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BIO-OXIDATIVE TREATMENT OF DAIRY WASTES

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"Deoxygenating wastes consist of all wastes which react with the oxygen dissolved in the receiving body of water and deplete or tend to deplete the amount of oxygen available for normal aquatic life." So stated DeLaporte at the First Ontario Industrial Waste Conference (1). Such a waste originates in the dairy and milk processing industry. Aerobic treatment is generally used for the disposal of dairy wastes because these wastes have a low concentration of solids and a high oxygen demand. There is, however, a record of failure as well as of success with aerobic treatment, and the underlying reason for the failures has been the lack of basic information on the aerobic process.

This report to the Conference presents results of our laboratory investigations, and contains basic information on the conversion of dairy waste by aerating sludge and on the oxygen requirement during the process. Much of the information may be applicable to other waste. Details are available in various publications and have been summarized (12, 13, 14, 16).

Milk Waste

Milk losses are inevitable. Under good housekeeping, 1% is a low operating loss, although as much as 3% or more of the milk or its equivalent may be found in the waste. Thus a plant handling 150,000 pounds of milk daily will discharge a minimum of 1,500 pounds fluid milk containing 180 pounds milk solids. Wash and cooling waters dilute this loss so that the dairy waste contains only 0.1% solids giving a concentration of 1,000 parts per million (ppm). The biochemical osygen demand (BOD) would be about 800 ppm, while the chemical oxygen demand (COD) is around 1,000 ppm (9). The daily pollution load from such a milk plant would equal that of a community of at least 430 people.

The soluble solids in dairy waste serve as an excellent nutrient for microbial growth as they contain about 53% lactose, 35% protein, and necessary salts. Extreme precautions are necessary to avoid the obnoxious conditions so generally known. An understanding of the biochemistry of the treatment process would help produce desirable effluents.

Gross Changes During Aeration

The problem was approached as one of aerobic fermentation of a very dilute solution. A laboratory fermentor was used throughout these studies (7). The device allows excess agitation and aeration. Malodors were absent when a simulated waste made from skim milk was fed continuously at the rate of one liter per hour into 20 liters of aerating solution. Examination of the non-settled mixed effluent showed that about 40 to 50% of the COD had disappeared. More detailed analysis showed that all the protein (determined as nitrogen) of the added waste was now in the cell or sludge solids. Further, 44 units of the original carbohydrate were completely gone while 9 units were used as cell substance. Of 88 units of organic matter in the waste, one-half had disappeared while one-half remained as cell substance. Similar results were observed when 20% of aerator capacity served as seed while waste was added so that the container filled in 4 hours. The seed contained about 500 ppm solids. After two hours there was a rapid decrease of total oxygen demanding material until by the sixth hour there was only about 50% of the amount present in the original waste (5). Removal of cells by centrifuge gave a solution with only about 10% of the original COD.

Oxygen Uptake

The changes that occur during aeration were determined in the Warburg apparatus by manometric measurements made at 30°C in buffered solutions containing sufficient nitrogen nutrient. A well-aerated sludge was used as inoculum. The rates of oxidation of skim milk, as well as of lactose and casein, the major components of skim milk, were high for the first six hours and then approached the rate of the unfed control (-). In each case between 32 and 40% of the total theoretical required amount of oxygen was used. The CO_2 formed in each vessel was equivalent to the O_2 removed. Further analysis showed that all soluble material had been removed. The fact that no other products were found in the solution suggested that aerobic treatment of dairy waste must occur thus:

$$\text{Milk solids} + O_2 \longrightarrow \text{sludge cells} + CO_2 + H_2O$$

Composition of sludge

A more detailed consideration of this system required a chemical analysis of the cells as well as of the ingredients utilized by the cells. Dried sludge and casein were analyzed. The empirical formulas and mole weights were calculated and are shown in Table I. The ash content of sludge has been omitted but when this is taken into consideration the "mole" weight becomes 124 units instead of 113 as shown for $C_5H_7NO_2$. With the analytical data in the table, and information collected in the Warburg apparatus, certain bio-chemical relationships were established (8).

