

ACCLIMATIZATION OF ACTIVATED SLUDGE TO LIME-SULFIDE UNHAIRING EFFLUENTS*

J. E. COOPER, W. F. HAPPICH, E. F. MELLON, AND J. NAGHSKI

*Eastern Regional Research Center†
Philadelphia, Pennsylvania 19118*

ABSTRACT

Activated sludge from sanitary wastes was acclimated to lime-sulfide, hair-pulping tannery effluents and used to reduce the organic nitrogen and sulfide components as well as biochemical oxygen demand (BOD), suspended solids, and chemical oxygen demand (COD) by 83 to 94 percent.

The sludge was acclimated in a completely mixed bio-oxidation reactor by periodic feeding with increasing increments of tannery unhairing wastes. The clarified effluent from the bio-oxidation unit was recirculated to dilute the unhairing waste (as received from the tannery) without evidence of inhibitor buildups. Under these conditions, there was no evolution of hydrogen sulfide gas. The aerobic process oxidized the sulfide ion in the waste without requiring the addition of catalysts such as manganous salts.

≈ ≈ ≈

INTRODUCTION

The utilization of activated sludge for the removal of carbonaceous materials from sanitary wastes was first reported by Ardern (1). The determination of the biochemical aspects of activated sludge was pioneered by Harris *et al.* (2) when they postulated that the chemical changes were attributable to enzymes rather than to direct bacterial action. The relationship between oxygen utilization and bacteria in sewage was demonstrated by Parsons and Wilson (3, 4). Their first-order differential equation was demonstrated to hold for the carbonaceous fermentation and not the nitrification stage of Gaunt and Abbott (5). During the second stage (nitrification), the assimilation of amino acids and peptides occurs at the same time the carbohydrate material is utilized by the bacteria for nutrition, energy, and growth.

The control of the activated sludge treatment process by management of the detention time and the mixed liquor suspended solids concentration (MLSS) was a breakthrough in the operation of the aeration process. Harris and Cock-

*Presented in part at the Sixty-ninth Annual Meeting of the American Leather Chemists Association, Ottawa, Canada, June 24-28, 1973.

†Agricultural Research Service, U. S. Department of Agriculture.

burn (6) proposed a mathematical relationship between the interfacial contact time and the sludge concentration, *i.e.*, that the percent sludge solids required to effect a given degree of treatment was inversely proportional to the detention time at a constant air pressure. Comparison between plug flow and complete mixing was studied by Grieves and Pipes (7). Garrett (8) was one of the first to effect control of activated sludge concentration through wasting.

As a continuous culturing device, the complete-mixed system has a useful application in the sanitary engineering field. A complete-mixed activated sludge implies that the influent is completely mixed with the contents of the aeration vessel (9). Various techniques have been used to accomplish this uniform dispersion. Kehr and von der Emde (10) designed a pilot plant to study the high-rate activated sludge process. Four parameters were determined with this unit: (A) the aeration tank volume required to handle a loading; (B) the most probable biochemical oxygen demand (BOD) removal; (C) the most suitable aeration system; and (D) the power consumption.

The standardization of procedures for sanitary engineering research was first published by Symons *et al.* (11) in a 1960 study of the aerobic, biological treatability of industrial wastes. A comprehensive study of the design and operation of laboratory and pilot plants for submerged culture studies was published by Chain *et al.* (12).

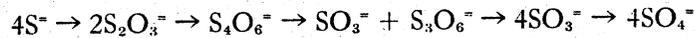
The biological treatment of industrial wastes requires a knowledge of the major constituents that contribute to the chemical oxygen demand (COD) and BOD of the influent that is to be sewered. In treating tannery wastes, two options are open: treating the total mixed effluents which are often highly variable in composition, or treating highly polluted process streams separately. The application of the activated sludge process to tannery composite wastes has been reported by Emerson (13) and Barkley (14). Parker (15) studied the biological treatment of tannin liquors, excluding the unhairing liquors. Removal of nitrogen from waste waters has been discussed by Eliassen (16) and McCarty (17).

Hair removal from hides by the lime-sulfide, hair pulping process results in a considerable amount of nitrogenous compounds, sulfide, fats, waste lime, and inorganic solids being discharged as an effluent, characterized by a high BOD and COD, high pH, and high suspended solids content. Bio-oxidation of these tannery unhairing liquors (which contain 70 percent of the pollution load from a side-leather tannery) has not been studied, although Hoppich *et al.* (18) and Niwa (19) have reported various methods for removing suspended solids from unhairing liquors in order to recover the dissolved proteins.

The rate of oxidation of sulfides by oxygen has been published by Bowers *et al.* (20) and Field (21). They indicated that a polysulfide was formed which determined the oxidation rate of the sulfide ion. Wallace *et al.* (22) found that the rate-determining step in the base-catalyzed oxidation of organic sulfides with molecular oxygen involves proton abstraction from the sulfide, forming a stable

carbanion, and that the rapid reaction between oxygen and the α -carbanion occurs at the alpha-position. The autoxidation of organic sulfides with oxygen is a function of the bisulfide concentration and the oxygen concentration. According to Hashimoto and Sunamoto (23) the disulfide ion is the reducing agent that forms a polysulfide ion, which catalyzes the autoxidation of the sulfide ion, and the overall reaction is a second order rate equation.

London and Rittenberg reported that *Thiobacillus thioporus* and *T. thiooxidans* (24) produce enzymes that completely oxidize sulfides, thiosulfate, tetra- and trithionate, and sulfite to sulfate.



The sulfide bio-oxidation is completed within five minutes under conditions used by Saxena and Aleem (25). The sulfide concentration is inhibitory to the oxidation process when the MLSS concentration is too low to produce a sufficient amount of oxidase.

Moriarty and Nicholas (26) determined that *Thiobacillus concretivorus* excreted enzymes that oxidized the inorganic sulfide ion and that the rate of oxidation was a linear function of the enzyme concentration. The conclusion was that the rate of sulfide oxidation is a function of the enzyme producers, the thiobacilli.

