Using an HBOD Probe to Measure Biochemical Oxygen Demands of Wastewaters

By Booki Min, David Kohler, Jason Brown, and Bruce Logan

New respirometric tests are being developed to more easily measure the strength of biodegradable organic matter in wastewater. Here it is shown that the headspace BOD (HBOD) test can provide data similar to that produced by the five-day biochemical oxygen demand (BOD_5). The advantages of the HBOD test have previously been shown to be: use of non-diluted samples, faster exertion of oxygen demand (the test is completed in 2 or 3 days), and a reduced sample preparation time. The HBOD test was originally conducted using a dissolved oxygen (DO) probe or a gas chromatograph (GC). Here we use a new instrument, which we refer to as an HBOD probe, to analyze oxygen concentrations in an HBOD test and to obtain data that is more precise than that obtained in a BOD test. The use of this probe greatly reduces sample analysis time in comparison to the previous HBOD and BOD protocols.

Introduction

The biochemical oxygen demand (BOD) test has been used for nearly a century at wastewater treatment plants to determine the strength of biodegradable organic matter in wastewaters. The test is rather time intensive, and relative to other measurement techniques now used in the laboratory, rather imprecise. The accuracy of the test has also always been a question, because the timing of the test (usually 5 days) is an arbitrary number originally chosen based on the time for the Thames River in England to flow to the ocean (Leblanc, 1974). Many researchers over the years have proposed alternatives to the BOD test, but none have seen wide application. For example, manometric methods based on the Warburg apparatus and the Barcroft device were used many years ago to measure biodegradable organic matter, but they failed to be widely adopted because they required expensive instruments and extensive operator training.

With instrumental and labware advances, it seems reasonable to expect that easier, more accurate methods to measure wastewater strength could be developed. The headspace BOD (HBOD) test was proposed several years ago in an effort to improve upon the BOD test (Logan and Wagenseller, 1993). The advantages of the HBOD test were: samples did not need to be diluted (oxygen was

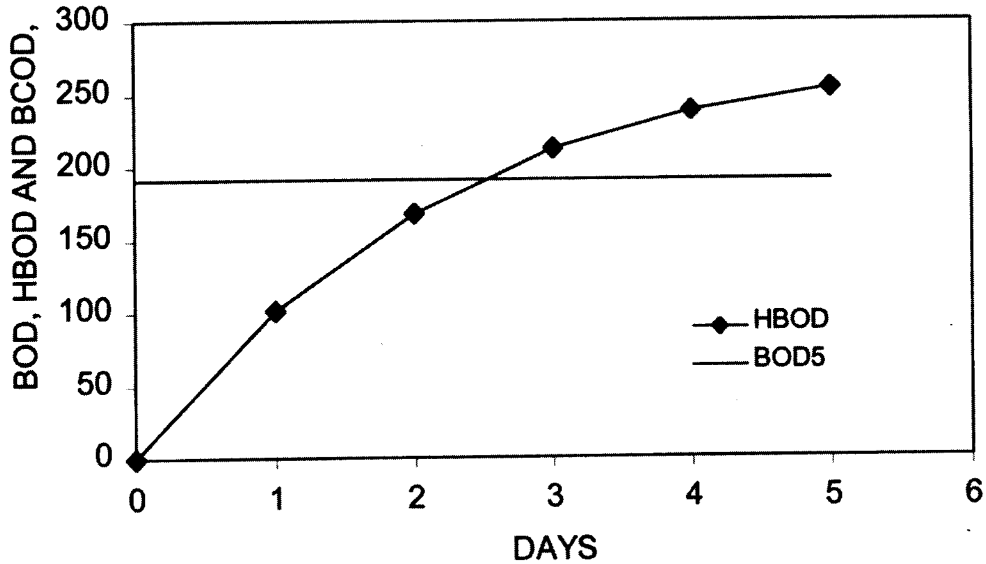

Figure 1. **Daily HBOD versus the BOD_5 of a primary clarifier effluent sample from the Penn State University Wastewater Treatment Plant. Notice that the BOD_5 is reached using the HBOD test in approximately 2.5 days.**

continuously added from the container headspace during sample shaking); only 2 to 3 days were necessary for sample incubation time to obtain values equivalent to the 5-day BOD test; smaller samples could be used; and the test appeared to be more precise than the BOD test. The most obvious disadvantage of the HBOD test, however, was measuring oxygen in a tube at the completion of the test. Either a gas chromatograph (GC) was necessary to measure oxygen in the tube headspace (Logan and Patnaik 1997), or the tube solution needed to be poured out of the bottle to measure the dissolved oxygen (DO) concentration (Logan and Wagenseller 1993). These procedures were either complicated (in the case of the GC) or somewhat messy (pouring samples for DO analysis). In both cases, the time required to measure the oxygen in the tubes was not reduced compared to that necessary for the BOD test.

