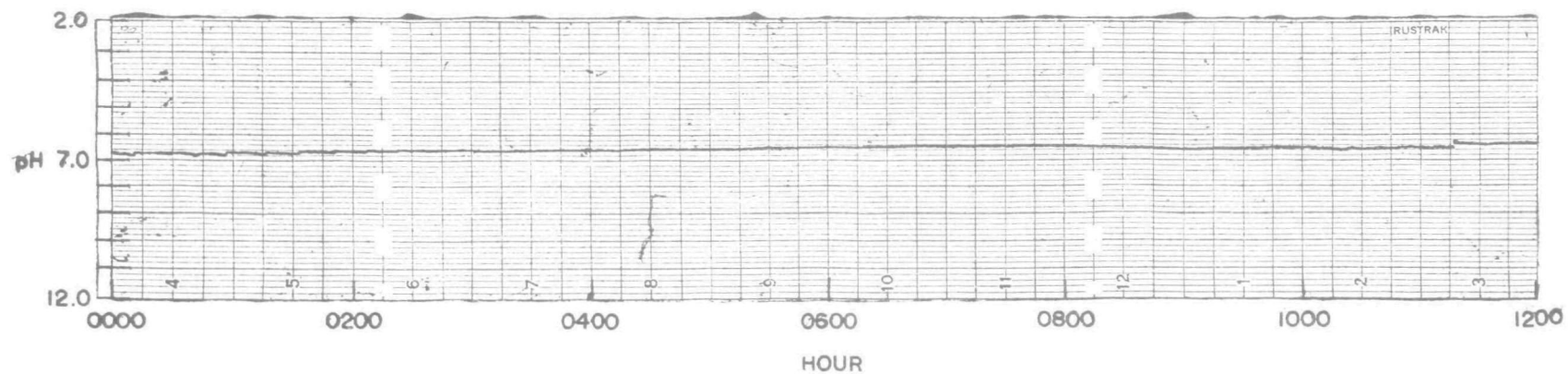

 FIGURE 12 EFFLUENT BOD₅ AND COD: PHASE IV

FIGURE 13 EFFLUENT BOD₅ AND COD: PHASE V

Effluent pH varied very little. It was observed that the variation between the phases was relatively small and the daily variation insignificant. Figure 14 shows a recording of the typical effluent pH.

Dissolved oxygen measurements were made of the lagoon effluent and in the lagoon, and samples were taken from bottom deposits. Resulting from effluent dissolved oxygen and dissolved oxygen in the lagoon are presented in Table 5 and Table 6, respectively. Sludge deposit data are presented in Table 7.

Temperature measurements were made of both the influent and effluent. (The effluent temperatures also represent the condition found in the lagoon.) Average monthly water temperatures for the influent and effluent are presented in Table 8. These data represent monthly averages as obtained from daily measurements made between the hours of 7:30 a.m. and 3:30 p.m.



(24-HR. pH, AUGUST 14, 1968)

FIGURE 14 TYPICAL EFFLUENT pH

TABLE 5 EFFLUENT DISSOLVED OXYGEN

<u>DATE</u>	<u>Dissolved Oxygen</u> <u>mg/ l</u>	<u>Temperature</u> <u>°C</u>	<u>Flow</u> <u>gpm</u>
8/8/68	3.7	27	15
8/19/68	3.8	27	15
11/22/68	9.6	7	20
3/5/69	3.3	7	30
6/19/69	0.8	22	68
6/25/69	1.6	25	70
7/2/69	0	25	110
7/28/69	0	25	130
8/4/69	2.8	25	120
8/15/69	0	27	110
8/20/69	2.2	27	130
9/10/69	0.8	22	145
9/17/69	0.5	22	165

TABLE 6 LAGOON DISSOLVED OXYGEN PROFILES⁽¹⁾

STATION, DATE	Depth, feet												
<u>Sta. 1</u>	0	1	2	3	4	5	6	7	8	9	10	11	12
8/19/68	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	3.2	-	0.0
11/22/68	9.6	9.6	9.6	9.6	9.6	9.6	9.2	-	3.0	-	-	-	0.0
3/5/69	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	
6/19/69	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
9/17/69	0.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
<u>Sta. 2</u>													
8/19/68	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.2	4.3	4.4	4.4
6/19/69	0.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
9/17/69	0.7	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
<u>Sta. 3</u>													
8/19/68	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	3.6	0.0	0.0
11/22/68	9.6	9.6	9.6	9.6	9.6	9.6	9.6	9.6	9.6	9.6	-	2.2	0.0
3/5/69	4.2	3.6	3.5	3.4	3.3	3.5	3.5	3.5	3.5	3.5	3.5	2.5	2.5
6/69/69	1.2	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
9/17/69	0.8	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

⁽¹⁾ Station 1 at Influent end, station 2 at center and station 3 at effluent end.

TABLE 7 SLUDGE DEPOSITS⁽¹⁾

<u>Date</u>	<u>Station</u>	<u>Sludge Depth, Feet</u>	<u>Volatile Solids, percent</u>	
			<u>Liquid Interface</u>	<u>Bottom</u>
8/19/68	1	1.5	-	-
	2	0.3	-	-
	3	1.5	-	-
11/22/68	1	1.5	79.8	81.9
	3	1.5	78.3	71.2
3/5/69	1	1.5	-	-
	3	1.5	-	-
6/19/69	1	1.3	82.6	75.3
	2	0.5	76.6	70.7
	3	2.5	72.8	67.9
9/17/69	1	1.5	72.1	-
	2	0.5	69.2(mixed)	-
	3	1.5	58.3(mixed)	-

⁽¹⁾ Samples taken with core type sampler.

TABLE 8 AVERAGE MONTHLY LAGOON INFLUENT AND EFFLUENT TEMPERATURES

<u>MONTH</u>	<u>Average Temperature, °C</u>	
	<u>Influent</u>	<u>Effluent</u>
January 1969	16	5
February 1969	15	6
March 1969	15	8
April 1969	17	15
May 1969	19	19
June 1969	21	22
July 1969	24	24
August 1969	23	24
September 1968 & 1969	20	22
October 1968	19	17
November 1968	17	9
December 1968	17	5

SECTION VIII

DISCUSSION

Field Demonstration Lagoon

Although the influent pH varied significantly due to the batch operations at the tannery, the effluent remained at a pH of 7.0 ± 0.5 . Dissolved oxygen in the system varied with temperature changes and waste load. The lagoon system was completely aerobic for operational phases one, two, and three (except at the sludge interface at the bottom of the lagoon). For the fourth operational phase (69 gpm) the lagoon surface carried a dissolved oxygen content of 1.0 mg/l and one foot below the surface the dissolved oxygen was zero. During the fifth operational phase only trace amounts of dissolved oxygen could be found at the lagoon surface. The different temperatures at which the operational phases were observed varied significantly. The average temperatures for the operational phases (each had a duration time of at least 12 weeks) were 24, 17, 7, 18 and 24°C for phases I through V, respectively. The alpha value for the waste water at 20°C was 0.72 and the BOD velocity constant (base 10) was 0.22 day^{-1} . For phases I and II the N:BOD₅, P:BOD₅, N:COD and P:COD ratios were 0.084, 0.0065, 0.020, and 0.0015, respectively. During phases III through V these same parameters were 0.091, 0.0063, 0.023, and 0.0016, respectively.

Since the aerators provided a lagoon turnover rate of once every 3 hours, the lagoon went from aerobic to what may be considered facultative rather than anaerobic-aerobic. The lagoon system became anaerobic-aerobic during the fourth operational phase (69 gpm) and remained anaerobic-aerobic through the fifth operational phase (127 gpm). Anaerobic conditions were observed in the bottom deposits which accumulated to an average depth less than 2.0 feet during the initial operation of the system and remained at that depth throughout the study period.

Results from the operation of the system are compared in Table 9 and the efficiencies are presented graphically in Figure 15. These data indicate that while the system was anaerobic-aerobic, doubling the load did not substantially change the lagoon characteristics, including the removal efficiency. Results from the system while aerobic are comparable to those observed for a laboratory completely mixed unit without recycle. Diluted tannins (diluted to 1000 mg/l of COD) fed a laboratory system with detention times of 12 to 49 hours resulted in soluble BOD₅ removal efficiencies from 60 to 75 percent and soluble COD removal efficiencies from 18 to 36 percent.

The system was sufficiently turbulent to consider the application of

$$E = 100 \frac{\bar{K}t}{1 + \bar{K}t}$$

(\bar{K} = BOD₅ removal rate, t = time and E = efficiency) to the data during

TABLE 9 COMPARISON SUMMARY OF OPERATIONAL PHASES⁽¹⁾

Analysis	Operational Phase				
	I	II	III	IV	V
Influent:					
Flow, gpd	21,600	28,800	47,500	99,300	183,000
Det. Time (Ave), days	49.6	37.4	16.2	7.8	4.2
BOD ₅ load, lbs/day	188	251	463	969	1,785
COD load, lbs/day	807	1,072	1,870	3,920	7,220
BOD ₅ load, lbs/1000 ft ³ /day	1.8	2.4	4.5	9.4	17.3
COD load, lbs/1000 ft ³ /day	7.9	10.4	18.2	38.1	70.0
Effluent:					
Ave. temp., °C	24	17	7	18	24
BOD ₅ , lbs/day	5	11	73	318	670
F-BOD ₅ , lbs/day	<1	4	36	168	341
COD, lbs/day	195	371	1,086	2,440	4,580
F-COD, lbs/day	-	111	754	1,540	3,060
BOD ₅ red, %	97	96	84	67	63
F-BOD ₅ red, %	99	98	92	83	81
COD red, %	76	65	42	38	37
F-COD, red, %	-	90	60	61	58
F-BOD ₅ red, lbs/day/B.hp ⁽²⁾	13	18	31	57	103
F-COD, red, lbs/day/B.hp ⁽²⁾	-	69	80	170	297
SS, lbs/day	89	213	242	584	982
VSS, lbs/day	68	179	157	467	772
F-BOD ₅ red. to SS	2.10	1.22	1.76	1.37	1.47
F-COD red. to SS	-	4.50	4.60	4.07	4.24
F-BOD ₅ red. to VSS	2.75	1.38	2.72	1.72	1.87
F-COD red. to VSS	-	5.37	7.10	5.10	5.38

⁽¹⁾ Total tannery flow: Batpool = 260,000 gpd and spent vegetable tannins = 32,000 gpd.

⁽²⁾ Converted to 7-day week rate; other data on 5-day work week basis except detention time averaged through 7-day week.