This paper reports the preparation and properties of acclimated-activated sludge and its use for denitrification, oxidation of the sulfide ion, and reduction of the BOD and COD concentrations of lime-sulfide unhairing waste liquors.

EXPERIMENTAL

Bio-oxidation Units

Acclimated-activated sludge was prepared in the Horizon Ecology Bench Scale Bio-oxidation apparatus[‡] illustrated in Figure 1. The unit, originally designed by A. Busch (27), Rice University, has been modified by the authors to accommodate domestic activated sludge and acclimated-activated sludge. An advantage of this unit is that it may be used either in a batch or in a continuous process. Another advantage is that it is a complete-mixed reactor and the sludge concentration is under control at all times by means of the pumps. The detention time of the sludge, and therefore the age of the sludge, can be controlled. The raw influent to be treated can be diluted with water, recycled treated effluent, or nutrient solutions in any desired ratio by the metering diaphragm pumps A and B shown in Figure 2. The influent mixture is injected into the mixed liquor chamber of reactor I (acclimated unit). The air rate is adjusted to keep the mixed liquors in motion and also to satisfy the oxygen demand of the sludge. The detention time of the unit may be controlled by the effluent pump rate or by

[‡]Reference to brand or firm name does not constitute endorsement by the U. S. Department of Agriculture over others of a similar nature not mentioned.

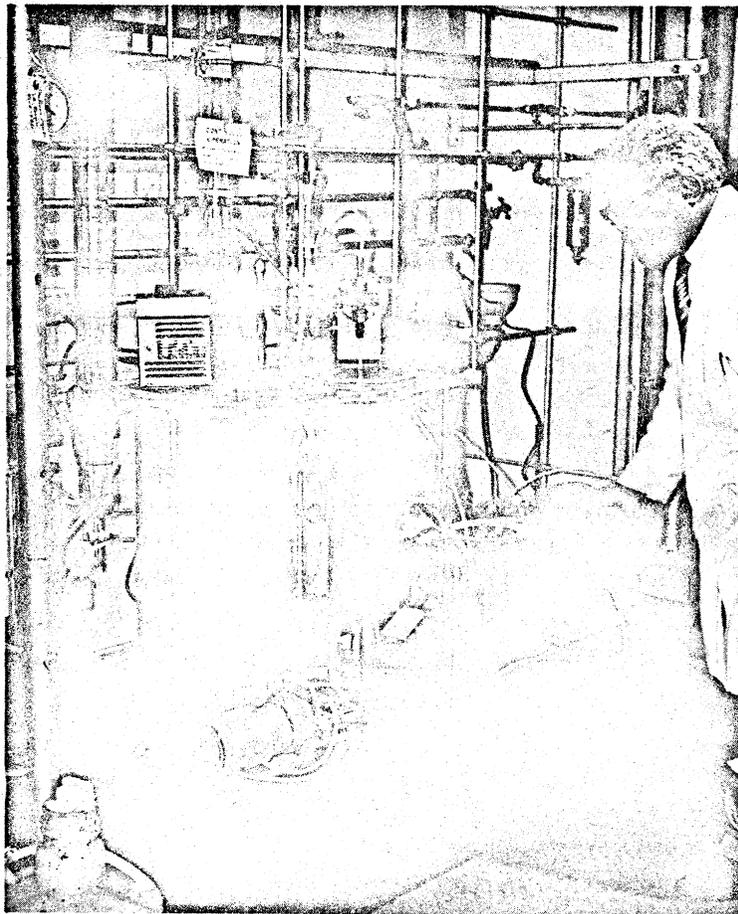


FIGURE 1.—Illustration of the bio-oxidation reactors: The unit on the left contains the acclimated-activated sludge; the activated sludge unit is on the right. The effluent pumps are located on top of each unit.

substituting inner chambers of various diameter. The MLSS concentration is controlled by pump D, which may be adjusted so that the solids can be pumped to waste or to reactor II (sanitary unit), or the mixed liquor solids may be pumped from reactor II to reactor I. The internal chamber is a quiescent zone where settling of the solids takes place. The final effluent is withdrawn at the top of the internal chamber by pump E and it is either wasted or returned to the influent and used as a diluent for the lime-sulfide unhairing liquors.

Activated Sludge

Return sludge was obtained from a local municipal sewage works and kept under aeration at our laboratory for use in the bio-oxidation units. Primary

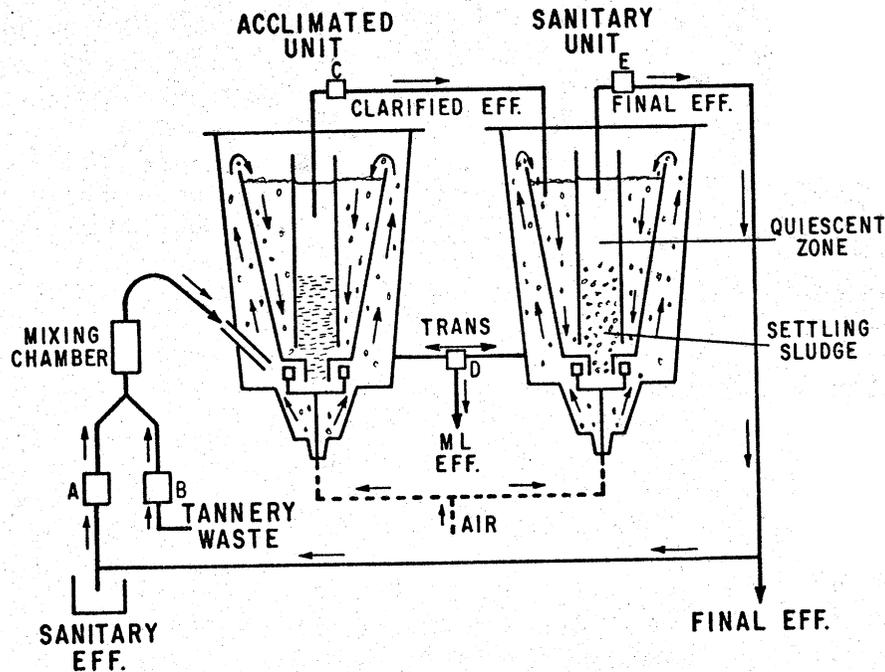


FIGURE 2.—Schematic of the bio-oxidation units. A,B and C,E are the influent and effluent pumps, respectively. D is the mixed liquor (ML) transfer pump. Working volume of each vessel is five liters.

effluent from the same treatment plant was used as a maintenance feed. The total solids, settleable solids, suspended solids, and pH were determined daily. The oxygen demand of the sludge was determined before adding to the bio-oxidation units.