Removal of Lactose

In the presence of a nitrogen source, lactose is readily removed from solution by aerated sludge. If complete oxidation of lactose occurred it could be represented by the well known equation showing that all carbon is oxidized, leaving none for the cells:

$$C_{12}H_{22}O_{11}\cdot H_2O + 12\ O_2 \longrightarrow 12\ CO_2 + 12\ H_2O \text{ or}$$

$$(CH_2O) + O_2 \longrightarrow CO_2 + H_2O$$

However, in order to obtain the 5 carbons in the cells, 5 sugar particles are needed:

$$5\ (CH_2O) + NH_3 \longrightarrow C_5H_7NO_2 + 3\ H_2O$$

But the Warburg studies showed that only about 37.5% of the theoretical amount of oxygen was used; thus burning up three-eights of available sugar to CO_2 and water, while the remainder was incorporated into cell substance. The utilization of sugar in the presence of NH_3 for cell synthesis must be therefore:

$$8\ (CH_2O) + 3\ O_2 + NH_3 \longrightarrow C_5H_7NO_2 + 3\ CO_2 + 6\ H_2O.$$

Removal of Protein

Similar reasoning showed how the casein, $C_8H_{12}N_2O_3$, was used by sludge organisms. Theoretically, complete oxidation would be:

$$C_8H_{12}N_2O_3 + 8\ O_2 \longrightarrow 8\ CO_2 + 2\ NH_3 + 3\ H_2O$$

Manometric data again showed that only 3 of the carbons were completely oxidized. Thus casein was removed from solution for assimilation and oxidation in this manner:

$$C_8H_{12}N_2O_3 + 3\ O_2 \longrightarrow C_5H_7NO_2 + NH_3 + 3\ CO_2 + H_2O.$$

Removal of Skim Milk Organics

From the above, a mole of organic cell substance of 113 units may be formed from 240 units of sugar or 184 units of casein. Fortunately, this approximated the proportions of sugar and protein in skim milk. This permitted the addition of the two equations to give one equation for the assimilation of skim milk:

$$8\ (CH_2O) + C_8H_{12}N_2O_3 + 6\ O_2 \longrightarrow 2\ C_5H_7NO_2 + 6\ CO_2 + 7\ H_2O$$

The nitrogen required for sugar assimilation is supplied by the protein. Therefore, 226 units of organic cell material may be produced from 424 units of organic milk solids, showing about 53% conversion to cells. The same value is obtained even when the ash and moisture content of the dried milk and of the sludge are taken into consideration. This approximates the values observed in many experiments.

Endogenous Respiration

Starving or unfed cells also have an oxygen demand and the Warburg studies showed that the organisms oxidized themselves thusly:

$$C_5H_7NO_2 + 5\ O_2 \longrightarrow 5\ CO_2 + NH_3 + 2\ H_2O.$$

In order to completely oxidize 113 units of cells, there are required 160 units of oxygen. This endogenous respiration goes on very slowly. During the tests, 10 microliters of oxygen were used per mg of cell per hour. This equals 14.3 micrograms of oxygen, and from the equation of endogenous respiration, represented a destruction of 10.2 micrograms of cell substance, an amount equal to about 1% of the original weight of cells. Rates as high as 1.25% were observed in field trials. Lower rates may be anticipated as the more easily oxidized materials are used up.

Rate of Oxidation

Polarographic studies showed that an oxygen concentration of 0.35 to 0.5 ppm was necessary to maintain aerobic conditions (8). When 500 ppm sludge were treated with milk, the rate of oxidation was constant above a milk concentration of 100 ppm. The speed of milk oxidation was related to the cell concentration. If the cell concentration is doubled, milk oxidation should take half as long, but the same amount of oxygen would be required. After assimilation was completed, the rate of oxygen demand by endogenous respiration alone continued at one-tenth the rate required during assimilation.