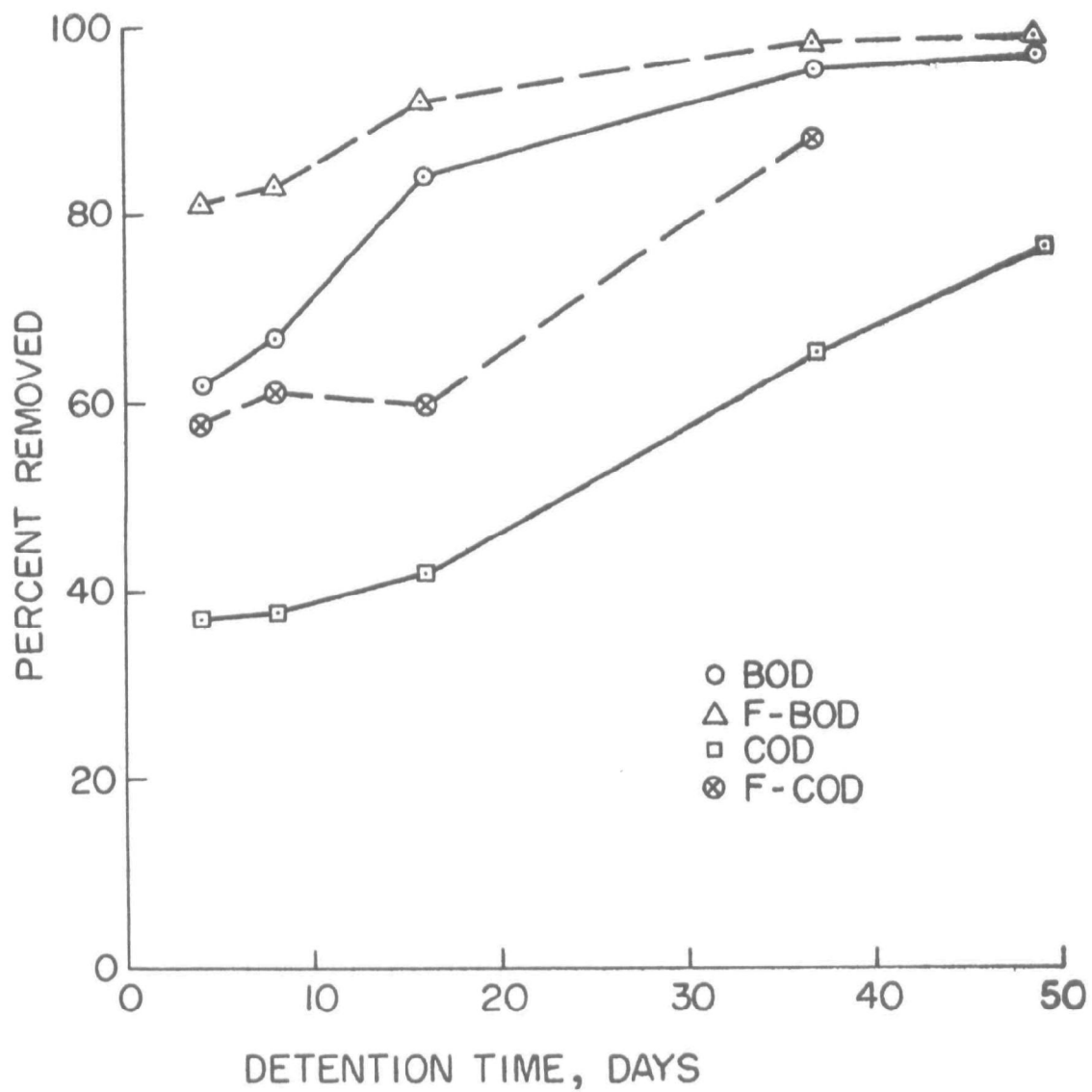


FIGURE 15 COD AND BOD₅ REMOVAL

aerobic conditions [7]. This assumes the lagoon acted as an aerobic stabilization basin and a first order reaction rate. Results from this work indicate a \bar{K} (corrected to 20°C) of 1.49 day⁻¹, 1.42 day⁻¹ and 1.82 day⁻¹ for phases I, II, and III, respectively. The fluctuation shown in phase III was probably due to temperature averaging.

The aerobic system should have approached the concept of total oxidation, therefore,

$$aL_r = b Sa$$

should be applicable [7]. In this equation a = synthesis to sludge ratio, b = rate of auto-oxidation (fraction/day), L_r = BOD removed (lbs/day) and Sa = average mixed liquor suspended solids (lbs). The data obtained in this work are not sufficient for the calculation of a and b , however, the ratio of a/b can be calculated from the field data. Since total oxidation implies an oxygen requirement equivalent to the ultimate BOD, an oxygen balance can be made for the aerobic phases. For phase III, taken at an average temperature of 7°C, the calculated dissolved oxygen in the lagoon was 2.6 mg/l compared to a measured dissolved oxygen concentration of approximately 3.2 mg/l.

Operational characteristics of aerated aerobic lagoons, anaerobic-aerobic lagoons and anaerobic contact processes are usually reported in terms of BOD₅ loads. It has been reported that BOD₅ removal efficiencies of 80 percent or more were achieved from aerated aerobic lagoons, anaerobic-aerobic lagoons and anaerobic contact units with BOD₅ loading ranges of 1 to 8, 8 to 15, and 100 to 300 lbs/1000 ft³/day, respectively [8], [9], [10], [11], [12]. Sawyer [8] has noted that loadings above 5 lbs/1000 ft³/day for anaerobic-aerobic lagoons are impractical because of the oxygen requirement. The lagoon system was loaded close to the above ranges reported for lagoons and the removal efficiencies were within the ranges that have been experienced; however, it appears that considerable amounts of the waste components, measured as COD, are not removed during biological treatment.

The anaerobic-aerobic system load may be better indicated in terms of lbs of BOD₅/1000 ft³/day/B.hp. Data from this work indicate loads of 0.94 and 1.73 lbs of BOD₅/1000 ft³/day/B.hp for phases IV and V, respectively.

Although the soluble BOD₅ removal efficiency was 80 percent or better, it is believed, from the waste characteristics and the operation of the lagoon system, that anaerobic-aerobic treatment in the same unit would be more efficient if the anaerobic and aerobic zones could be distinctly separated. Because of the toxic effects of oxygen on the anaerobic process and mixing between the anaerobic and aerobic zones, it is difficult to enhance both aerobic and anaerobic conditions in a lagoon. It may be more desirable to operate an anaerobic contact system with special design considerations for providing an aerobic zone. The work of Steffen and Bedker [10], Gates, Smith, Lin and Ris [11], and McCarty [12] offer

interesting approaches to the anaerobic contact process and an anaerobic-aerobic system. A variation of the anaerobic systems reported by these investigators may have application in tannery waste treatment.

Color Removal Problem

In addition to reporting results from the observed biological systems it is significant to note the problem of color. Color was not reduced by biological treatment. Although the color of the diluted tannins could not be matched with platinum-cobalt units, the color of the diluted spent vegetable tannins used in the lagoon study was estimated to be 5000 color units. It was observed that color of the influent and effluent could be reduced by blending with lime waste waters or by coagulating with a common chemical coagulant. Influent precipitation resulted in a bulked stringy sludge with poor settling characteristics with sludge volumes between 50 and 90 percent of total liquid volume. Removal of color from the lagoon effluent (best results from highly stabilized effluent) was more successful since the sludge volume produced was 20 to 30 percent of the total volume and color removal was between 90 and 95 percent. However, sludge produced from the colored effluent raises a serious question on treatment methods. The sludge volume resulting from the effluent indicates that it is about equal in volume to the total volume of concentrated spent vegetable tannins that originally caused the color. (In addition, lime waste water is high in sulfides which must be considered in its disposal.) Color removal is a significant consideration in selecting the proper method of treating spent vegetable tannins and must be thoroughly evaluated if a high degree of treatment is to be accomplished.

SECTION IX

BACTERIAL GROWTH USING SPENT VEGETABLE TANNINS

General

The need for putting tannery waste water treatment on a sound basis and providing a systematic approach to treatment of tannery waste waters in a biological system requires evaluation of biological data that is useful in design concepts that are technologically sound. Modeling of continuous bacterial cultures and the use of this concept in waste design has been recognized and is receiving more attention by designers. Therefore, spent vegetable tannins were used as the substrate in a completely mixed aerobic growth unit and the results were put in terms of bacterial growth kinetic parameters.

Kinetics of Bacterial Cultures: A Brief Review

It has been recognized that waste treatment facilities are designed on some correlation between operational variables and performance. This has been necessary because of various waste characteristics that are encountered and the unknown composition of the medium. Although chemical oxygen demand parameters (or biochemical oxygen demand) do not provide fundamental relations for kinetics of substrate utilization by bacterial cultures, the sanitary engineer has to rely upon these parameters in modeling waste treatment processes. Limitations on the use of these parameters in bacterial growth kinetics must be recognized and the fundamentals of enzyme-substrate interactions must be understood by those responsible for design of biological waste treatment systems. All engineers interested in kinetic descriptions of biological processes using waste as a substrate should recognize that COD and BOD are operational parameters and are not an actual measurement of substrate [13].

A lot of attention has been directed to kinetic equations that can be used in analysis and design of biological waste treatment systems. Studies have been made using one substrate, multiple substrate, and synthetic waste for kinetic description of continuous flow systems and batch systems with mixed and pure bacterial cultures. Concepts and theories have been well defined and the literature does indicate sufficient agreement on kinetic models of biological oxidation for its application to be put on a sound technological basis [14]. It is not the purpose of this work to evaluate the many theories and kinetic models; however, it is essential that disagreement among investigators be pointed out.

There are two views that are expressed in regard to effective yield, Y . One view is that the relationship between synthesis and nature of the compound (substrate) is fixed and independent of the nature of the organic matter being assimilated and the other is that cell yield varies with the chemical nature of the substrate [15], [16], [17], [18]. Hetling,

Washington, and Rao [19] indicate that yield varies with substrate, organisms, and detention time. In addition, these investigators concluded that mixed cultures give higher yield than pure cultures and, also, complex media give higher yield than simple media. Although evidence indicates otherwise, the concept of constant yield for a specific substrate has been used with some degree of success [14], [20], [21].

Controversy exists about the variability of endogenous respiration rate, k_e . (Endogenous respiration is defined as the utilization of cellular material by the microorganism for the energy needed to replace protoplasm. Specific organism decay rate, k_d , will be used here for the organism decay rate due to a decrease in cellular mass.) It has not been clearly resolved as to whether the rate of organism decay varies with substrate; however, within limits, the "engineering concept" of a constant organism decay rate has apparently met with some success [21].

The simple relationship between growth rate, μ , of microorganisms and substrate concentration (or nutrient),

$$\mu = \hat{\mu} \left(\frac{S}{S + K_s} \right), \quad (1)$$

developed by Monod [22] has been very successful and is widely accepted. This expression is the same as the generally accepted Michaelis-Menten relationship for enzyme-substrate interaction. Other relationships have been developed that fit growth kinetic data. Hetling and Washington [23] studied the relationship of substrate concentration to growth rate where substrate was measured as COD. These investigators found that a function,

$$\mu = \hat{\mu} \left(\frac{S_1 - A}{S_1 + B} \right), \quad (2)$$

similar to the Michaelis-Menten equation adequately represented the relationship.

Mathematical Model

A number of mathematical models have been developed for kinetic description of biological systems and the translation of growth kinetic parameter to waste treatment technology [14], [20], [21], [24], [25]. Sound models of continuous and batch cultures have been developed from the following relationships (see Section XIII for notations):

$$\mu = \hat{\mu} \left[\frac{S}{K_s + S} \right] \quad (1)$$

$$\frac{dX}{dt} = \mu X \quad (3)$$

$$\frac{dX}{dt} = k_d X \quad \left[\text{or } \frac{dX}{dt} = k_e X \right] \quad (5)$$

and

$$\frac{dX}{dt} = Y \frac{dS}{dt} \quad (6)$$

Both continuous flow growth units and batch growth units have been used to evaluate Y , k_d (or k_e), $\hat{\mu}$, and K_s . A material balance,

$$\left[\Delta \text{ cells, reactor} \right] = \left[\Delta \text{ cells, growth} \right] - \left[\Delta \text{ cells, organism decay} \right] - \left[\Delta \text{ cells, effluent loss} \right],$$

and substrate balance,

$$\left[\Delta \text{ substrate, reactor} \right] = \left[\Delta \text{ substrate, influent} \right] - \left[\Delta \text{ substrate, organism growth} \right] - \left[\Delta \text{ substrate, effluent loss} \right]$$

for a completely mixed continuous flow reactor (growth unit) without recycle of suspended solids lead to a set of equations,

$$\frac{S_0 - S_1}{X_1} = \frac{k_d}{Y} \theta + \frac{1}{Y} \quad (7)$$

and

$$\frac{\theta}{1 + k_d \theta} = \frac{K_s}{\hat{\mu}} \left[\frac{1}{S} \right] + \frac{1}{\hat{\mu}}, \quad (8)$$

useful for determining descriptive parameters from laboratory data. When equation 2 is used for the relationship between growth rate and substrate, measured as COD, equation 8 becomes

$$\frac{\theta}{1 + \theta k_d} = \frac{A + B}{\hat{\mu}} \left[\frac{1}{S_1 - A} \right] + \frac{1}{\hat{\mu}} \quad (9)$$

Spent Vegetable Tannin Analyses

Spent vegetable tannins were obtained from Virginia Oak Tannery, Inc., Luray, Virginia as needed and as near the same hour of day as possible. The tannin operation, a batch process, produces an effluent that varies in strength during the day as well as from day to day. Table 10 is a summary of analyses that were made on spent vegetable tannins collected over a period of approximately six months. (The complete data is given in Table A-11 of the Appendix.) Figure 16 shows the BOD exerted for two different samples of tannins.