Acclimated Activated Sludge

The acclimated activated sludge was prepared by adding quantities of diluted unhairing waste, one part waste to 20 parts tap water, to Unit I, which contained the activated sludge. The dilution of the unhairing waste was based on the immediate dissolved oxygen demand (IDOD) and the BOD of the waste after screening through a 65-mesh screen. After five days, the sludge is acclimated and can then accept higher concentrations of unhairing waste effluent, or treatment at 20 to 1 dilution can be continued by dilution with recycle effluent from the reactor.

Protein Removal

The removal of dissolved keratin and other nitrogenous compounds was determined by measuring the Kjeldahl organic nitrogen and the total nitrogen concentrations of the influent and effluent, respectively.

Lime-Sulfide Unhairing Effluent Liquors

Unhairing waste liquors were obtained from a side-leather tanner who used the high-sulfide, hair-pulping, paddle vat process. The concentrated effluent was obtained directly from the unhairing operation and did not include any washwaters. A chemical analysis was performed on the effluent as received. The unhairing liquor was passed through a 65-mesh polypropylene screen to remove the larger solids. The screened effluent was divided into portions for further treatment and analysis. The BOD's of all portions were estimated by determining the Oxygen Demand Index (28).

ANALYTICAL METHODS

The dissolved oxygen concentration was measured with a Weston and Stack Model 3 galvanic probe and a Model A-30 BOD agitator with a digital readout. The output of the readout was coupled to a Honeywell Electronic Model 19 recorder across a 10 K ohm variable resistor. Flocculation was accomplished with a Phipps and Bird Stirring Apparatus in accordance with the procedures of ASTM Designation D2035-68 (29). The BOD was estimated by measuring the Oxygen Demand Index according to the method of Westerhold (28).

The official methods of analysis of The American Water Works Association, American Public Health Association, and The Water Pollution Control Federation were used for pH, BOD, COD, total oxidizable carbon (TOC), total solids, volatile solids, settleable solids, suspended solids, and volatile suspended solids (30). The dissolved oxygen (D.O.) concentration was measured using the Alsterberg (azide) method (30). Nitrogen was determined by the semi-micro Kjeldahl method. Sodium sulfide was determined by the Official Method of Analysis of the Society of Leather Trades' Chemists (31).

ASTM procedure D2329-68 (29) was modified to estimate activity of activated and acclimated activated sludges.

RESULTS AND DISCUSSION

Composition of Unhairing Effluent

The analysis of a typical batch of unhairing liquors as received from the tannery is shown in Table I. The pH of 12.5 shows that hydroxide alkalinity is present. The total alkalinity of 11,386 mg./l. (CaCO_3) indicates that solid lime is in the unhairing liquor. The organic nitrogen of 4500 mg./l. represents undissolved and dissolved keratin as well as albuminoids. The IDOD is very high, as shown by both the 15 minute and the 30 minute BOD values. There is excellent agreement between the five-day BOD (BOD_5) and the TOC. The total oxidizable material of 72,800 mg. COD/l. includes carbohydrates, fats, and soluble and insoluble nitrogenous materials that do not oxidize appreciably in TOC or BOD_5 tests. Elemental analyses of a series of samples of dissolved

protein which had been exhaustively dialyzed yielded empirical formulae identical to that calculated for keratin. The COD/g. of these samples were consistent with the calculated value for keratin of 1.4, as shown in Table II.

TABLE I
LIME-SULFIDE UNHAIRING EFFLUENT
(Fresh Hides, Paddle)

pH	12.5
Na ₂ S	3,500 mg./l.
Total Nitrogen	4,900 mg./l.
Organic Nitrogen	4,500 mg./l.
Total Alkalinity (CaCO ₃)	11,386 mg./l.
Total Solids	5.59%
Total Volatile Solids	52.0%
Settleable Solids	200 ml./l.
Suspended Solids	33,680 mg./l.
Volatile Suspended Solids	30%
15 Min. BOD (IDOD)	280 mg./l.
30 Min. BOD	480 mg./l.
BOD Five-Day	21,600 mg./l.
COD	72,800 mg./l.
TOC	20,700 mg./l.

BOD — biochemical oxygen demand; COD — chemical oxygen demand; TOC — total organic carbon; IDOD — immediate dissolved oxygen demand.

TABLE II
COMPARISON OF CHEMICAL OXYGEN DEMAND TO WEIGHT OF
SOLUBLE PROTEIN FROM UNHAIRING LIQUORS

Sample Source	COD mg./l.	R = COD/gm. Protein
Tannery B	1405*	1.4
Tannery B	1440*	1.4
Tannery C	1225	1.2
Tannery A	1260	1.3
Tannery A	1585*	1.6
Tannery A	1281	1.3
Tannery A	1273	1.3
Tannery A	1354*	1.4
Tannery A	1316*	1.3
Tannery A	1412*	1.4
Tannery A	1396*	1.4
Tannery A	1260	1.3
Tannery A	1244	1.2

*Samples were dialyzed and lyophilized. Other samples were precipitated at pH 4.2 from screened unhairing wastes, centrifuged, and dried at 101°C. and are designated as crude protein.

Treatability

The biological treatability of the waste was determined from the ratio of the BOD/COD (11). From Table I: BOD = 21,600 mg./l., COD = 72,800 mg./l., and BOD/COD = $21,600/72,800 = 0.29$. This low value of BOD/COD indicated that acclimation of the sludge would be necessary to obtain adequate removal of the BOD (11). However, the value of 0.29 indicated that it should be treatable after acclimatization.

