POLLUTION POTENTIAL MEASUREMENTS OF BEEF CATTLE WASTES

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INTRODUCTION

A knowledge of the amount of oxygen required by decomposable matter in a livestock waste is important for several reasons. Firstly, it may be used as a general measure of the oxidizable matter contained in a waste. Secondly, it may be used as a means of predicting the progress of aerobic decomposition in polluted waters and the degree of self-purification that may be achieved in a given time. Thirdly, it may be used as a measure of the removal of pollutants that accompanies different treatment processes.

Though the oxygen demand of a waste may be determined by several tests, the biochemical oxygen demand (BOD) test is the one most widely used. This test is normally the primary basis of any assessment of the pollution potential or strength of a waste.

In a recent study by Aasen and McQuitty (1) reported elsewhere, an oxygen demand index (ODI) test was used in addition to the BOD test in a comparison of aerobic and anaerobic storage of beef cattle wastes. The material presented here is the result of further analyses and study of data pertaining to these tests. Their relationship to other measured waste strength characteristics also was considered.

TESTS

Biochemical Oxygen Demand

The BOD of a waste is the amount of dissolved molecular oxygen required to stabilize the decomposable matter present under aerobic conditions (2, 3, 9, 11). This oxygen demand is exerted by three classes of materials (2, 3): (a) an initial demand by chemical reducing compounds (ferrous ion, sulphite and sulphide); (b) carbonaceous organic matter usable as a food source for aerobes; and (c) oxidizable nitrogen that serves as a food source for nitrogen bacteria. The latter two demands form the BOD with the carbonaceous breakdown as the first stage and nitrification as the second.

Only the first stage is sufficiently constant to be generalized in mathematical terms (3). The general equation for the BOD curve is given by:

\[ Y = L (1 - 10^{-kt}) \]

where

\[ Y = \text{BOD at time } t; \]
\[ L = \text{ultimate BOD of a waste; and} \]
\[ k = \text{reaction rate constant of bacterial population.} \]

The use of the equation is dependent upon the determination of \( L \) and \( k \) for a given waste. Several methods have been developed for determining these constants, including: (a) the "log-difference" method – Fair 1936 (4); (b) the "slope" method – Thomas 1937 (12, 13); and (c) the "moment" method – Moore et al. 1950 (8).

Oxygen Demand Index

The ODI test\(^a\) is a modification of the chemical oxygen demand (COD) test which is a measure of the chemically oxidizable organic matter in a waste (3). The ODI test, involving chemical oxidation, uses potassium dichromate \((K_2Cr_2O_7)\) as an oxidizing agent. During the redox reaction, the yellow color of the hexavalent dichromate ion \((Cr_2O_7^{2-})\) is reduced to the green-color trivalent state \((Cr^{+++})\) by organic matter. The degree of color change is proportional to the amount of organic matter present and can be measured on a spectrophotometer at a wavelength of 600 nm.


Simpson\(^a\), in a comparison of oxygen demand tests, noted that ODI test results were similar to those obtained by the COD tests. The primary advantage of the ODI test over the COD test lies in the fact that the former requires only a few minutes to carry out compared to several hours in the case of the latter.

EXPERIMENTAL PROCEDURES

The beef cattle wastes were collected in four storage pits beneath slatted floors (1). Pits 1 and 2 were operated as oxidation ditches, with one rotor located in the former and two in the latter to maintain two levels of aeration. Pits 3 and 4 received no treatment and hence operated anaerobically.

Samples were collected weekly from each pit for the last 19 wk of a 30-wk trial period (1). The sample analyses were conducted in the Environmental Laboratory, Department of Civil Engineering, University of Alberta.

BOD tests were carried out using the Hach Manometric BOD apparatus. The standard 5-d BOD test requires a constant temperature of 20°C. However, because no facilities were available to control temperatures of the solutions in the Hach units, the BOD data \((\text{BOD}_{5T})\) were obtained in this trial at an average temperature of 24°C (22-27°C). The procedures followed were in accordance with the manual (7) accompanying this apparatus. Tool (14) observed that this Hach unit yielded results within ±5% of the standard dilution method. It has the advantages that it was designed for use by an unskilled operator and has the capability of handling wastes with high BOD values. Readings were taken twice daily and the first-stage BOD curve was plotted for each of duplicate samples.

Initially, the procedures for the ODI test as documented by Westerhold and cited by Simpson\(^a\) were followed. These later were modified to those adopted by Simpson using standard COD reagents.
No apparent differences were observed between respective ODI values during a comparison of the two procedures.

In addition to the BOD and ODI tests, the samples were analyzed for pH, total solids (TS) and volatile total solids (VTS). The methods used in these determinations were in each case in accordance with those set out in "Standard Methods" (2) for samples with high solids content.