Descriptive Parameters

A continuous flow completely mixed aerobic laboratory growth unit as shown in Figure 17 was fed spent vegetable tannins that were: (1) diluted to a COD concentration of 1000 mg/l with deionized water and (2) same strength as collected. The waste was used as collected and no attempt was made to alter nutrient concentration or eliminate any toxic substance that may have been present. Hence the results presented

TABLE 10 SPENT VEGETABLE TANNIN ANALYSES

	<u>Maximum</u>	<u>Minimum</u>	<u>Average</u>
COD, mg/l	44,790	13,380	26,500
BOD, mg/l	9,200	2,500	4,648
Total Solids, mg/l	22,280	7,940	13,639
Total Volatile Solids, mg/l	16,822	6,788	10,984
Organic Nitrogen, mg/l	63.7	24.4	54.6
Ammonia Nitrogen, mg/l	20.2	7.6	12.0
Total Phosphorus, mg/l	21.5	4.8	13.1
pH	5.1	4.6	-
1st Stage BOD velocity constant (k_1) at 20°C, day ⁻¹	-	-	0.17
Oxygen Transfer ratio, alpha	-	-	0.5
Color:			
(as collected)			
dominant wavelength, mμ			601
hue			orange red
luminance, %			5.9
purity, %			100
(pH adjusted to 7.6)			
dominant wavelength, mμ			645
hue			red
luminance, %			2.8
purity, %			100

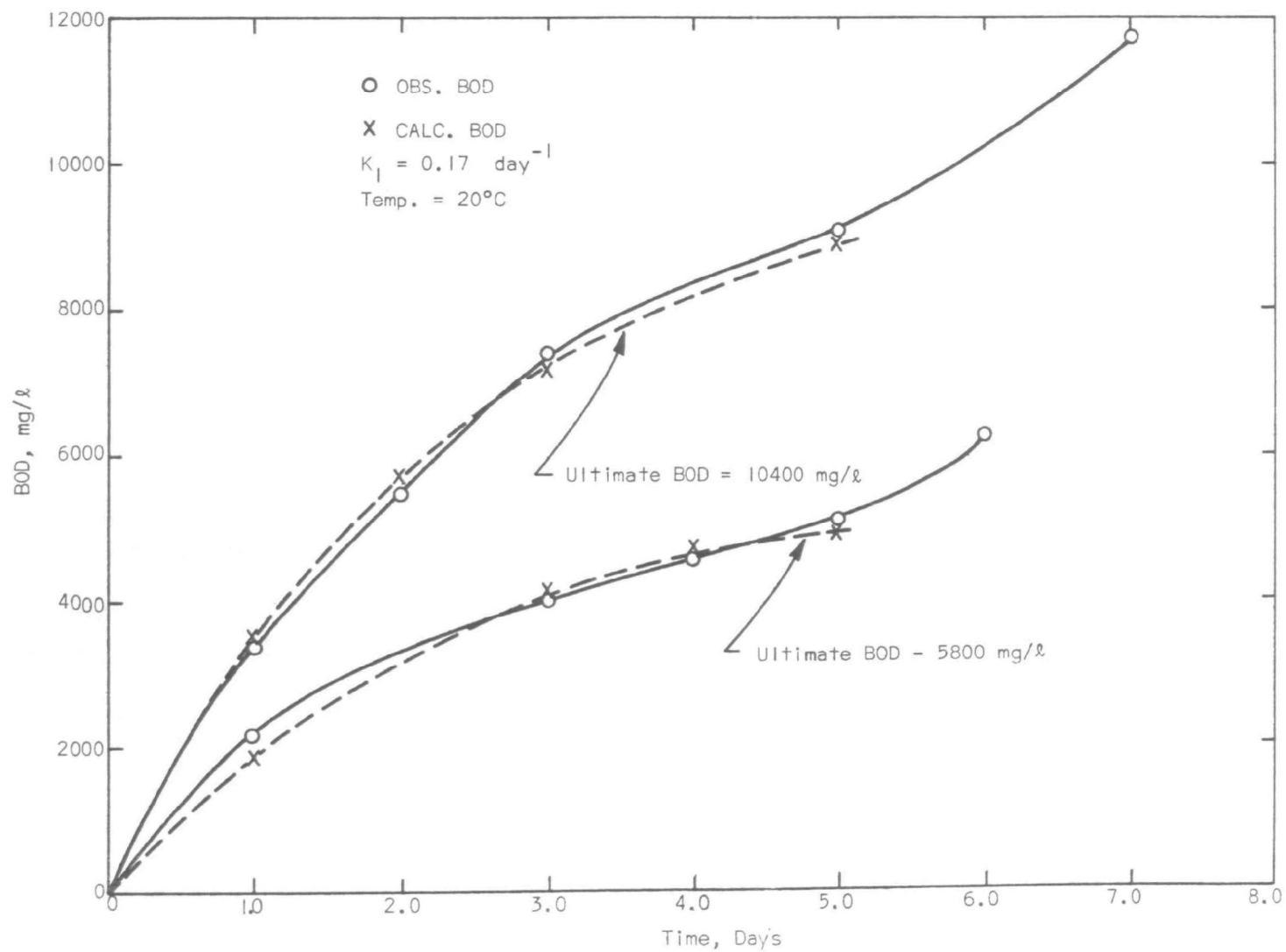


FIGURE 16 ULTIMATE BOD FOR CONCENTRATED TANNINS

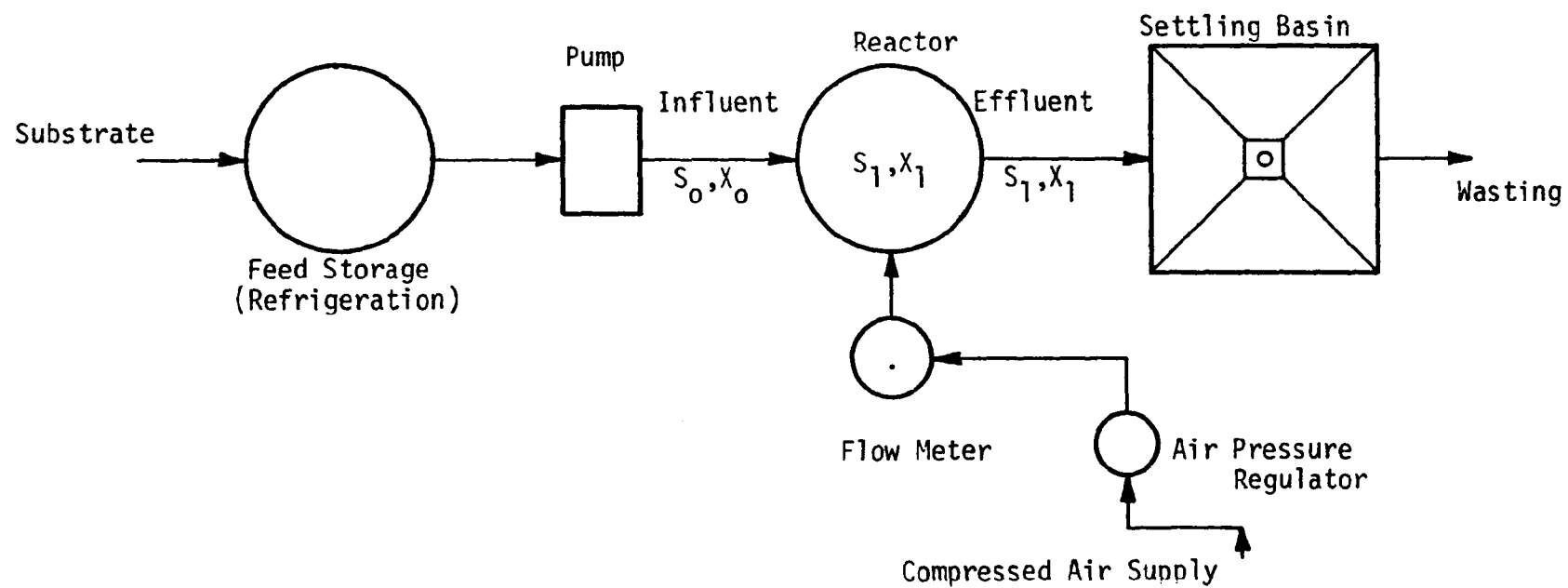


FIGURE 17 FLOW DIAGRAM OF COMPLETELY MIXED CONTINUOUS FLOW SYSTEM

here represent unaltered spent tannins, except for dilution. These data are given in Table A-11 and Table A-12 of the Appendix. Changes in BOD_5 and suspended solids and COD with aeration time until steady-state is reached are shown in Figure 18 and Figure 19, respectively.

Results for diluted tannins are presented in Table 11 in the form used for graphical solution of equation 7. Figure 20 shows the graphical solution for X measured as MLSS and MLVSS. Table 12 and Figure 21 show data resulting from the feed of concentrated spent vegetable tannins.

Values of k_d and Y for the diluted waste were 0.045 hr^{-1} and $0.62 \frac{\text{mg MLVSS}}{\text{mg COD}}$ for X as MLVSS, and 0.041 hr^{-1} and $0.78 \frac{\text{mg MLSS}}{\text{mg COD}}$ for X as MLSS. The concentrated waste indicates a k_d of 0.061 hr^{-1} and a Y of $0.91 \frac{\text{mg MLSS}}{\text{mg COD}}$.

Rearrangement of the data from the diluted waste for solution of equation 8 and equation 9 is shown in Figure 22 and Figure 23, respectively. Since Figure 22 represents a condition that cannot exist, negative growth rate, the Michaelis-Menten relationship does not describe the data. For the relationship shown in Figure 24, $A = 590$, $B = -491$, and $\hat{\mu} = 0.21 \text{ hr}^{-1}$. (In order to solve equation 9 constant A was obtained separately from a plot of $1/\theta$ vs. S_1 and extending the curve to obtain dissolved COD for $1/\theta = 0$, i.e., $A = S_1$ when $1/\theta = 0$ [16].)

Discussion of Results

Both MLSS and MLVSS as a measure of cell concentration for the waste were acceptable. The yields coefficients obtained can be related for the diluted waste by using the average ratio of $\frac{\text{MLVSS}}{\text{MLSS}}$, 0.78, at steady-state for the observed resident times. Values of k_d and Y are higher than values that have been reported for other waste and known substrate [14], [19]. Higher yield coefficients have been associated with mixed cultures and complex media [19]. These data tend to support this conclusion.

The use of concentrated waste for description of k_d and Y may be questionable. In addition, as indicated in Table 12, the feed concentration varied significantly and, therefore, the assumptions upon which equation 7 is based may not be valid. However, the assumptions of $k_d = \text{constant}$ and $Y = \text{constant}$ implies a correlation for concentrated waste; therefore, the organism decay rate and yield coefficient for the concentrated waste may be considered indicative of values for tannins of the indicated strength. The yield coefficient and organism decay rate for the concentrated waste is significantly greater than that obtained with the diluted waste.

These data do not resolve the question of the variability of k_d and Y; however, it does serve as a warning to the designer that caution must be