Two types of loads are applied on activated sludge units: (A) hydraulic loads which establish the basis for the hydraulic design of the aeration unit, and (B) loads of removable substance which control the process design of the aeration unit. The process load of a biological treatment unit is usually expressed in terms of the BOD applied per unit of time, *i.e.*, pounds of five-day BOD (20°C.)/day. Other parameters may also be used as process loads, such as suspended solids, COD, organic nitrogen, or bacteria. Unhairing wastes contain a large amount of organic nitrogen to be treated by the aerobic treatment process, suggesting the use of the pounds of organic nitrogen applied per unit of time rather than the BOD (20°C.) which is based on glucose-like carbohydrates.

The problem is further complicated because the unhairing waste contains a high concentration of sulfide ion, which does not require organisms initially for oxidation but creates a high instantaneous oxygen demand that can lead to an oxygen deficit severe enough to inhibit microbiological oxidation and possibly lead to anaerobic conditions. Therefore, the first factor should be the calculation of the sulfide loading to be applied to the aeration tank in a unit of time per pound of available D. O. Second, the loading of organic nitrogen per day per 1000 pounds of MLSS per hour of aeration must be calculated. The third factor that governs the aeration process is the rate at which oxygen can be supplied as D. O., to meet the oxygen requirements of both the biological flora and the nonbiological constituents that exert an oxygen demand.

Guidelines for Initial Operation of Bio-Unit on Tannery Unhairing Effluent

While removal of sulfide, protein, nitrogen, and total oxidizable material (COD) as well as BOD₅ and suspended solids are of concern, the removal of BOD₅ was taken as the basis for planning since operational criteria based on extensive experience are reported in the literature in terms of BOD₅ loading for 90 percent BOD₅ removal from sanitary sewage.

McCabe and Eckenfelder (33) recommend loadings below 500 mg. BOD/day per 1000 mg. MLSS for diffuse air plants operating with a 4- to 12-hour aeration time in influent of 150 to 350 p.p.m. BOD, with MLSS in the 2000 to 3000 p.p.m. range.

For our five l. bio-unit operating with an MLSS of 3000, allowable BOD loading would be

$$500 \times \frac{3000}{1000} \times 5 = 7500 \text{ mg. BOD per day}$$

assuming a ten-hour aeration time sets an influent flow rate of $\frac{5}{10} = 0.5$ l. per hour. Allowable BOD₅ per liter is $\frac{7500}{0.5 \times 24} = 625$ mg./l.

For an intensive mixing type of plant operating at MLSS levels of 6000 to 12000 mg./l., 90 percent reductions of BOD₅ have been reported at loadings up to 500 lbs. BOD₅ per day per 1000 cu. ft. of aeration volume (10). This is equivalent to a loading of 8014 mg./l. or 40,070 mg./day for our five l. unit.

This data predicts an allowable loading of $\frac{40,070}{.5 \times 24} = 3339$ mg. BOD/l. at a 0.5 l./hr. influent rate and ten-hour aeration time.

Since the unhairing effluent to be treated (Table I) had a BOD₅ of 21,600 mg./l., predilution by a factor between $21,600/625 = 35/1$ and $21,600/3339 = 6.5/1$ prior to treatment was indicated.

An arbitrary dilution factor of 20/1 was chosen for initial experiments at a 0.5 l./hr. feed rate. This choice gave an aeration time of ten hours and a loading of 12,960 mg. BOD₅/day with an influent BOD₅ of 1080 mg./l.

Could sludge age under these conditions, based on 3000 mg./l. MLSS concentration and a suspended solids content of $33,680/20 = 1684$ mg./l. in the influent, would be

$$\frac{3000 \times 5}{0.5 \times 1684 \times 24} = 0.74 \text{ days,}$$

between the normal range of 0.2 to 0.7 for high rate processes and 3 to 9 for conventional activated sludge plants (33).

Air requirements would be between $\frac{0.0309 \times 12,960}{24(60)} = 0.28$ l./min. and $\frac{0.0618 \times 12,960}{24(60)} = 0.56$ l./min., based on values of 500 to 1000 cu. ft. of air per lb. BOD removed (0.0309 to 0.0618 l. air per mg. BOD) reported in the literature.

Sulfide Oxygen Requirement Based on Sulfide Concentration

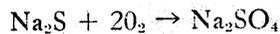
The oxidation-reduction potential (ORP) of the unhairing liquor was - 650 mv., and that of the activated sludge + 236 mv. When the unhairing liquor was aerated for one-half hour, the ORP was - 450 mv. which quickly dropped to - 650 mv. after standing for three minutes. The DO was zero under these

conditions. This strongly reducing condition is characteristic of anaerobic environments. Bisulfide ion, which is present at pH 12 or greater, produces the ORP of - 650 mv. Preaeration of the unhairing liquor before loading to an aerobic process, until the ORP was around - 50 mv., lowered the bisulfide ion concentration to a great extent.

The 280 mg./l. IDOD of the unhairing waste was due mainly to the sulfide ion concentration. Sulfide is rapidly oxidized at pH 9 or less by thiobacilli as whole cells or by their extracts. The very rapid change in the oxidation potential in an oxygen environment, as indicated by the change from - 650 mv. to - 450 mv., which quickly dropped back to - 650 mv. when the air was cut off, demonstrates that oxygen is necessary for the reaction to occur.

Feeding rate of influent must be adjusted on the basis of the sulfide ion concentration in the influent to ensure that sulfide ion does not build up to toxic levels.

The COD of sodium sulfide was determined as follows: since



the weight of oxygen consumed is directly proportional to the weight of sodium sulfide present, grams oxygen/grams sodium sulfide = 64/78 or 0.82 g. O₂ per g. Na₂S, or 1000 mg./l. Na₂S = 820.0 mg./l. O₂ (COD).