DATA ANALYSIS AND RESULTS

k and L Determinations

A Fortran computer program was written to determine values for k (rate constant) and L (ultimate BOD) for the first-stage BOD curve. All three methods listed above for determining k and L were incorporated in the program. Initially, the program was not able to handle the BOD data as recorded, due to minor fluctuations of the Hach unit readings. Therefore, a logarithmic transformation of the time (h) of the BOD readings plotted against BOD (mg per liter) was used to determine the straight line regression of the data (Figure 1). The values determined from the regression then were transformed back to the original units to give the "best-fit" BOD curves (Figure 1).

The analyses of the computed values for k and L were carried out using the t-test and analysis of variance procedures (10), both of which gave the same results. A comparison of the means of the L values for the two storage treatments indicated that the difference was highly significant (P < 0.01). There was no significant difference (P < 0.05) between the means of L for the aerobic pits 1 and 2 or between the means of L for the anaerobic pits 3 and 4. The means and standard deviations of values of L obtained are shown in Table I. The weekly changes in computed ultimate BOD's are shown in Figure 2 and are the mean of the three methods used. The treatment mean values of L obtained in this study were 10,100 and 18,700 mg per liter, respectively, for the aerobic and anaerobic treatments.

No significant differences between the means of L for the methods used for L determination were found for the aerobic decomposition. However, a significant difference between the three methods was indicated for the anaerobic system. The means of the anaerobic L values then were tested using Duncan's new multiple range test (10) at the 0.01 level of probability. The results of this test indicated that the overall mean from the method of moments was not significantly different from the means of either of the other two methods, while the means of the log-difference and the slope methods were significantly different from each other.

Analysis of the means of k (Table II) between the two storage treatments showed highly significant differences. The analysis of variance for the means of k indicated that there was no significant difference between the two aerobic pits 1 and 2 or between the three methods used for determining k. Figure 3 shows the weekly change in computed k values.

The analysis for the means of k in the anaerobic treatments indicated that the differences between the three methods used to determine k were highly significant. However, the difference of the means of k between the anaerobic pits 3 and 4 was not significant.

The use of Duncan's multiple range test (P < 0.01) showed that the overall means of k for the slope and moment methods were not significantly different from each other. The test also showed that both these methods were significantly different from the log-difference method. The treatment mean values for k obtained were 0.132 and 0.236 days⁻¹, respectively, for the aerobic and anaerobic treatments.

Waste Characteristics

The concentration and quantity means

| Table I: Means and Standard Deviations of the Ultimate BOD (L), mg per liter |
|--------------------------|----------------------|----------------------|----------------------|----------------------|
| Method                  | 1                    | 2                    | 3                    | 4                    |
| Log difference          |                      |                      |                      |                      |
| Mean                    | 9,300                | 10,800               | 19,800               | 19,100               |
| SD                      | 3,800                | 4,300                | 5,000                | 4,400                |
| Slope                   |                      |                      |                      |                      |
| Mean                    | 9,200                | 10,500               | 18,300               | 17,800               |
| SD                      | 4,000                | 4,300                | 4,800                | 4,200                |
| Moment                  |                      |                      |                      |                      |
| Mean                    | 9,560                | 11,000               | 19,100               | 18,200               |
| SD                      | 4,100                | 4,800                | 4,000                | 3,900                |
| Gross pit:              |                      |                      |                      |                      |
| Mean                    | 9,300                | 10,800               | 19,100               | 18,400               |
| SD                      | 3,900                | 4,400                | 4,700                | 4,100                |
| Treatment:              | Aerobic              | Anaerobic            |                      |                      |
| Mean                    | 10,100               | 18,700               |                      |                      |
| SD                      | 4,200                | 4,400                |                      |                      |
there was an increase in both concentration and quantity for all the variables.  

Significant differences were found for the concentrations between the two forms of decomposition between the anaerobic pits 3 and 4, but the aerobic and anaerobic systems only showed no significant differences were found between VTS concentrations.  

Weekly changes of reaction rate constant (k) for the aerobic (pits 1 and 2) and anaerobic (pits 3 and 4) treatments.

Multiple Regression Analysis

The 5-d time period required for the BOD test may be a major disadvantage where information concerning the strength characteristic of a waste is needed promptly. An approximation of BOD₅ may be made using the 2.5-day, 35°C BOD test (14), but again the time delay may be too long. Accordingly, multiple regression equations were determined to estimate BOD₅.

Only TS and ODI were used as the independent variables in the analysis. The reasons for doing so were that the tests in both instances are fairly simple to run and that the equipment required for both tests normally is available in a laboratory. The use of VTS as a variable was discarded on the basis that most laboratories are not equipped with the necessary muffle furnace while, in any case, VTS was found to contribute little to the reduction of the sum of squares. A further reason for using only two variables was to keep the regression equations as simple as possible.