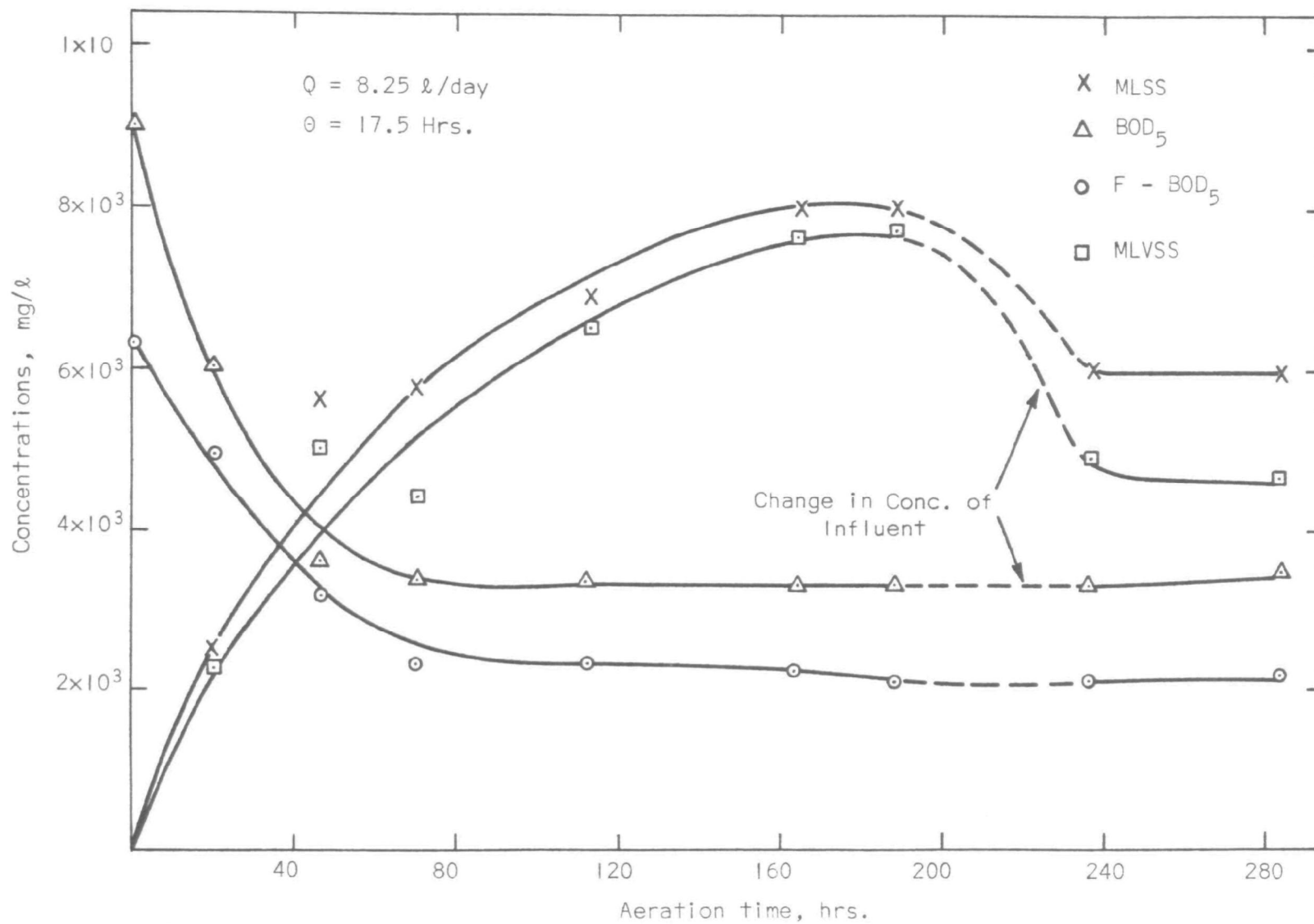


FIGURE 18 TYPICAL PROGRESSIVE BOD REMOVAL AND SUSPENDED SOLIDS PRODUCTION

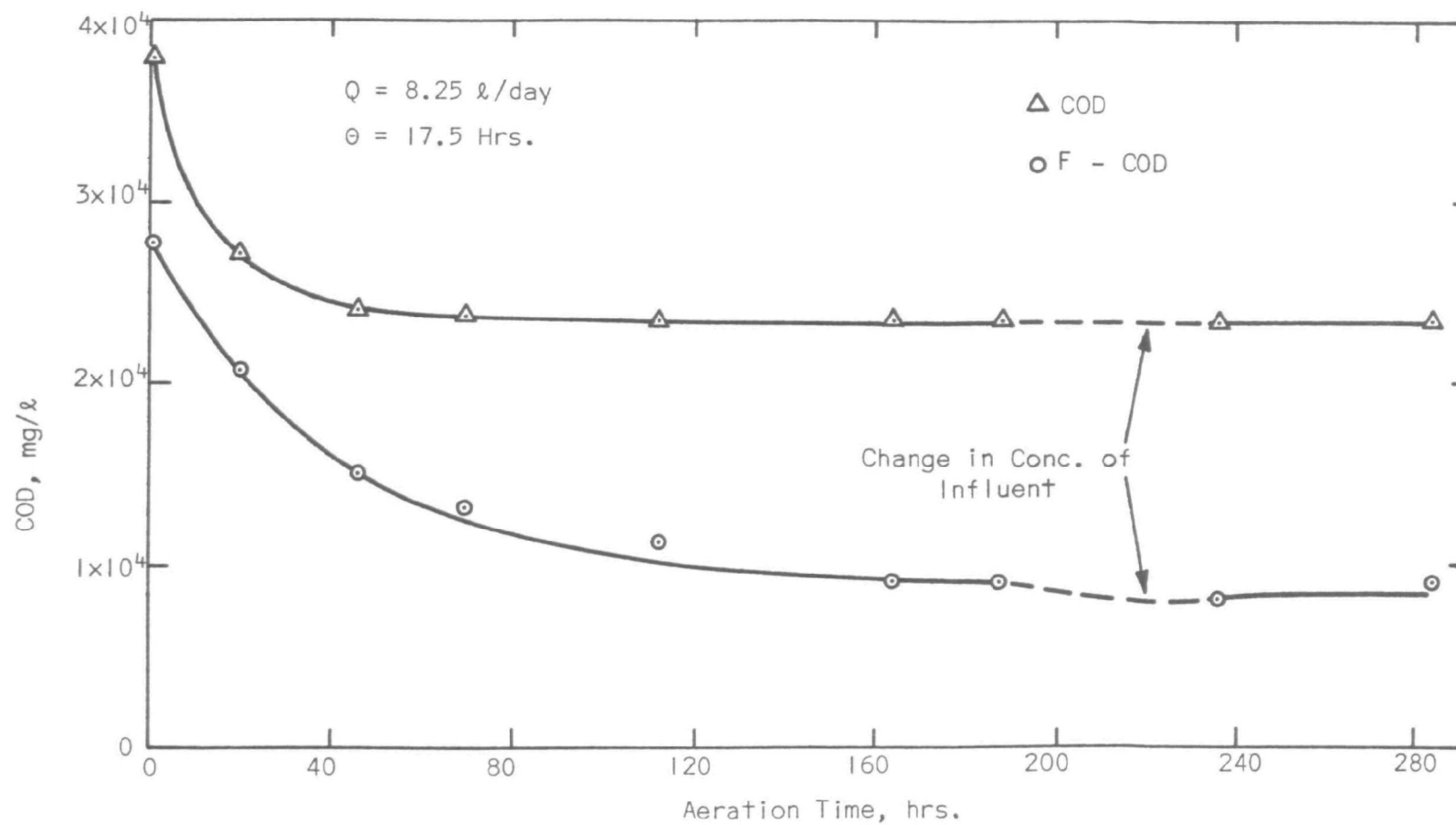


FIGURE 19 TYPICAL PROGRESSIVE COD REMOVAL

TABLE 11 COD AND SUSPENDED SOLID CHANGES FOR DILUTED TANNINS

θ , Hrs.	S_o , COD, mg/l	S_i , COD, mg/l	X_i , MLSS, mg/l	1X_i , MLVSS, mg/l
49.0	996	636	92	70
24.4	936	644	112	90
16.2	910	696	96	74
12.1	890	728	84	65

TABLE 12 COD AND SUSPENDED SOLID CHANGES FOR CONCENTRATED WASTE

θ , Hrs.	S_o , COD, mg/l	S_i , COD, mg/l	X_i , MLSS, mg/l	1X_i , MLVSS, mg/l
46.0	11,860	6,652	1280	1060
22.2	32,800	7,766	8892	7746
22.2	24,800	6,980	7785	7141
17.5	27,880	9,050	8003	7703
17.5	21,360	9,050	6084	4682
12.2	19,742	12,840	3638	3170
12.2	20,192	13,552	4195	3975
5.2	17,200	16,160	(WASHOUT)	-
5.2	12,280	11,540	(WASHOUT)	-