In the hair pulping process, two to three percent Na₂S, based on the hide weight, is customarily used. It is usual practice, when employing drums or paddle vats, to add 250 pounds of water per 100 pounds of hide as the float ratio, resulting in a sodium sulfide solution of 8,000-12,000 mg./l. Approximately 50 percent of the sodium sulfide is utilized during the unhairing process, leaving 4000-6000 mg./l. of Na₂S to be disposed of in the waste liquor. The COD due to Na₂S would then range from 3280-4920 mg./l. In the case of an uncontrolled loading, one could have a COD range of 6560-9840 mg./l. Samples of effluent, analyzed on a volume basis, contained 0.55 percent or 5500 mg./l. sodium sulfide after unhairing.

According to Saxena (25) the optimum sulfide concentration for rapid oxidation is 0.33 mM (25 mg./l.). The concentration of sulfide in the lower range (3280 mg./l.) is 131 times greater than the optimum sulfide concentration for loading to aeration tanks and oxidation could be inhibited.

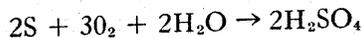
In our experiments, the unhairing waste was diluted with water or aeration effluent in the ratio of 1:20, before feeding to ML reactor. With this dilution aerobic conditions could be maintained and the sulfide ion concentration could be reduced 90 percent by aerating the mixture with acclimated-activated sludge for two hours, or 96 percent at five hours' retention.

Microscopic examination of the acclimated-activated sludge and the clarified effluent (32) showed zoogloal masses and large numbers of vibrio forms of bacteria. These are probably *Beggiatoa alba*, which are normally found in sewage

polluted streams and feed on hydrogen sulfide. It is well known that metabolism of the thiobacteriales in the absence of sunlight is not photosynthetic and that hydrogen is transferred to oxygen, requiring aerobic conditions (22). The acclimated-activated sludge is composed of large masses of thiobacteriales, which utilize hydrogen sulfide and sulfur as sources of energy for the assimilation of carbon dioxide and for the synthesis of their cell substances. The probable bacterial mechanism is



Thiobacilli are known to carry out the following reaction aerobically:



The latter reaction contributes to the drop in pH of the diluted lime-sulfide influent from 10.2 to 8.8 during the retention period in the reactor. The thiobacteriales are autotrophic and aerobic, requiring D.O. as demonstrated in the equations.

Activated Sanitary Sludge

Five l. of activated sludge from a municipal wastes plant was aerated at a rate of one l. of air/min. in the biooxidation sanitary unit (Unit I). Primary effluent from the same treatment plant was used as a feed. After two hours of aeration, the pH, total nitrogen, suspended solids, BOD, COD, and sulfide ion concentrations were determined on the influent, the complete-mixed reactor, and the effluent, respectively. The data in Table III indicate that the return sanitary sludge was not in a highly activated state. Although there was appreciable reduction in BOD and COD, there was no removal of either the total nitrogen or the organic nitrogen. The suspended solids content in the effluent was two and one half times greater than in the influent.

TABLE III
SANITARY ACTIVATED SLUDGE IN DENITRIFICATION STAGE

	Influent	Activated Sludge	Effluent
pH	7.4	7.5	7.5
(mg./l.)			
Total Nitrogen	77	130	68
Organic Nitrogen	26	63	67
Suspended Solids	100	816	240
BOD	1860	—	66
COD	6360	—	228
S ²⁻	0.00	0.00	0.00

BOD — biochemical oxygen demand.
COD — chemical oxygen demand.

The activated sludge was in the denitrification stage, obtaining its oxygen supply from the nitrates that are dissolved in the water, and releasing nitrogen and carbon dioxide gases. This condition was corrected by doubling the air rate (to two l. of air/min.), to maintain a D.O. concentration of one mg./l. in the ML. Under the new increased air rate, sufficient oxygen was supplied to meet the metabolic needs of the micro-organisms.

Conventional operation of a ML system maintains the MLSS around 2500 mg./l. The activated sludge from the municipal waste plant in the experiment above was 816 mg./l. MLSS or one third of the desired concentration of solids. The final effluent contained 240 mg./l. SS and was returned to the reactor in order to assimilate the unmetabolized organic matter of 1860 mg./l. BOD of the incoming influent.

Our purpose in allowing the MLSS to increase was to create food limiting conditions before attempting to acclimate the municipal sludge to the tannery unhairing liquors.

Comparing the Food/Mass (F/M) or BOD/MLSS ratios under the endogenous conditions above of $1860/816 = 2.27$, with the BOD/MLSS ratio of $452/1600 = 0.28$ when the activated sludge was operating properly in a growth stage on primary sanitary effluent (Table IV) and of $1438/3960 = 0.36$ when an acclimated activated sludge was operating at steady state on unhairing effluent feed (Table V) illustrates the importance of monitoring these ratios to assure proper operation.

American sanitary sewage treatment experience teaches that F/M ratios less than 0.50 are required to effect 90 percent or better removal of BOD under conditions practical for continuous plant operation (McCabe and Eckenfelder, Reference #33, see pp. 262-263). The F/M ratio of 2.27 was further evidence that the municipal sludge must be returned to the aeration unit to obtain food limiting conditions rather than a microbial limiting environment. The state of

TABLE IV
UTILIZATION OF NITROGEN BY ACTIVATED SANITARY SLUDGE*

	Influent	Mixed Liquors	Effluent	% Removal
pH	7.6	7.9	7.5	—
Total Nitrogen (mg./l.)	37	51	16	57
Organic Nitrogen (mg./l.)	17	49	6.2	64
Suspended Solids (mg./l.)	90	1600	7.6	92
BOD (mg./l.)	452	—	10	98

*Return sludge from a municipal waste treatment plant.
BOD — biochemical oxygen demand.

activity of the activated sludge after conditioning was determined by adding a sanitary waste to the mixed liquor tank and following the oxygen uptake with a membrane probe which had been standardized with the Winkler procedure (30) as shown in Figure 3. The experiment was carried on for 16 days. Fifty percent of the carbonaceous BOD was oxidized in three days. The reaction appears to be a first order rate equation, wherein the velocity constant, k , is very