Application of Data

From the data presented to this point, information is available on the amount of oxygen required for complete oxidation of a waste, the amount required during the rapid assimilation process, and the amount required for endogenous respiration. The rate at which oxygen is used by the sludge during assimilation and during endogenous respiration is also known. In addition, the amount of new solids produced can be calculated as well as the time required for such production.

Table II following shows calculations made for a single feeding of 100 lb of milk solids at 1,000 ppm concentration when acted upon by 500 ppm active sludge.

TABLE II

Calculations for Oxidation of 100 lb of Milk Solids (1,000 ppm Concentration) by 50 lb of Active Sludge (500 ppm concentration)

	Assimilation Phase	Endogenous Respiration	Total
Oxygen Required			
Per Cent	37.5	62.5	100.0
Pounds	45.3	76.1	121.4
Pounds per hour	7.5	0.75	
Time required (hours)	6		
New Cells produced (pounds)	50		
Cell solids oxidized (per cent per hour)		0.5-1.0	

Non-Accumulation of Sludge

A study of the above tabulation shows that conditions may be established favoring nonaccumulation of sludge. If it is assumed that 2,500 ppm sludge solids are in an aerator and endogenous respiration proceeds at 1% per hour, a total of 20% or 500 ppm will disappear in 24 hours. The addition of 1,000 ppm of skim milk will produce 500 ppm of new cells to replace the amount destroyed. In this way, it is theoretically possible to maintain a constant level of sludge while destroying waste. Kountz has successfully applied this principle to

Purification

Actually, the process is more than the simple assimilative oxidation of organic matter with subsequent oxidation of the cells by their own endogenous respiration. The rate of purification or removal of waste from solution is much greater than the rate of oxidation, as shown so well by Gellman and Heukelekian (3). They found the average rate of purification for seven industrial wastes to be six times the rate of oxidation. Our studies showed that when 1,000 ppm simulated milk waste were added to 1,000 ppm sludge in a single dose, purification rates were ten or more times greater than oxidation rates (6). In 30 minutes, one-half of the oxygen demanding substances was removed from the waste. According to the above equations, the expectation would be that the removal of nutrients would be eight-thirds or 2.67 times the rate of oxidation. Gellman and Heukelekian obtained such values for some wastes, but wider ratios were obtained with higher carbohydrate-type wastes. Since oxidation does not occur immediately, material is apparently accumulated for subsequent oxidation.

Storage and Oxidation

Further study with dairy waste showed that purification consists of several interrelated processes: removal from solution, synthesis, storage, and oxidation (15). A glycogen-like substance was the major storage product and was readily oxidized. It was estimated that during purification an active aerated sludge may store as much as 50% of its own weight. One would then anticipate that rapid and complete purification could be accomplished in about 20 to 30 minutes if 1,000 ppm of soluble organic substances were mixed with 3,000 ppm well aerated, starved sludge. The loaded sludge could be removed leaving a clear effluent. The concentrated sludge may be aerated to burn the stored material. The starved cells may be reused for seed or a portion of the loaded sludge may be disposed of by other means. Eckenfelder and associates have applied this process of purification and aeration of sludge slurry to various organic wastes (2).

Summary

Laboratory studies on dairy wastes have made available basic information of value to sanitary engineers. Specifically, each pound of oxygen demand requires a pound of oxygen for complete combustion. The high rate of oxygen utilization during assimilative growth must be satisfied to prevent obnoxious conditions. This phase of assimilation requires at least 37.5% of the total oxygen demand within a relatively short period depending upon the concentration of the sludge and of the solids. Oxygen is utilized at a much slower rate during endogenous respiration, and air flow may then be reduced about ten times. A significant amount of sludge is oxidized during the first 24 hours and may amount to as much as 20% of the sludge weight.

Equations of assimilation and endogenous respiration showing these changes have been developed and detailed data are presented.

The biological treatment is a complex process of water purification involving the multifold activities of microorganisms. Waste removal is a combination of cell synthesis, conversion for temporary storage, and oxidation. Application of basic information on synthesis, storage, and oxidation should be of prime consideration in designing biochemical treatment plants for waste disposal.