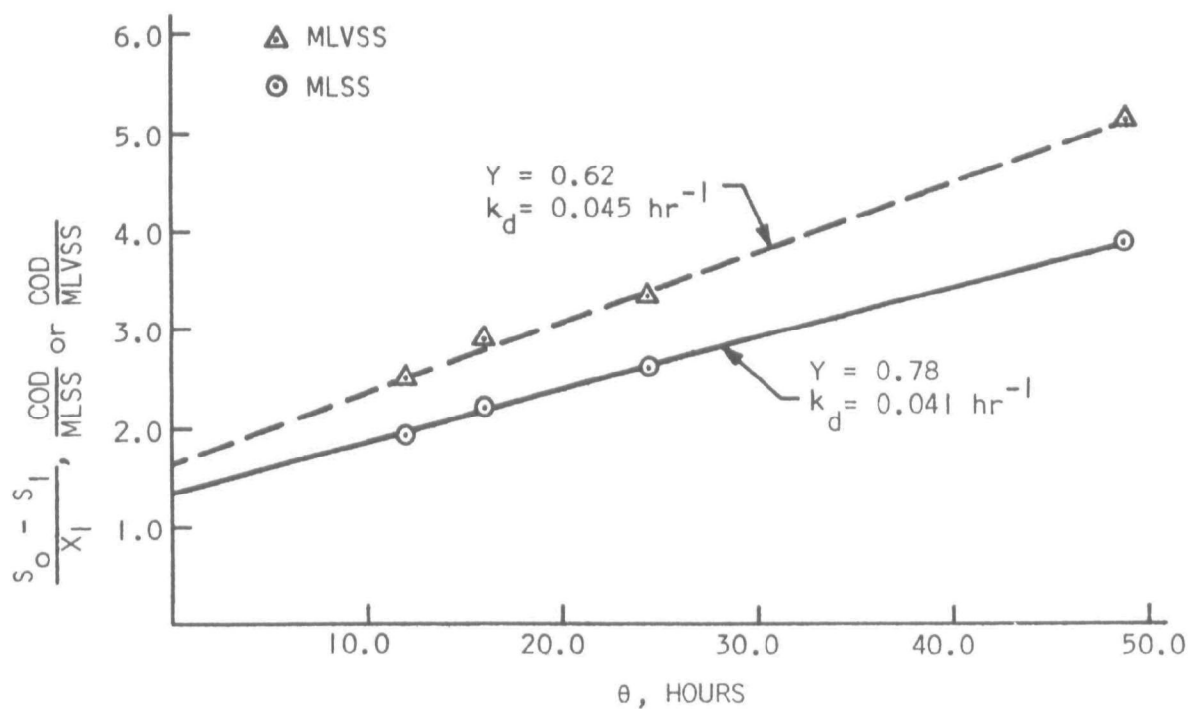


FIGURE 20 YIELD AND ORGANISM DECAY RATE FOR DILUTED TANNINS

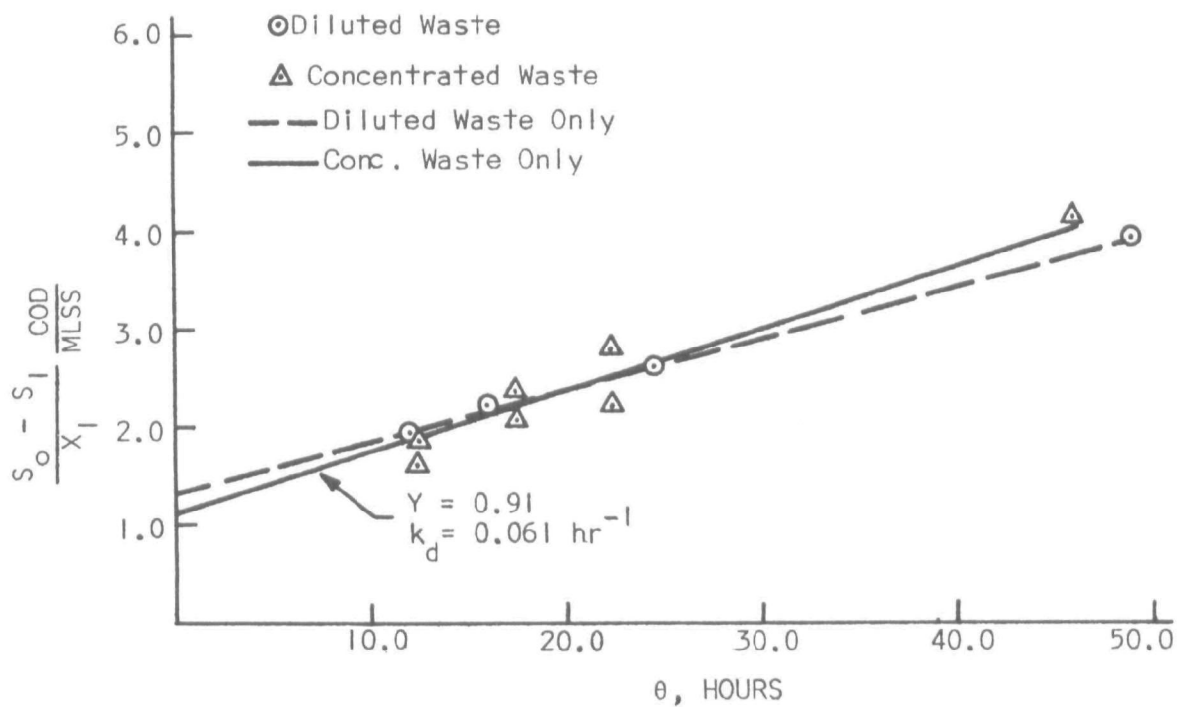


FIGURE 21 YIELD AND ORGANISM DECAY RATE FOR CONCENTRATED TANNINS

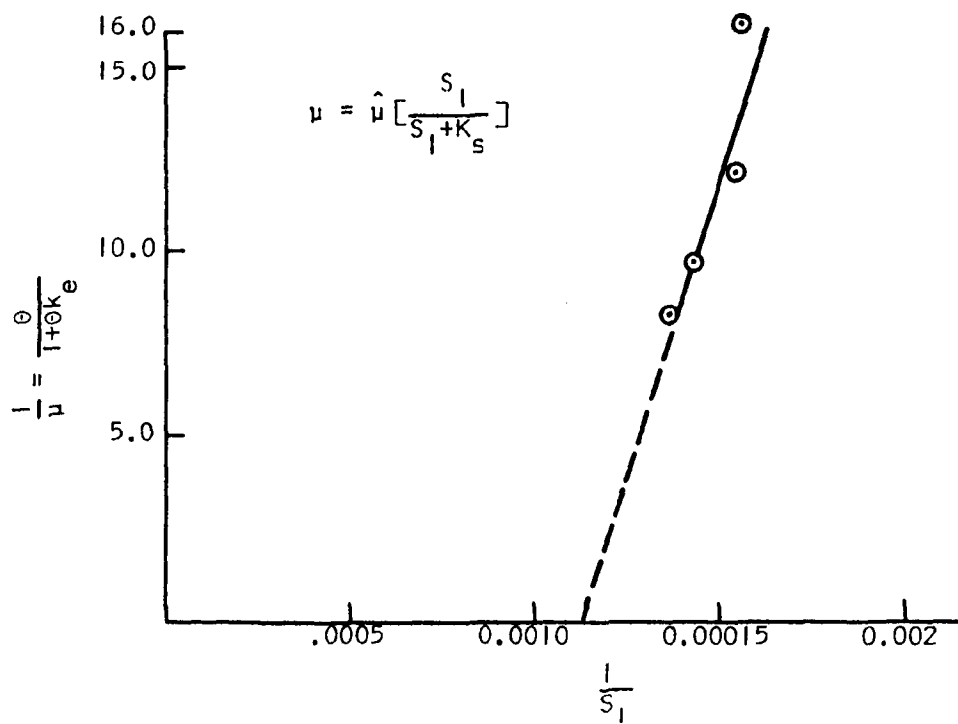


FIGURE 22 GROWTH RATE: MICHAELIS-MENTEN ENZYME-SUBSTRATE INTERACTION

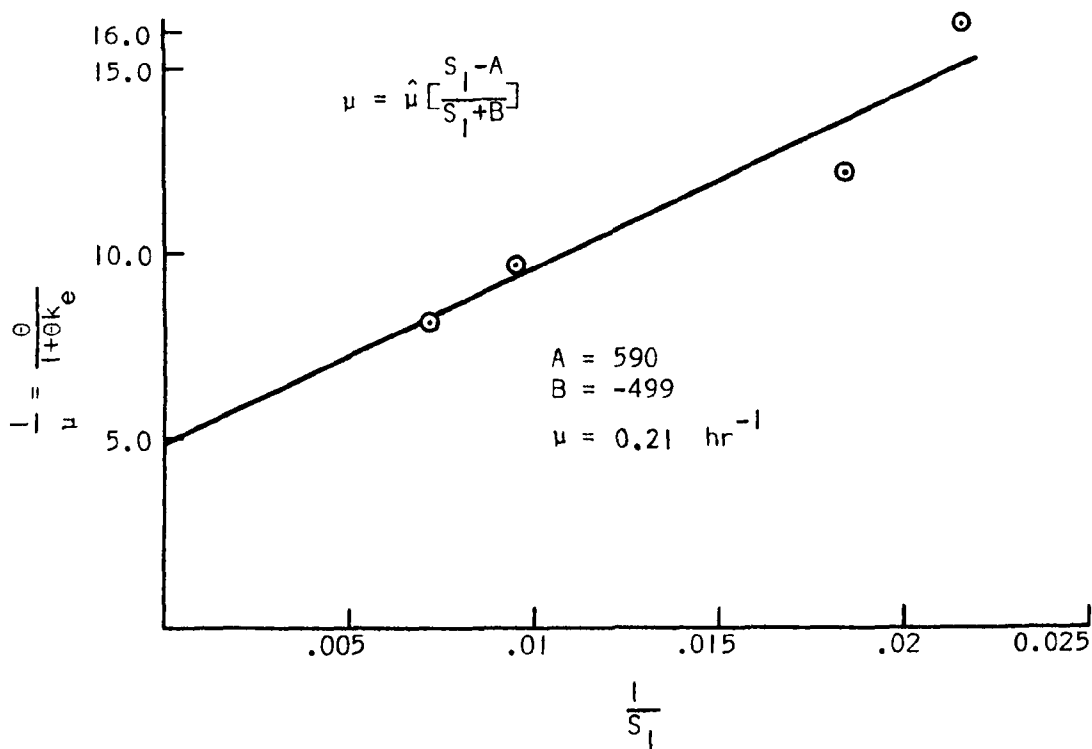


FIGURE 23 GROWTH RATE: RELATIONSHIP SUGGESTED BY HETLING AND WASHINGTON [16]

exercised in the selection of these parameters. If biological waste treatment design is to be technologically sound, laboratory investigations may not only be desirable but necessary, even for like wastes with different strengths.

Obviously, since a negative growth rate would result, the Michaelis-Menten expression for substrate-growth interaction, using COD as substrate, does not apply for this waste. The equation,

$$\mu = \hat{\mu} \frac{S_1 - A}{S_1 - B}, \text{ adequately represents the data with substrate measured}$$

as COD. Although use of this type of expression may be regarded by some as curve fitting, it does provide a means of evaluating a relationship between growth and COD for an industrial waste.

Five-day BOD analyses were made on all samples but it was found that COD results provided a better fit of the data. While BOD₅ may be used as an operational parameter and for the translation of descriptive parameters to biological waste treatment, COD was found to be more applicable in this investigation.

SECTION X

ACKNOWLEDGMENTS

The support of Mr. Stephan J. Blaut and Mr. A. Nollert of Virginia Oak Tannery, Inc. is acknowledged with sincere thanks. Mr. P. Cabbage of Virginia Oak Tannery, Inc. provided valuable assistance during operation of the facility.

An expression of gratitude is directed to Mr. David Cottrell and Mr. Indu Thaker who performed the analytical work.

The support of the project by the Federal Water Quality Administration and the assistance provided by Mr. Harold J. Snyder, Jr., Project Officer, is acknowledged.

SECTION XI

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SECTION XII

PUBLICATIONS AND PATENTS

No patent has been produced as a result of this work.

The following publications have been produced as a result of this project:

(1) Parker, C. E. and Thaker, I. H., "A Study of Kinetic Parameters Using Spent Vegetable Tannins," Proc. of the 3rd Mid-Atlantic Ind. Waste Conf., University of Maryland, November 1969.

(2) Parker, C. E., "Biological Treatment of Spent Vegetable Tannins," Proc. of the 25th Ind. Waste Conf., Purdue University, May 1970.

SECTION XIII

NOTATIONS

A	= constant in Hetling-Washington expression
a	= synthesis to sludge ratio
B	= constant in Hetling-Washington expression
b	= rate of auto-oxidation
B.hp	= brake horsepower
BOD ₅	= 5-day biochemical oxygen demand at 20°C
C _O	= initial DO at beginning of an observation
C _S	= DO saturation
C ₊	= DO after time, t
COD	= chemical oxygen demand
DO	= dissolved oxygen
E	= efficiency
F-prefix	= analysis of the filtrate (soluble fraction)
FSS	= fixed suspended solids
K	BOD velocity constant (common log)
\bar{K}	= BOD ₅ observed removal rate
k _d	= specific organism decay rate hours ⁻¹
k _e	= endogenous respiration, hours ⁻¹
K _L	= oxygen transfer coefficient
K _S	= constant in Michaelis-Menten expression
L _r	= BOD removed
MLSS	= suspended solids in aeration unit
MLVSS	= volatile suspended solids in aeration unit
N:BOD ₅	= nitrogen to BOD ₅ ratio

N:COD	= nitrogen to COD ratio
NH ₃ -N	= ammonia nitrogen
ORG-N	= organic nitrogen
P:BOD ₅	= phosphorus to BOD ₅ ratio
P:COD	= phosphorus to COD ratio
pH	= hydrogen ion concentration
Q	= flow rate
S	= substrate in aeration unit in terms of influent substrate
S _a	= average mixed liquor suspended solids
S ₁	= waste concentration in aeration unit as COD, mg/l
S ₀	= waste concentration of aeration unit influent as COD, mg/l
Set. S.	= settleable solids
SS	= suspended solids
T	= temperature, °C
t	= time
TKN	= total Kjeldahl nitrogen
TFS	= total fixed solids
TP	= total phosphorus
TS	= total solids
T. Sulf.	= total sulfides
TVS	= total volatile solids
VOTAN	= Virginia Oak Tannery, Inc.
VSS	= volatile suspended solids
X	= cell concentration
X ₁	= MLSS as measure of cell concentration, mg/l
'X ₁	= MLVSS as measure of cell concentration, mg/l

- Y = yield coefficient, mg MLSS or MLVSS per mg COD (for fundamental relationship: mg cells per mg substrate).
- θ = aeration unit retention time, hours
- μ = observed specific growth rate, hours⁻¹
- $\hat{\mu}$ = maximum specific growth rate, hours⁻¹

SECTION XIV

APPENDIX

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DETERMINATION OF TOTAL PHOSPHORUS

Reagents

Sulfuric acid, H_2SO_4 , concentrated reagent grade

Sodium nitrate, NaNO_3 , reagent grade

Sodium hydroxide, NaOH , concentrated (approximately 15 N)

Phenolphthalein indicator

Molybdate reagent. Dissolve 50 gm of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, in 400 ml of 10 N sulfuric acid and 500 ml of water, make up to 1 liter, and store in a paraffin-lined bottle.

Sulfuric acid, (Approximately N) Dilute 114 ml of conc. sulfuric acid to 4 liters.

Stannous chloride stock soln., 10 gm $\text{SnCl}_2 \cdot 6\text{H}_2\text{O}$ or 7.5 gm $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 25 ml of conc. HCl . Store in a small glass-stoppered brown bottle.

Stannous chloride dilute soln. Dilute 1 ml of stock soln. to 200 ml with approximately N sulfuric acid just before use.

Isobutyl Alcohol. Comm. grade, with a boiling range 106° to 110°C.

Ethyl Alcohol. 95%.

Standard phosphate soln. Recrystallize A.C.S. grade monobasic potassium phosphate 3 times from water, dry at 110°C, and store in a desiccator over concentrated sulfuric acid. Dissolve 4.3929 gm of the dry salt in 300 ml of water and 200 ml of approximately N sulfuric acid. Add a few drops of 0.1 N potassium permanganate as preservative and make up to 1 liter with water. This stock soln., 1.0 mg of P per ml is stable. Dilute as needed.

Analytical Procedure

Place 100 ml of the sample (or suitable aliquot) in an 500 ml Kjeldahl flask and add 20 ml conc. H_2SO_4 . Heat to boiling and add about 1.5 gm NaNO_3 . Be careful of extreme foaming. Boil down to conc. acid. (Solution may not be clear.) Add a small amount of NaNO_3 and solution should become clear. Cool, add 40 ml water, and boil for 2-3 minutes. Cool and neutralize to faint pink phenolphthalein color with conc. NaOH (about 1.5 N). Be very careful of splattering. (White solid may form.) Transfer to 200 or 250 ml volumetric flask. Rinse Kjeldahl flask thoroughly with small amounts of water until correct volume is reached. (White solid should dissolve.) Transfer 15 ml of diluted solution to separatory funnel and add 5 ml of molybdate solution. Add 10 ml butyl alcohol and shake for 30 sec., removing aqueous layer.