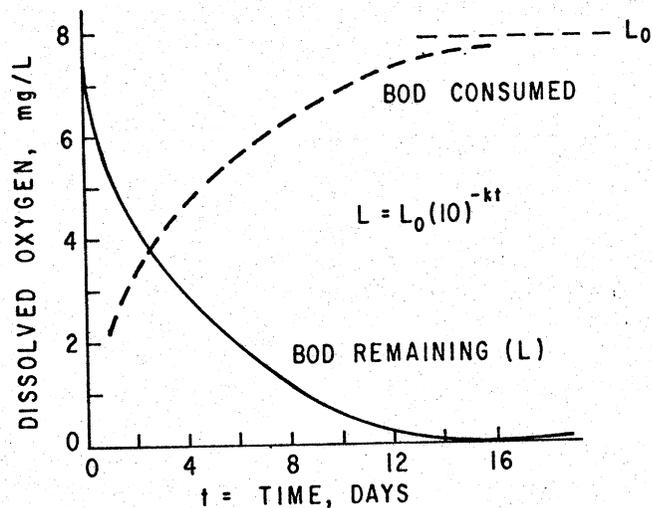


FIGURE 3.—Typical oxygen demand curve in BOD determination. Dotted curve represents the oxygen consumed (BOD). Solid line represents the fraction of unreacted BOD remaining.

close to 0.1. This is characteristic of carbohydrate oxidation by aerated sewage sludges (34). The upper curve is the fraction of total carbonaceous material oxidized at time, t . The fraction of BOD remaining to be oxidized at time t is given by the lower curve, which approximates the equation:

$$L = L_0 (10^{-kt})$$

where L_0 is the ultimate carbonaceous BOD and L the BOD at anytime “ t .”

The Effect of Shock Loading on Activated Sludge

Figure 4 shows the effects of adding a shock load (0.5 l./hr., 32,040 mg./l BOD) to the activated sludge, which resulted in bacteriostasis, an unsatisfactory condition of the activated sludge. The D.O. concentration remained constant for over five hrs., indicating that the carbonaceous loading was not degraded. Two conditions are represented here: catalytic inhibition and respiratory failure of the organisms. The sludge under this condition does not settle, but floats. Under these conditions the influent pumps were cut off and the ML were aerated

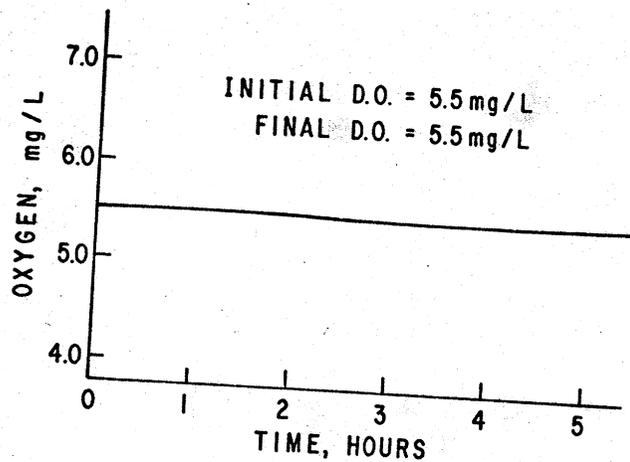


FIGURE 4.—This oxygen demand curve of inhibited biomass was the recorded response of a membrane probe.

for 24 hrs. to oxidize the sulfide ion. Two l. of the ML was then sewerred. Synthetic sewage was added to the reactor and the ML continuously aerated until food limiting conditions were established. In normal plant practice, the entire aeration tank would have been sent to the lagoons. It is important that graphs of this type should have the time and date, especially in municipal plants where occasional "spills" are impressed on the aeration system, thus poisoning the activated sludge.

Acclimated Activated Sludge

The activated sludge in Unit II was fed small increments of diluted lime sulfide-unhairing wastes (500 ml. per day) for four days. The sludge became acclimated to the unhairing waste, as evidenced by ability to maintain a sludge density index of 2.6 with the ML concentration 3960 mg./l. and settleable solids equal to 15 percent ($SDI = 3960/1500 = 2.6$) at a sludge age of 0.32 days.

After acclimating the sludge as described above, the unit was operated for several days on a continuous influent of tannery unhairing effluent diluted one to 20 with tap water. Feed rate was at the condition previously calculated, 0.5 l. per hr., to give a detention or aeration time of ten hrs. MLSS concentration was initially 3000, rising to 3900 mg./l. after 24 hrs. This gave a Gould sludge age initially of 0.74 days, increasing to 0.96 days during most of the run. The sludge density index and settling properties remained satisfactory. An air rate of 1.0 l./hr. provided sufficient oxygen and agitation to maintain aerobic conditions.

Averaged influent, effluent analyses, and percent removals of BOD, suspended solids, sulfide, nitrogen, and COD over a four-day period are shown in Table V. The reductions in BOD_5 and suspended solids are near the values expected for

TABLE V
REMOVAL OF MAJOR CONSTITUENTS IN TANNERY UNHAIRING
EFFLUENTS BY ACCLIMATED-ACTIVATED SLUDGE*

	Influent	Effluent	Removal	% Removal
(mg./l.)				
BOD ₅ †	1584	289	1296	85
Suspended Solids	1228	71	1157	94
Total Nitrogen	228	89	139	61
Organic Nitrogen	195	36	159	82
Sulfide	175	14	161	92
COD	2219	370	1849	83

*Data averaged over four-day period. Feed rate 0.5 l./hr. of tannery unhairing effluent diluted one to 20.

†BOD₅ — five-day biochemical oxygen demand.

this loading of sanitary sewage. This indicates no significant inhibition or poisoning of the acclimated activated sludge even at the high (1584 mg. BOD₅/l.) influent concentration, and high pH (near ten) of the influent.

Nitrogen and COD removals were much higher than anticipated at this low sludge age, where little nitrification and denitrification normally occurs. This point will be of interest in future studies and may be very advantageous to tanneries in meeting future nitrogen limitations in effluents.

Sulfide removal (92 percent) was good as expected from the preliminary batch treatment tests showing 90 percent removal in two hrs. and 96 percent after five hrs.