References

1. DeLaporte, A. V. Deoxygenating Wastes. First Ontario Industrial Waste Conference, p 36-39. June 1954.

2. Eckenfelder, W. W., Jr., and O'Connor, D. J. The Aerobic Biological Treatment of Organic Wastes. Proc. 9th Ind. Waste Conf., Purdue Univer., p 512-530 (1954)

3. Gellman, I., and Heukelekian, H. Studies of Biochemical Oxidation by Direct Methods. III. Oxidation and Purification of Industrial Wastes by Activated Sludge. Sewage and Ind. Wastes 25: 1196-1209. (1953).

4. Hoover, S. R., Jasewicz, L., Pepinsky, J. B., and Porges, N. Assimilation of Dairy Wastes by Activated Sludge. Sewage and Ind. Wastes 23: 167-173. (1951).

5. Hoover, S. R., Pepinsky, J. B., Jasewicz, L., and Porges, N. Aeration as a Partial Treatment for Dairy Wastes. Proc. 6th Ind. Waste Conf., Purdue Univ. 313-319. (1951).

6. Hoover, S. R., Jasewicz, L., and Porges, N. Biochemical Oxidation of Dairy Wastes. Relationship Between the Rate of Purification and Rate of Oxidation and Graphical Estimation of First Order Velocity Constants. Proc. 9th Ind. Waste Conf. Purdue Univ., 71-79. (1954).

7. Hoover, S. R., and Porges, N. Treatment of Dairy Waste by Aeration. II. Continuous Aeration Studies. Proc. 5th Ind. Waste Conf., Purdue Univ., 137-144. (1949).

8. Hoover, S. R., and Porges, N. Assimilation of Dairy Wastes by Activated Sludge. II. The Equation of Synthesis and Rate of Oxygen Utilization. Sewage and Ind. Wastes, 24: 306-312. (1952).

9. Hoover, S. R., and Porges, N. Treatment of Dairy Waste by Aeration. U.S. Dept. Agr. Bur. Agr., and Ind. Chem., AIC-332 (ERRL) 7pp. Mar. 1952.

10. Kountz, R. R., Big Problem: Dairy Wastes. Striking Solution: Bio-Oxidation. Food Eng., 26 (10): 89-90. (1954).

11. Kountz, R. R., Dairy Waste Treatment. J.Milk and Food Tech., 18: 243-245. (1955).

12. Porges, N., Rapid Bio-Oxidation Method of Waste Disposal. 1955. Proc. of Am. Soc. Brewing Chem. p 56-64.

13. Porges, N., Waste Treatment by Optimal Aeration -- Theory and Practice in Dairy Waste Disposal. J.Milk and Food Tech., 19: 34-38. (1956).

14. Porges, N., Jasewicz, L., and Hoover, S. R., A Microbiological Process Report. Aerobic Treatment of Dairy Wastes. Applied Microbiology, 1: 262-270. (1953).

15. Porges, N., Jasewicz, L., and Hoover, S. R. Biochemical Oxidation of Dairy Wastes. VII. Purification, Oxidation, Synthesis and Storage. Proc. 10th Ind. Waste Conf., Purdue Univ., 135-146 (1955).

16. Porges, N., Jasewicz, L., and Hoover, S. R., Principles of Biological Oxidation. Presented at Conference on Biological Waste Treatment, Manhattan College, April 1955.

TABLE I

Analytical and Empirical Composition of Milk Ingredients and Sludge

	Lactose	Casein	Sludge
Composition in %			
Carbon	39.98	52.85	42.26
Hydrogen	6.72	6.48	5.69
Nitrogen	0	15.12	11.27
Oxygen	53.30	24.76	27.00
Ratio of Atoms = % /atomic weight			
Carbon	3.33	4.40	3.94
Hydrogen	6.71	6.43	5.65
Nitrogen	0	1.08	0.81
Oxygen	3.33	1.55	1.69
Formula:	$C_{12}H_{24}O_{12}$	$C_8H_{12}N_2O_3$	$C_5H_7NO_2$
Mole Weight	360	184	113