Add 10 mL of approximately 1 N sulfuric acid and shake for 30 sec., removing aqueous layer. Add 16 mL of stannous chloride solution and shake for 30 sec., removing aqueous layer after the blue color separates. Transfer blue alcoholic layer to 50 mL volumetric flask, rinse funnel with ethanol, and dilute to 50 mL with ethanol. Let color develop for 1 hr 15 min. Record percent transmittance at 630 mμ against a blank of 15 mL distilled water treated as the waste sample. Read mg phosphorus off calibration curve made from standard phosphorus solution curve. Make correction to find mg/L in original sample of 100 mL.

TABLE A-1 OXYGEN TRANSFER: LAGOON INFLUENT

Dissolved Oxygen, mg/ℓ	LAGOON INFLUENT			DISTILLED WATER	
	T=31°C, C _S =6.0mg/ℓ			T=26°C, C _O =6.6mg/ℓ	
	T=26°C, C _O =7.5mg/ℓ				
	time,min.	time,min.	time,min.	time,min.	time,min.
1.0	0	0	0	0	0
1.5	0.3	0.3	0.3	0	0.2
2.0	0.6	0.7	0.7	0.4	0.4
2.5	1.0	1.1	1.1	0.8	0.7
3.0	1.5	1.5	1.4	1.1	0.9
3.5	2.1	2.1	2.0	1.6	1.1
4.0	2.6	2.7	2.6	2.1	1.4
4.5	3.4	3.6	3.5	2.8	1.8
5.0	4.2	4.6	4.5	3.6	2.1
5.5	6.4	-	6.8	5.0	2.6
6.0	-	-	-	-	3.2
6.5	-	-	-	-	4.3
7.0	-	-	-	-	5.8

TABLE A-2 ULTIMATE BOD: LAGOON INFLUENT

Time, Days	Biochemical Oxygen Demand, mg/l (T = 20°C)			
	(By Date Collected)			
	7/11/68	7/16/68	8/8/68	9/18/69
0.5	-	-	-	270
1.0	-	619	550	590
2.0	-	-	-	903
3.0	1600	1062	918	980
4.0	-	-	-	1170
5.0	1850	1250	1100	1230
7.0	2000	1462	-	1475
9.0	-	1600	-	1725
11.0	-	1800	-	1825
13.0	-	-	-	1875
14.0	-	1650	-	-
15.0	-	1700	-	-
17.0	-	1700	-	-
20.0	-	1700	-	-

TABLE A-3 AVERAGE WEEKLY FLOW

DATE	Flow, gpm	DATE	Flow, gpm
15-21 Dec. 68	30*	4-10 May	65
22-28	25*	11-17	65
29 Dec. 68-4 Jan. 69	36*	18-24	60
4-11 Jan. 69	31*	25-31	68*
12-18	40	1-7 Jun	60
19-25	41	8-14	58
26 Jan.-1 Feb.	32	15-21	92
2-8 Feb.	34	22-28	70
9-15	36	29 Jun.-5 Jul.	80
16-22	41	6-12 Jul.	125
23 Feb.-1 Mar.	29	13-19	143
2-8 Mar.	31*	20-26	147
9-15	29	27 Jul.- 2 Aug.	115
16-22	24	3-9 Aug.	120
23-29	35	10-16	115
30 Mar.- 5 Apr.	24	17-23	125
6-12 Apr.	80*	24-30	120
13-19	60	31 Aug.- 6 Sept.	105
20-26	65	7-13 Sept.	134
27 Apr.- 3 May	72	14-20 Sept. 69	145

* 5-day flow, all others 7-day flow.

TABLE A-4 INFLUENT DATA: BATEPOOL, SOAK AND TANNINS WITH BLEACH⁽¹⁾

Date	BOD ₅	COD	ORG-N	NH ₃ -N	TKN	TS	TFS	TVS	SS	FSS	VSS	Set. S.	pH	Total Sulfide	Total Phosphorus
4/30/68 ⁽²⁾	4400	-	-	-	-	21635	10623	11012	-	-	-	-	-	-	-
5/7/68 ⁽²⁾	2300	-	-	-	-	14326	9938	4388	-	-	-	-	-	-	-
5/14/68	1200	-	-	-	-	9835	6893	2942	-	-	-	-	-	-	-
5/20-21/68	800	-	-	-	-	8856	6858	2008	-	-	-	-	-	-	-
5/28-29/68	925	-	-	-	-	8523	6024	2498	-	-	-	-	-	-	-
6/4-5/68	1825	5829	44.2	51.0	95.2	11031	6888	4143	-	-	-	-	-	-	-
6/11-12/68	1150	5380	48.3	44.0	92.3	10612	7156	3456	-	-	-	-	6.2	-	-
6/18-19/68 ^{(2),(3)}	725	3640	47.8	32.3	80.1	4116	1728	2388	566	2	564	1.0	3.4	-	-
(Tannery vacation, 10 work days zero flow)															
7/11-12/68	1850	-	-	-	-	10168	6490	3678	-	-	-	-	5.7	-	-
7/15-16/68	1250	5663	38.0	46.8	84.8	7584	4355	3229	643	182	461	0.2	5.7	-	-
7/17-18/68	1213	5352	37.0	53.2	90.2	5955	3860	3138	463	-	-	0.3	5.5	-	-
7/22-23/68	975	4352	32.9	66.3	99.2	7856	5144	2712	376	-	-	0.6	6.2	-	-
7/24-25/68	775	5951	39.5	40.5	90.0	9856	6647	3209	350	0	350	0.2	5.6	-	-
7/30-31/68	800	4275	33.4	51.5	84.9	6892	4349	2545	460	75	385	0.2	5.2	1.7 ²	-
8/1-2/68	775	3353	35.1	59.4	94.5	6781	4743	2038	392	-	-	0.3	6.6	-	-
8/6-7/68	1250	5711	47.3	52.1	99.4	11835	8438	3397	975	0	975	122.0	4.6	-	-
8/8-9/68	1100	5128	32.6	46.4	79.0	7184	3935	3249	282	-	-	0.5	5.4	-	-
8/12-13/68	-	-	-	-	-	7773	5731	2042	882	30	852	5.5	7.3	1.8 ²	4.46
8/14-15/68	763	-	-	-	-	-	-	-	-	-	-	-	6.0	0.3	8.47
8/20-21/68	-	5129	40.6	40.2	80.8	-	-	-	-	-	-	1.0	7.6	-	7.67
8/27-28/68	775	2642	-	-	-	-	-	-	-	-	-	1.0	6.8	1.0	-
9/3-4/68	-	-	-	-	-	10004	7567	2437	-	-	-	8.0	8.6	-	-
9/10-11/68	950	-	-	-	-	10691	8955	1736	-	-	-	4.0	6.0	-	-
9/17-18/68	998	2701	-	-	-	-	-	-	-	-	-	-	4.0	-	-
9/24-25/68	1018	-	45.3	36.1	81.4	10111	7486	2625	-	-	-	70	3.2	-	-
10/1-2/68	846	1937	-	-	-	7963	6820	1143	-	-	-	0.5	6.9	-	-
10/8-9/68	950	2714	35.3	62.7	98.0	9051	3435	1616	-	-	-	0.6	6.5	-	-
10/22-23/68	1075	6616	38.8	23.8	62.6	13307	8880	4427	-	-	-	85	3.5	-	-
10/29-30/68 ⁽⁴⁾	850	547	31.0	48.7	79.7	12907	8680	4227	-	-	-	50	9.3	-	-
11/21-22/68	950	2879	40.3	40.3	80.6	-	-	-	-	-	-	15	7.5	-	-
12/3-4/68	725	3757	28.3	58.2	86.5	6931	5206	1725	-	-	-	0.1	7.0	-	-
12/11/68 ^{(2),(5)}	5100	>7640	2.2	5.9	8.1	23044	1874	21170	-	-	-	0.0	4.5	-	-
12/19-20/68 ⁽²⁾	750	3826	64.4	26.6	101.0	5768	3595	2113	-	-	-	1.0	6.8	-	-
1/7-8/69	1190	5769	74.7	27.7	102.4	15845	13675	2170	-	-	-	0.5	7.2	-	-

(1) Results in mg/l except pH and SS. SS in ml/l

(2) Grab sample

(3) No soak wastewater

(4) No tannins

(5) Tannins only

TABLE A-5 INFLUENT DATA: BATEPOOL AND TANNINS⁽¹⁾

Date	BOD ₅	COD	ORG-N	NH ₃ -N	TKN	TS	TFS	TVS	Set. S.	pH	Total Sulfide	Total Phosphorus
1/14-15/69	1000	2349	-	-	-	-	-	-	>40	9.6	-	-
2/11-12/69	1850	7775	26.8	53.8	80.6	4730	2350	2380	1.5	6.6	-	-
2/18-19/69	1175	4720	49.0	66.4	115.4	4733	2320	2313	1.0	6.5	-	-
3/4-5/69	1000	5860	65.5	69.4	134.9	5637	2990	2647	2.5	7.6	-	-
3/18-19/69	1000	3980	29.4	73.3	102.7	3664	1865	1799	1.5	6.4	-	8.80
4/8-9/69	725	4660	65.2	40.4	105.6	-	-	-	2.0	6.5	-	-
4/24-25/69	1125	4490	-	-	-	3805	1024	2781	-	6.5	-	-
5/7-8/69 ⁽²⁾	475	2000	-	-	-	1848	958	890	1.5	6.9	-	-
5/20-21/69 ⁽²⁾	350	1920	24.7	39.8	64.5	1625	850	775	0.5	6.8	-	-
6/3-4/69	850	5540	27.4	39.8	67.2	5042	1702	3340	0.5	6.2	-	-
6/17-18/69	2000	7340	28.8	34.2	63.0	2556	660	1896	0.5	6.7	-	7.60
6/19-20/69 ⁽³⁾	775	-	-	-	-	-	-	-	7.5	6.2	-	-
6/25-26/69	1600	6120	51.5	33.1	84.6	4904	1622	3286	8.0	5.8	-	-
7/16-17-69	850	4421	-	-	-	2902	900	2002	6.0	6.5	-	-
7/23-24/69	1050	4660	52.7	36.9	89.6	3119	946	2173	7.5	6.5	-	-
7/29-30/69	900	3760	35.5	66.1	101.6	3092	1267	1825	15	6.9	1.2	-
8/5-6/69	750	2520	37.8	59.1	96.9	2920	1536	1384	>40	7.8	-	-
8/14-15/69	1200	3666	29.3	92.2	121.5	5050	2211	1839	18	7.3	0.4	-
8/20-21/69	1000	3820	52.4	65.8	118.2	4108	2074	2034	10	6.3	-	-
8/27-28/69	1250	6700	-	-	-	5975	2245	3730	6.0	6.3	-	-
9/10-11/69	2050	3980	109.4	99.6	209.0	7579	3410	4169	5.0	7.0	0.4	5.61
9/17-18/69	1215	3720	-	-	-	6034	2363	3671	5.0	6.9	-	-

(1) Results in mg/l except pH and SS. SS in ml/l

(2) No tannins

(3) Aerator near effluent end off.