In other experiments comparable satisfactory operation and removals were obtained using recycled effluent to dilute the raw unhairing waste in a ratio of one to 20, indicating no buildup of soluble toxicants.

The biomass remained in a viable exogenous state when the loading was

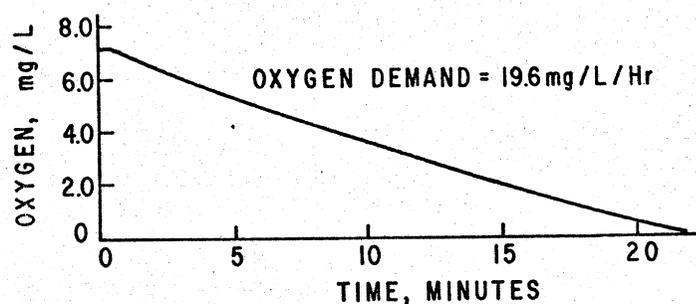


FIGURE 5.—Oxygen demand curve of acclimated activated sludge in unhairing effluent diluted one to ten.

doubled by using a one to ten dilution at the same feed rate, although MLSS built up rapidly and reductions were poorer. The exogenous state at high aerator BOD levels is indicated by the oxygen demand rate of 19.6 ml. per l. per hr. shown in the oxygen demand rate curve in Figure 5, obtained on acclimated activated sludge feeding on lime sulfide unhairing waste diluted one to ten with

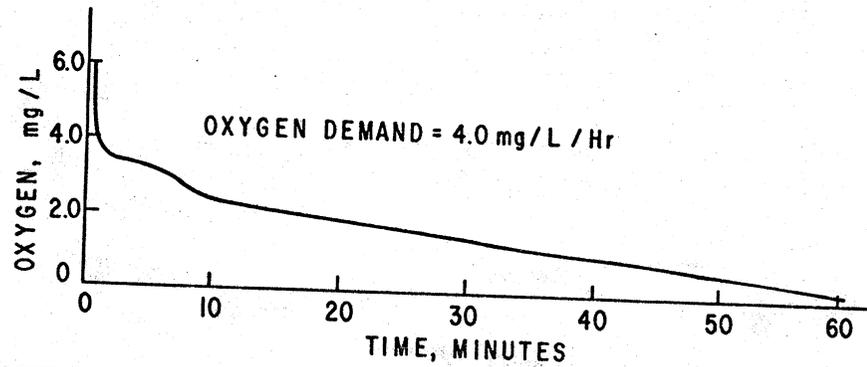


FIGURE 6.—Oxygen demand curve of acclimated activated sludge maintained 24 hrs. without feed.

bio-unit effluent, compared to the basal endogenous demand rate of 4.0 mg. per l. per hr. of a similar sludge which had been maintained without feed for 24 hrs. (Figure 6). The typical foaming due to oxidative decomposition of the sludge in the endogenous state was observed in this sample.

CONCLUSION

This work has demonstrated that unhairing effluents can be successfully treated in an activated sludge system provided that the principles governing the operation of activated sludge systems are recognized and the unit is operated within established limits of treatment parameters: (A) The biomass is properly acclimated to the new type of influent; (B) The pH of the biomass is maintained below 9.0 by dilution of influent or other means; and (C) the loading is adjusted so that the system operates aerobically and without inhibiting levels of waste components.

It is important to recognize the high initial BOD requirement in this type of waste due to the presence of sulfide and operate with a sufficient amount of D.O. to satisfy this high initial oxygen demand as well as that due to bio-oxidation of carbonaceous and nitrogenous compounds.

It is also clear from this study that direct introduction of tannery unhairing effluents into a conventional activated sludge system without consideration of the above factors can result in unsatisfactory operation of an activated sludge unit.

ACKNOWLEDGMENTS

The authors thank Laverne H. Scroggins for the analysis of the recovered proteins and E. Graves and staff, Industrial Wastes Laboratory, Northeast Pollution Works, City of Philadelphia, Pennsylvania, for the COD and TOC analyses. Special thanks are expressed for the co-operation of Ocean Leather Corporation, S. B. Foot Tanning Company, and Pfister and Vogel Tanning Company.

REFERENCES

1. Ardern, E. *Surveyor*, 72, 409 (1927).
2. Harris, F. W., Cockburn, T., and Anderson, T. *Surveyor*, 70, 30, 53 (1926).
3. Parsons, A. S., and Wilson, H. *Surveyor*, 72, 490 (1927).
4. Parsons, A. S., and Wilson, H. *Surveyor*, 72, 221, 252 (1927).
5. Gaunt, P., and Abbott, W. E. *J. Soc. Chem. Ind.*, 47, 14 (1928).
6. Harris, F. W., Cockburn, T., and Anderson, T. *Eng. Contr., Water Works Issue*, 66, 24 (1927).
7. Grieves, R. B., and Pipes, W. O. *Proc. Ind. Waste Conf.*, 18th, 636 (1963).
8. Garrett, M. T., Jr. *Sewage Ind. Wastes*, 30, 253 (1958).
9. Gaudy, A. F., Jr., Engelbrecht, R. S., and Dettoss, R. D. *Appl. Microbiol.*, 8, 298 (1960).
10. Kehr, D., and von der Emde, W. *J. Water Pollut. Contr. Fed.*, 32, 1066 (1960).
11. Symons, J. M., McKinney, R. E., and Hassis, H. H. *J. Water Pollut. Contr. Fed.*, 32, 841 (1960).
12. Chain, E. B., and Gualandi, G. *Rendicont. Istituto Superiore Di Sanita*, XVII, English Ed., Roma: Fondazione Emanuele Paterno (1954).
13. Emerson, D. B., and Nemerow, N. L. *Proc. Ind. Waste Conf.*, 24th, 867 (1969).
14. Barkley, W. A., King, P. H., Myers, R. H., and Randall, G. W. *Proc. Ind. Waste Conf.*, 25th, 69 (1970).
15. Parker, C. E. *Proc. Ind. Waste Conf.*, 25th, 678 (1970).
16. Eliassen, R., and Tchobanoglous, G. *Proc. Ind. Waste Conf.*, 23rd, 35 (1968).
17. McCarty, P. L., and Haug, R. T. in "Microbial Aspects of Pollution," Sykes, G., and Skinner, F. A., Editors, Academic Press, London, New York (1971), p. 215.
18. Happich, W. F., Happich, M. L., Cooper, J. E., Feairheller, S. H., Taylor, M. M., Bailey, D., Jones, H. W., Mellon, E. F., and Naghski, J. *JALCA*, 69, 50 (1974).
19. Niwa, Y. *Hikaku Gijutsu*, 11, 14 (1969).
20. Bowers, J. W., Fuller, M. J. A., and Packer, J. E. *Chem. Ind. (London)* 1966 (1); 65.
21. Field, L., Parsons, T. F., and Pearson, D. E. *J. Org. Chem.*, 31, 3550 (1966).
22. Wallace, T. J., Pobiner, A., Baron, F. A., and Schriessheim, A. *J. Org. Chem.*, 30, 3147 (1965).
23. Hashimoto, S., and Sunamoto, J. *Bull. Chem. Soc., Japan*, 39, 1297 (1966).
24. London, J., and Rittenberg, S. C. *Proc. Nat. Acad. Sci., USA*, 1183 (1964).
25. Saxena, J., and Aleem, M. I. H. *Can. J. Biochem.*, 51, 560 (1973).
26. Moriarty, D. J. W., and Nicholas, D. J. D. *Biochim. Biophys. Acta*, 184, 114 (1969).
27. Busch, A. W., and Myrick, N. G. *J. Water Pollut. Contr. Fed.*, 32, 949 (1960).
28. Westerhold, A. F. *The Digester*, XXII, (1), p. 4 (1965).
29. 1970 Annual Book of ASTM Standards, part 23, Water; Atmospheric Analysis. Published by the American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103.
30. Standard Methods for the Examination of Water and Wastewater, 13th edition, 1971,