Although the analysis, due to the nature of the project, could not show a relationship between ODI and BOD₅, highly significant simple correlations (P < 0.01) existed between the two variables for both storage systems. Slightly lower correlations were found between TS and BOD₅, but they were still significant at the same probability level. A relationship is known to exist between BOD and TS, since organisms largely use the dissolved organic portion of the TS for food (5).

A computer program (6) for a stepwise multiple regression was used to determine the relationship between the dependent and independent variables. The general model considered for the regression was

\[
\text{BOD}_5 = a + b_1 \text{TS} + b_2 \text{ODI}
\]

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\]
TABLE IV REGRESSION ANALYSIS FOR AEROBIC BOD$_5$

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>df</th>
<th>Sum of squares</th>
<th>Mean squares</th>
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<td>Total</td>
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</table>

** Significant at the 0.01 level of probability.
Regression equation: BOD$_5$ = -2970 + 0.219(ODI) + 0.0660(TS).
Multiple correlation coefficient = 0.836.
Cumulative proportion of sum of squares reduced = 0.709.
Standard error of the estimate = 1200 mg/liter.

TABLE V REGRESSION ANALYSIS FOR ANAEROBIC BOD$_5$

<table>
<thead>
<tr>
<th>Source of variation</th>
<th>df</th>
<th>Sum of squares</th>
<th>Mean squares</th>
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<td>Total</td>
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<td>273,007,616</td>
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</table>

** Significant at the 0.01 level of probability.
Regression equation: BOD$_5$ = 4540 + 0.279(ODI) + 0.0957(TS) + 23100($^\ast$).
Multiple correlation coefficient = 0.821.
Cumulative proportion of sum of squares reduced = 0.696.
Standard error of the estimate = 1850 mg/liter.

The results of the analyses concerning the time constant ($k$) and the ultimate BOD ($L$) for the first-stage BOD curve are of interest. Both values were found to be significantly lower ($P < 0.01$) for the aerobic than for the anaerobic treatments, thus suggesting the need for the use of values appropriate not only to a waste for a particular class of animal but also to the type of treatment involved prior to BOD determinations.

**DISCUSSION**

The importance of making comparisons between the aerobic and anaerobic treatments on a dry matter basis for the various waste characteristics tested in this project has been made elsewhere (1).

Highly significant concentration differences existed between the strength characteristics tested for the two storage treatments. With the effect of dilution removed, a highly significant difference was observed only for the quantity of BOD$_5$. Differences between the quantities of the other variables were not significant even at the 0.05 level of probability.

The following conclusions are drawn from this study:

1. The BOD constants for reaction rate ($k$) and ultimate BOD ($L$) for anaerobically stored beef cattle wastes are significantly higher than for those stored aerobically. The respective treatment mean values for $k$ were 0.236 and 0.132 days$^{-1}$ and for $L$, 18,700 and 10,100 mg/liter.

**CONCLUSIONS**

The accuracy of the regression equations found in this study may be questioned to some degree, since the BOD$_5$ values used in their determination were obtained at a mean temperature of 24.0°C rather than the standard 20.0°C. There also were some limitations from a statistical viewpoint with regard to control of all the variables affecting the storage treatments, since the project was conducted under practical conditions. Hence, the regressions for BOD$_5$ and the values of $L$ and $k$ determined in this study require to be evaluated to determine their general applicability to other livestock wastes, including those from beef cattle maintained under conditions of environment and feeding different from those prevailing during this project.
2. Significant differences exist for the anaerobic, but not the aerobic, wastes between the values of both $L$ and $k$ for the three standard methods of determining these constants.

3. Regression equations using values for total solids and the oxygen demand index as independent variables may be used to approximate the BOD$_5$ of beef cattle wastes.

4. Seeding of beef cattle wastes undergoing aerobic or anaerobic treatment has no effect on the BOD lag period.

SUMMARY

The wastes of housed beef cattle were collected and stored in pits beneath slatted floors over a 30-week period. The contents of two pits were stored anaerobically, while aerobic conditions were maintained in another two pits. Samples, collected weekly from each pit over the last 19 weeks of the test period, were analyzed for biochemical oxygen demand, oxygen demand index, pH, total solids and volatile total solids. The BOD constants for reaction rate ($k$) and ultimate BOD ($L$) were determined by three methods: moment, slope and log-difference.

Results indicated that values for $k$ and $L$ are both significantly higher for anaerobically stored wastes than for aerated wastes. Differences between the values of the constants exist for the three methods of determination, these being significant in the case of the anaerobic, but not in the aerobic, treatment. Regression equations were determined to estimate BOD$_5$, using the oxygen demand index and total solids values as independent variables.

REFERENCES