TABLE A-6 EFFLUENT DATA: PHASE I (Q = 15 GPM)⁽¹⁾

Date	ANALYSIS											Set. S.	pH	Total Sulfide	Total Phosphorus
	BOD ₅	COD	ORG-N	NH ₃ N	TKN	TS	TFS	TVS	SS	FSS	VSS				
4/30/68 ⁽²⁾	400	-	-	-	-	5507	3767	1730	-	-	-	-	-	-	-
5/7/68 ⁽²⁾	180	-	-	-	-	6045	4180	1865	-	-	-	-	-	-	-
5/14/68	130	-	-	-	-	6480	4709	1771	-	-	-	-	-	-	-
5/20-21/68	100	-	-	-	-	6809	5474	1335	-	-	-	-	-	-	-
5/28-29/68	97	-	-	-	-	7361	5988	1372	-	-	-	-	-	-	-
6/4-5/68	85	2256	37.1	36.0	73.1	7609	5947	1662	-	-	-	-	-	-	-
6/11-12/68	53	1341	20.9	29.0	49.9	7208	6202	1006	-	-	-	-	7.4	-	-
6/18-19/68	27	1426	22.8	30.1	52.9	7104	6042	1062	673	242	431	39.0	7.2	-	-
7/11-12/68	50	-	-	-	-	6156	5460	696	-	-	-	-	6.9	-	-
7/15-16/68 ⁽²⁾	48	838	21.0	18.2	39.2	6106	6369	737	221	60	161	6.5	7.2	-	-
7/17-18/68	50	891	14.3	19.6	33.9	6272	5636	636	183	86	97	2.0	7.0	-	-
7/22-23/68 ⁽²⁾	39	1202	17.9	23.0	40.9	6274	5339	935	311	15	296	13.0	7.0	-	-
7/24-25/68	11	1177	16.9	23.4	40.3	6110	5314	796	198	12	186	16.0	7.0	-	-
7/30-31/68 ⁽²⁾	32	1205	19.0	25.2	44.2	6053	5073	980	469	125	344	22.0	6.9	0	-
8/1-2/68 ⁽²⁾⁽³⁾	21	710	11.7	25.8	37.5	5615	5032	583	-	-	-	-	7.1	-	-
8/6-7/68 ⁽²⁾	29	1157	20.4	26.9	47.3	6057	5115	932	629	152	477	27.0	7.0	-	-
8/8-9/68	30	832	14.2	25.8	40.0	5854	5175	679	-	-	-	-	7.2	-	-
8/12-13/68 ⁽²⁾	25	-	-	-	-	6077	5155	922	502	61	441	23.0	7.3	0	2.22
8/14-15/68	24	-	-	-	-	-	-	-	-	-	-	24.0	7.1	0 ⁽²⁾	2.45

⁽¹⁾ Results in mg/l except pH and SS. SS in ml/l

⁽²⁾ Grab sample

⁽³⁾ Aerator off for 1 hr. prior to sample collection

TABLE A-7 EFFLUENT DATA: PHASE II (Q = 20 GPM)⁽¹⁾

DATE	BOD ₅	F-BOD ₅	COD	F-COD	ORG-N	F-ORG-N	NH ₃ -N	F-NH ₃ -N	TKN	F-TKN	TS	TFS	TVS	SS	FSS	VSS	Set. S.	pH	Total Sulfide	Total Phosphorus
8/20-21/68	-	-	749	-	-	-	-	-	-	-	-	-	-	-	-	-	28.0	7.6	-	7.67
8/27-28/68	35	-	1042	-	23.3	-	25.9	-	49.2	-	-	-	-	-	-	-	-	7.2	0	-
9/3-4/68 ⁽²⁾	-	-	-	-	-	-	-	-	-	-	7196	6505	691	-	-	-	10.0	7.4	-	-
9/10-11/68	42	-	-	-	-	-	-	-	-	-	6996	6315	681	-	-	-	25.0	7.2	-	-
9/17-18/68	37	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	7.0	-	-
9/24-25/68	43	-	-	-	28.8	-	23.3	-	52.1	-	7631	6829	802	-	-	-	40.0	6.3	-	-
10/1-2/68	48	26	1243	382	-	-	-	-	-	-	7787	6687	1100	813	146	667	48.0	6.9	-	-
10/8-9/68	41	16	1330	352	35.6	7.4	30.2	25.2	65.8	32.6	7533	6531	1002	926	180	746	48.0	6.7	-	-
10/22-23/68	42	20	1545	461	44.1	5.0	28.5	27.3	72.6	32.3	7682	6586	1096	-	-	896	31.0	6.9	-	-
10/29-30/68	43	14	1720	484	21.6	4.0	28.5	27.6	50.1	31.6	7615	6480	1135	-	-	915	24.0	7.2	-	-
11/21-22/68	-	-	1708	532	23.4	8.9	25.8	24.3	49.2	33.2	-	-	-	-	-	-	20.0	7.2	-	-
12/3-4/68	51	10	1748	562	36.1	5.6	37.8	33.9	73.9	39.5	6312	5222	1090	937	425	512	11.0	7.3	-	-

⁽¹⁾ Results in mg/l except pH and SS. SS in ml/l⁽²⁾ Sampled after long weekend holidayTABLE A-8 EFFLUENT DATA: PHASE III (Q= 33 GPM)⁽¹⁾

Date	BOD ₅	F-BOD ₅	COD	F-COD	ORG-N	F-ORG-N	NH ₃ -N	F-NH ₃ -N	TKN	F-TKN	TS	TFS	TVS	SS	FSS	VSS	Set. S.	pH	Total Sulfides	Total Phosphorus
12/10-11/68	66	23	1704	712	3.8	7.8	35.7	20.7	39.5	28.5	6761	5693	1068	1567	910	657	11.0	7.9	-	-
12/19-20/68	773	47	1548	1372	38.1	12.9	42.0	33.9	80.1	46.8	6157	5219	938	1030	638	392	14.0	7.0	-	-
1/7-8/69	169	774	2012	1328	35.0	6.1	41.7	40.6	76.7	46.7	5304	4334	970	681	276	435	0.5	7.3	-	-
1/14-15/69	161	79	2101	1411	-	-	-	-	-	-	-	-	-	-	-	-	3.5	7.3	-	-
2/11-12/69	114	50	1936	1376	39.0	9.3	31.6	30.5	70.6	39.9	2190	1295	895	330	95	235	1.5	7.4	-	-
2/18-19/69	130	87	1760	1416	35.6	9.0	30.5	28.3	66.1	37.3	2187	1285	902	327	74	243	4.0	7.3	-	-
3/4-5/69	122	38	2038	1248	35.9	8.1	37.8	36.1	73.7	44.2	2621	1575	1046	650	279	371	0.7	7.5	-	-
3/18-19/69 ⁽²⁾	155	68	2408	1528	49.8	16.8	32.2	30.0	82.0	46.8	3180	1555	1625	770	-	-	0.7	7.4	0	5.6

⁽¹⁾ Results in mg/l except pH and SS. SS in ml/l⁽²⁾ Aerator near effluent off.

TABLE A-9 EFFLUENT DATA: PHASE IV (Q = 69 GPM)⁽¹⁾

DATE	BOD ₅	F-BOD ₅	COD	F-COD	ORG-N	F-ORG-N	NH ₃ -N	F-NH ₃ -N	TKN	F-TKN	TS	TFS	TVS	SS	FSS	VSS	Set. S.	pH	Total Sulfides	Total Phosphorus
4/8-9/69	400	230	3876	2480	49.8	17.9	33.3	30.5	83.1	48.4	-	-	-	-	-	-	0.8	6.8	-	-
4/24-25/69	260	120	2408	1472	-	-	-	-	-	-	3017	1418	1599	358	78	280	1.0	7.3	-	-
5/7-8/69	85	50	1600	992	-	-	-	-	-	-	1370	640	730	395	91	304	0.8	7.2	-	-
5/20-21/69	90	70	1576	1008	15.3	5.3	19.9	15.7	35.2	21.0	1685	615	1070	430	70	360	0.3	7.1	-	-
6/3-4/69	248	155	1738	1232	19.3	5.6	17.9	17.1	37.2	22.7	2027	805	1222	422	93	329	0.2	7.0	-	-
6/17-18/69	276	118	2192	1375	14.0	5.3	17.6	16.5	31.6	21.8	2614	818	1795	664	65	599	0.5	7.0	0	5.8
6/19-20/69	345	170	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.0	7.1	-	-
6/25-26/69	240	160	-	-	38.0	25.8	27.2	20.2	65.2	46.0	2475	924	1549	568	165	403	2.5	6.9	-	-

⁽¹⁾ Results in mg/l except pH and SS. SS in mL/l.

TABLE A-10 EFFLUENT DATA: PHASE V (Q = 127 GPM)⁽¹⁾

DATE	BOD ₅	F-BOD ₅	COD	F-COD	ORG-N	F-ORG-N	NH ₃ -N	F-NH ₃ -N	TKN	FTKN	TS	TFS	TVS	SS	FSS	VSS	Set. S.	pH	Total Sulfide	Total Phosphorus	F-Phos- phorus
7/16-17/69	420	260	2520	1848	-	-	-	-	-	-	2082	879	1203	510	214	296	3.0	7.0	-	-	-
7/23-24/69	410	275	2552	2042	38.6	27.9	31.6	25.5	70.2	53.4	2184	971	1213	572	273	299	3.5	7.0	-	-	-
7/29-30/69	253	103	1632	1296	11.5	7.0	44.2	34.2	55.7	41.2	1933	788	1145	399	2	397	1.5	7.1	0.5	-	-
8/5-6/69	175	60	1352	784	10.3	6.7	42.0	31.6	52.3	48.3	1797	867	930	494	0	494	0.8	6.8	-	-	-
8/14-15/69	240	85	2104	1240	35.9	7.0	41.7	40.0	77.6	47.0	2397	1054	1343	537	0	537	1.5	7.0	0.4	-	-
8/20-21/69	250	60	2088	1352	30.5	4.1	44.0	42.6	74.5	46.7	2399	1245	1154	304	0	304	3.0	6.8	-	-	-
8/27-28/69	260	130	2040	1016	-	-	-	-	-	-	2481	1195	1288	414	104	310	1.5	6.7	-	-	-
9/10-11/69	390	210	2392	1592	16.8	15.4	45.1	36.7	61.9	52.1	2307	1110	1097	429	58	371	1.0	6.8	0.0	3.6	2.9
9/17-18/69	410	250	2335	1705	-	-	-	-	-	-	2752	1230	1522	477	230	247	1.8	6.9	-	-	-

⁽¹⁾ Results in mg/l except pH and SS. SS in mL/l.

TABLE A-11 CONCENTRATED VEGETABLE TANNIN ANALYSES^{(1),(2)}

Date	BOD ₅	F-BOD ₅	COD	F-COD	TS	TFS	TVS	SS	FSS	VSS	Temp.	pH	TKN	F-TKN	NH ₃ -N	F-NH ₃ -N	ORG-N	F-ORGN	TP	F-TP
4/10/69	5900	3400	44790	32800	20494	3672	16822	4222	308	3914	24	4.7	78.4	59.4	15.7	13.4	62.7	45.9	20.1	14.1
4/20/69	-	-	34640	24800	-	-	-	-	-	-	24	4.8	-	-	-	-	-	-	-	-
5/11/69	3300	2300	25600	19742	11816	1470	10346	2226	220	2006	24	5.1	58.3	35.8	7.8	5.6	50.4	30.2	8.3	6.0
5/15/69	4000	2450	24992	20192	12430	1710	10720	2570	286	2234	24	4.7	-	-	-	-	-	-	-	-
6/6/69	3000	2200	20880	14600	10194	1520	8674	1868	278	1590	24	4.9	74.8	55.4	13.8	11.9	61.0	43.5	14.8	11.7
6/17/69	4150	2600	27680	21585	11050	1510	9540	2100	218	1882	24	4.6	-	-	-	-	-	-	-	-
6/22/69	9000	6300	37996	27880	22000	5668	16332	1384	228	1156	24	4.8	68.3	51.6	8.4	5.6	59.9	46.0	16.00	14.2
6/30/69	9200	6550	28160	21360	22280	7300	14980	2560	498	2062	24	5.0	83.40	67.2	20.16	15.68	63.2	51.5	21.5	16.8
7/18/69	3450	2300	20480	17200	10222	1582	8640	1906	342	1564	24	4.7	69.44	56.56	10.08	8.12	59.4	48.4	6.4	5.3
7/25/69	2500	1950	13380	11920	7960	960	7000	1230	138	1092	24	4.8	-	-	-	-	-	-	-	-
7/31/69	1975	1650	13850	11860	7940	1152	6780	640	152	588	24	5.1	31.92	23.5	7.6	6.2	24.4	17.4	4.8	3.9
8/21/69	11250	7580	57865	43580	25880	7460	18420	3220	390	2830	24	4.9	-	-	-	-	-	-	-	-

(1) Data in mg/l except temperature and pH. Temperature in °C

(2) Grab samples

TABLE A-12 REACTOR DATA FOR DILUTED TANNINS⁽¹⁾

θ	Q	Time	F-BOD ₅	F-COD	TS	TFS	TVS	SS	FSS	VSS	Temp.	pH
49	2.94	0	230	996	588	248	340	58	28	30	-	5.2
STEADYSTATE		142	70	636	886	264	622	92	48	69	24	6.4
24.4	5.9	0	220	936	544	223	321	64	24	40	-	5.4
STEADYSTATE		162	55	644	848	223	625	112	22	90	25	6.5
16.2	8.9	0	215	910	568	230	338	72	32	40	-	5.1
STEADYSTATE		168	75	696	646	158	488	96	24	72	24	6.2
12.0	12.0	0	212	890	610	258	352	66	34	32	-	5.3
STEADYSTATE		144	85	728	760	210	550	84	18	66	25	6.1

(1) θ in hours, Q in l/day, time in hours and temp in °C. All others in mg/l except pH.