- prepared and published jointly by American Public Health Association, American Water Works Association, Water Pollution Control Federation. Publication office, American Public Health Association, Inc., 1740 Broadway, New York, New York 10019.
31. Official Methods of Analysis, 1965, of the Society of Leather Trades' Chemists, 4th revised edition, 52 Crouch Hall Lane, Redbourn, Herts, England.
 32. Frobisher, Martin, Jr. "Fundamentals of Bacteriology," 3rd Ed., W. B. Saunders (1946).
 33. McCabe, J. and Eckenfelder, E. E., Jr. (Editors) "Biological Treatment of Sewage and Industrial Wastes," Vol. I, New York, Reinhold Pub. Corp., 1956.
 34. Moore, E. W., Thomas, H. A., Jr. and Snow, W. B., Simplified Method for Analysis of B.O.D. Data, Sewage Ind. Wastes, 22, 1343 (1950).

Received June 25, 1975.

DISCUSSION

MR. CARL F. ACKERBAUER (Ackerbauer Laboratories, Inc.): Thank you, Mr. Cooper, for presenting some interesting data and, surely, food for thought. Tanners are at this time especially interested in all factors that might help us solve our problem, with air and water pollution. Tanneries are striving to eliminate contaminating substances in their wastewaters. Federal guidelines are and will continue to be motivated by the research and development results from well conducted and oriented programs of private industry and governmental agencies. The EPA must have a sound basis for its standards and regulations. Data such as those in this paper will not only help us treat our wastewaters but also enable us to present to the regulating agencies the latest in industrial waste treatment technology.

I have two questions. Joe, the activated sludge which you used from a sanitary source undoubtedly varies with regard to the solids content. First, what was the solids content and how important is this? Second, what were the BOD₅, COD, and suspended solids in the final effluent?

MR. J. E. COOPER: The sludge from the Abington sewage works had a solids content around 2400 p.p.m. I did not feed it for four hours and dropped the solids from 2400 to 1700 p.p.m. by aeration. The final effluent ran from 20 to 40 p.p.m. BOD₅.

MR. S. S. SARYAN (Wolverine World Wide, Inc.): Do you have any hydrogen sulfide gas being evolved, and does that bother you? Second, do you have any foam formed, and is that a problem?

MR. COOPER: The reason I am here today is that I have solved these problems. There is no hydrogen sulfide because when you aerate you convert the sulfide to sulfur. You do not need to add manganese.

MR. SARYAN: Before you have an opportunity to oxidize the sulfide, doesn't some of the hydrogen sulfide come off?

MR. COOPER: No, you get no hydrogen sulfide above pH 10. I use the final effluent to lower the pH to 10 while pumping oxygen in to get sulfide oxidation. Foaming occurs only when the unit is underfed. You must have a strong feed of tannery waste for the system to work without foaming. I have worked in a municipal treatment plant and the only time we got foaming was when we had too little air and too little food coming into the sludge. You can get foaming if you try to lower the pH by adding acids since this drives off a gas. Grease also promotes foaming.

MR. DON CHARNIAK (C. E. Bauer): Mr. Cooper, what type of screening are you considering to remove the coarse solids?

MR. COOPER: Fresh hair pulping wastewaters will contain hair fragments ranging from 0.05 mm. to two mm. in length. We used three screen mesh sizes, 20, 40, and 65 mesh.

MR. SATYENDRA MOHAN DE (Chestnut Operating Company): What was the mixed liquor volatile suspended solids in your system?

MR. COOPER: On the activated sludge before it is acclimated it ran about 60 percent volatile. After acclimation it went up to about 75 to 80 percent.

MR. DE: What was your rate constant or k_1 value for the reaction?

MR. COOPER: It was about 0.4 for the sulfide reaction. It is a very rapid oxidation.

MR. GEOFFREY J. GOETZ (PPG Industries): Joe, what is the net cost or net savings if someone is already hooked into a municipal sewage treatment plant and they were to install a system such as you describe.

MR. COOPER: I have design information available. I estimate maximum cost for modifying paddle vats and pumps and piping of \$10,000 for 20,000 gallons per day.

MR. ACKERBAUER: Thank you, Joe. I would like to express the association's appreciation by giving you this certificate.