TABLE A-13 REACTOR EFFLUENT FOR CONC. TANNINS: 5.2 HR. D.T. ^{(1),(2)}

Time	Date	BOD ₅	F-BOD ₅	COD	F-COD	TS	TFS	TVS	SS	FSS	VSS	Temp.	pH	TKN	F-TKN	NH ₃ -N	F-NH ₃ -N	ORG-N	F-ORGN	TP	F-TP
00	7/18/69	3450	2300	20480	17200	10222	1582	8640	1906	342	1564	-	4.7	69.4	56.6	10.1	8.1	59.3	48.5	6.4	5.3
(INFLUENT)																					
40	7/20/69	3050	1850	18480	16720	10332	1522	8810	1432	194	1238	26	5.8	-	-	-	-	-	-	-	-
90	7/22/69	2550	1450	18280	16440	10440	1568	8892	1788	346	1442	24	5.9	-	-	-	-	-	-	-	-
134	7/24/69	2350	1425	17880	16160	10564	1420	9140	1750	192	1558	24	5.8	-	-	-	-	-	-	-	-
00	7/25/69	2500	1950	13380	11920	7960	960	7000	1230	133	1092	-	4.8	-	-	-	-	-	-	-	-
(INFLUENT)																					
208	7/27/69	2150	1350	13280	12280	9640	1160	8480	1450	122	1328	24	5.6	-	-	-	-	-	-	-	-
256	7/29/69	1975	1300	13560	11680	9760	1120	8640	1040	125	915	24	6.0	-	-	-	-	-	-	-	-
306	7/31/69	1950	1238	13440	11540	9840	1040	8800	1024	164	860	23	5.9	65.0	58.2	3.4	1.7	61.6	56.5	4.1	3.8

(1) Time in hours and temperature in °C; Other data in mg/l except Date and pH

(2) $Q = 27.6$ M/dayTABLE A-14 REACTOR EFFLUENT FOR CONC. TANNINS: 12.2 HR. D.T. ^{(1),(2)}

Time	Date	BOD ₅	F-BOD ₅	COD	F-COD	TS	TFS	TVS	SS	FSS	VSS	Temp.	pH	TKN	F-TKN	NH ₃ -N	F-NH ₃ -N	ORG-N	F-ORGN	TP	F-TP
00	5/11/69	3300	2300	25600	19742	11816	1470	10346	2226	220	2006	-	5.1	58.2	35.8	7.8	5.6	50.4	30.2	8.3	6.0
(INFLUENT)																					
49	5/13/69	1800	950	20000	13360	11052	1638	9414	3012	482	2630	25	6.3	-	-	-	-	-	-	-	-
97	5/15/69	1850	825	18960	12840	12238	1624	10614	3638	468	3170	25	6.4	-	-	-	-	-	-	-	-
00	5/15/69	4000	2450	24992	20192	12430	1710	10720	2570	286	2284	-	4.7	-	-	-	-	-	-	-	-
(INFLUENT)																					
147	5/17/69	1950	837	20112	10776	13010	1766	11244	4058	266	3792	24	6.4	-	-	-	-	-	-	-	-
190	5/19/69	2000	975	20200	13600	12344	2100	10244	4198	274	3924	24	6.7	-	-	-	-	-	-	-	-
262	5/22/69	1950	1025	17800	13552	12991	2450	10541	4195	220	3975	24	6.8	56.5	33.7	4.5	3.4	52.0	30.3	8.0	3.8

(1) Time in hours and temperature in °C; Other data in mg/l except Date and pH

(2) $Q = 11.8$ M/day

TABLE A-15 REACTOR EFFLUENT FOR CONC. TANNINS: 17.5 HR. D.T. (1), (2)

Time	Date	BOD ₅	F-BOD ₅	COD	F-COD	TS	TFS	TVS	SS	FSS	VSS	Temp.	pH	TKN	F-TKN	NH ₃ -N	F-NH ₃ -N	ORG-N	F-ORGN	TP	F-TP
00	6/22/69	9000	6300	37996	27880	22000	5668	16332	1384	228	1156	-	4.8	68.32	51.6	8.4	5.6	59.92	46.00	16.00	14.2
(INFLUENT)																					
20	6/23/69	6050	4950	26960	20920	21610	5456	16154	2500	278	2222	24	5.8	-	-	-	-	-	-	-	-
46	6/24/69	3600	3200	24080	15120	22468	6560	15908	5678	674	5004	28	6.6	-	-	-	-	-	-	-	-
70	6/25/69	3400	2300	23750	13180	22466	7722	14744	5854	1462	4392	27	7.2	-	-	-	-	-	-	-	-
42	6/27/69	3400	2320	23360	11400	22628	4040	18588	6878	420	6458	30.0	6.5	-	-	-	-	-	-	-	-
163	6/29/69	3350	2200	23760	9040	20496	3806	16690	8026	398	7628	28.5	6.7	-	-	-	-	-	-	-	-
187	6/30/69	3325	2110	23550	9050	21528	3540	17988	8003	300	7703	29.0	6.6	-	-	-	-	-	-	-	-
00	6/30/69	9200	6555	28160	21360	22280	7300	14980	2560	498	2062	28.0	5.0	83.4	67.2	20.16	15.68	63.24	51.52	21.5	16.8
(INFLUENT)																					
235	7/2/69	3350	2162	23550	8280	22465	7200	15265	6015	1150	4865	26.5	6.6	-	-	-	-	-	-	-	-
283	7/4/69	3450	2225	23840	9050	23420	7124	16296	6084	1402	4682	27.0	6.7	68.40	56.6	7.8	6.8	60.6	49.8	15.8	14.2

(1) Time in hours and temperature in °C; Other data in mg/l except Date and pH

(2) $Q = 8.25$ l/day

TABLE A-16 REACTOR EFFLUENT FOR CONC. TANNINS: 22.2 HR. D.T.^{(1),(2)}

Time	Date	BOD ₅	F-BOD ₅	COD	F-COD	TS	TFS	TVS	SS	FSS	VSS	Temp.	pH	TKN	F-TKN	NH ₃ -N	F-NH ₃ -N	ORG-N	F-ORGN	TP	F-TP
00	4/10/69	5900	3400	44790	32800	20494	3672	16822	4222	308	3914	-	4.7	78.4	59.4	15.7	13.4	62.7	45.9	20.1	14.1
(INFLUENT)																					
26	4/11/69	5600	2475	31800	25800	-	-	-	1336	112	1224	25	5.5	-	-	-	-	-	-	-	-
43	4/12/69	4300	1775	30720	23800	-	-	-	3100	750	2350	25	6.2	-	-	-	-	-	-	-	-
53	4/13/69	-	-	28320	18920	-	-	-	4210	600	3610	25	6.5	-	-	-	-	-	-	-	-
92	4/14/69	2900	1100	28810	14721	-	-	-	7000	300	6700	25	6.6	-	-	-	-	-	-	-	-
117	4/15/69	2850	950	26885	10240	20118	3312	16806	7236	1210	8026	25	6.7	-	-	-	-	-	-	-	-
141	4/16/69	2800	1050	26760	9200	19798	3352	16446	8128	976	7152	26	6.7	-	-	-	-	-	-	-	-
164	4/17/69	2400	1100	26000	10080	20132	3660	16472	8998	1396	7602	25.5	6.9	-	-	-	-	-	-	-	-
189	4/18/69	2400	1250	26480	7798	20496	4326	16170	8896	1208	7688	25	6.8	-	-	-	-	-	-	-	-
209	4/19/69	2375	1250	24965	7766	20198	4148	16050	8892	1146	7746	23	6.8	76.2	56.0	4.5	2.3	70.3	53.8	10.8	13.6
00	4/20/69	-	-	34640	24800	-	-	-	-	-	-	-	4.8	-	-	-	-	-	-	-	-
(EFFLUENT)																					
256	4/21/69	-	-	18080	6880	19868	4060	15808	7768	760	7008	24	6.8	-	-	-	-	-	-	-	-
306	4/23/69	-	-	18240	6960	19456	3571	15885	7788	688	7100	23	6.8	-	-	-	-	-	-	-	-
330	4/24/69	-	-	18400	6980	9500	3504	15996	7785	644	7141	24	6.7	-	-	-	-	-	-	-	-

(1) Time in hours and temperature in °C; Other data in mg/l except Date and pH

(2) $Q = 6.5 \text{ L/min}$

TABLE A-17 REACTOR EFFLUENT FOR CONC. TANNINS: 46 HR. D.T.,⁽¹⁾,⁽²⁾

Time	Date	BOD ₅	F-BOD ₅	COD	F-COD	TS	TFS	TVS	SS	FSS	VSS	Temp.	pH	TKN	F-TKN	NH ₃ -N	F-NH ₃ -N	ORG-N	F-ORG-N	TP	F-TP
00	7/31/69	1875	1650	13850	11860	7940	1152	6788	740	152	588	-	5.1	31.92	23.5	7.6	6.2	24.3	17.3	4.8	3.9
(INFLUENT)																					
46	8/2/69	1000	550	12360	11200	5520	1212	4305	946	164	782	25	6.4	-	-	-	-	-	-	-	-
116	8/5/69	-	-	11040	8200	5820	1296	4524	1052	208	844	25	6.5	-	-	-	-	-	-	-	-
198	8/8/69	-	-	9160	6840	5376	1040	4336	1080	248	832	25	6.6	-	-	-	-	-	-	-	-
258	8/11/69	-	-	9995	6680	5856	1692	4164	1156	266	890	24	6.7	-	-	-	-	-	-	-	-
306	8/13/69	675	300	10200	6652	6480	1698	4782	1280	226	1060	25	6.7	27.4	17.3	3.3	2.2	24.1	15.1	3.4	2.9

⁽¹⁾ Time in hours and temperature in °C; Other data in mg/l except Date and pH

⁽²⁾ Q = 3.15 g/day

1	<i>Accession Number</i>	2	<i>Subject Field & Group</i>	SELECTED WATER RESOURCES ABSTRACTS INPUT TRANSACTION FORM	
		5-D			
5	<i>Organization</i> University of Virginia, Dept. of Civil Engineering, Charlottesville, Virginia				
6	<i>Title</i> Anaerobic-Aerobic Lagoon Treatment for Vegetable Tanning Wastes				
10	<i>Author(s)</i> Clinton E. Parker		16	<i>Project Designation</i> FWQA Project WPD-199	
			21	<i>Note</i>	
22	<i>Citation</i> <div style="display: flex; justify-content: space-between; margin-top: 5px;"> <div style="width: 45%;"> Date: June 1970 No. pp.: 84 </div> <div style="width: 30%;"> No. tables: 29 No. Fig.: 23 No. Ref.: 25 </div> <div style="width: 20%; text-align: right;"> No. appendix: 1 </div> </div>				
23	<i>Descriptors (Starred First)</i> Biological treatment, oxidation lagoons, lignins, aerobic conditions, anaerobic conditions.				
25	<i>Identifiers (Starred First)</i> Spent tannins, tannery waste waters, anaerobic-aerobic lagoon, biological treatment, biological growth units.				
27	<i>Abstract</i> <p>A field demonstration lagoon was operated at Virginia Oak Tannery, Inc., Luray, Virginia to evaluate the effectiveness of an anaerobic-aerobic lagoon in treating spent vegetable tannins blended with batepool and soak waste waters. The anaerobic-aerobic lagoon system was used to treat combined waste streams with a BOD₅ concentration of approximately 1000mg/l. Operational phases were designed to cause the system to go from aerobic conditions to anaerobic-aerobic. After reaching anaerobic-aerobic conditions, doubling the BOD₅ load did not result in a significant decrease in BOD₅ removal efficiency. Efficiency, measured in terms of soluble BOD₅, at a BOD₅ load of 17.3 lbs/1000 ft³/day (anaerobic-aerobic condition) was 81 percent compared to a 92 percent efficiency for a BOD₅ load of 4.5 lbs/1000 ft³/day (aerobic conditions).</p> <p>Although the lagoon system proved successful in removing degradable organics, color of the waste water was not reduced by this method of treatment. Color of spent vegetable tannins is a major problem and will dictate the most desirable approach to treating this waste water.</p> <p>A completely mixed aeration unit was used in the laboratory to study the biological degradation of spent vegetable tannins. It was found that approximately 60 percent of the COD of spent vegetable tannins is not biological degradable and the generally accepted substrate-growth interaction relationship required modification to take into account the non-degradable fraction of COD.</p>				
	<i>Abstractor</i> C. E. Parker		<i>Institution</i> University of Virginia		