Recent advances in oxygen measurement technologies have made it possible to greatly simplify the HBOD test. Using a newly developed fiber optic probe, we call the HBOD probe, it is possible to measure oxygen in the tubes within just a few seconds. Using the HBOD Probe, and anaerobic test tubes with crimp sealed tops (not available 100 years ago), we report in this paper that it is possible to measure the concentration of biodegradable matter in a wastewater much more easily than in a BOD test. Using data from two wastewater treatment plants, we demonstrate that HBOD values are obtained in only 2 to 3 days that are similar to the BOD_5 values, and that the HBOD values are more precise than those obtained in the BOD test.

Experiments

Wastewater samples were collected in 1-L Nalgene bottles from either the Penn State University (primary effluent, 24-h composite) or the University Area Joint Authority (UAJA) wastewater treatment plants. Within 2 hours of collection, BOD_5 and HBOD analyses were performed in a constant temperature room (20°C). BOD tests were done using 60-mL BOD bottles, according to *Standard Methods* (APHA et al. 1999). DO measurements were made with an YSI meter and DO probe (Model 50B, Yellow Spring Instruments, OH). Dilution water was prepared by adding one BOD nutrient buffer pillow (HACH Company) into the 6L of distilled water.

Prior to HBOD analysis, the HBOD probe (Ocean Optics Corp.) was compared to oxygen measurements made using a GC (SRI Instruments, Torrence, CA) equipped with a molecular sieve column and thermal conductivity detector. Samples were degassed in an anaerobic chamber (Coy Scientific Products) to remove all of

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the oxygen, removed from the chamber, and then briefly exposed to oxygen in the room. Oxygen measurements were then made on the samples using the GC followed by the HBOD probe. The GC and HBOD probe provided identical measurements over a range above 2% of oxygen in the samples. This range is sufficient for HBOD tests because oxygen demand by wastewater samples is not accurate at very low dissolved oxygen concentrations. Note that a DO concentration of 1 mg/L under standard conditions is approximately a headspace oxygen concentration of 2%.

HBOD samples were performed according to procedures in Logan and Patnaik (1995), except oxygen in the tube headspace was measured using an HBOD probe, and are only briefly summarized here. For HBOD tests, wastewater samples were placed in 1000-mL bottles, and the appropriate volume of sample was transferred into a 28-mL HBOD tube (BellCo) using a 5 mL digital dispensette (Brinkman, Westbury, N.Y.). The sample volume was selected based on the strength of the wastewater using a table in Logan and Patnaik (1997). For example, a 23-mL wastewater sample is used for wastewaters to measure oxygen demands in the range of 7 to 50 mg-HBOD/L, while 8-mL is used for samples in the range of 51-364 mg-HBOD/L. After tubes were filled, they were immediately sealed with a rubber stopper and an aluminum crimp top. Tubes were incubated in the dark on a shaker table (Lab Line Model 4626) at 150 rpm. For HBOD tests, no dilution step is necessary because oxygen in the headspace is used to replenish the DO in the liquid phase during the test. The HBOD was measured using the HBOD probe either: daily over a five-day period, or only on the second and third days. The HBOD probe was calibrated with a 0% oxygen sample prepared in an anaerobic chamber (Coy Scientific) and laboratory air (assumed to hold 20.9% oxygen). Barometric pressure, relatively humidity and temperature were measured using a Cole Parmer weather guage (Cole-Parmer Instrument Company). The HBOD was calculated (Logan and Patnaik, 1997) using:

$$HBOD_n = (P_o - 0.01 p_{o,w} r_o)\left(1 - \frac{O_n}{O_{o,n}}\right)\left[\frac{107.2}{(T_o + 273.15)}\left(\frac{V_T}{V_l} - 1\right) + \frac{DO}{760 - p_{o,w}}\right]$$

Where: $HBOD_n$ is in mg/l

P_o = total pressure of laboratory air on day 0 recorded from barometer [mm Hg]

$P_{o,w}$ = vapor pressure of water at temperature of sample on day 0 form table of water vapor pressures [mm Hg]

r_0 = relative humidity of air on day 0 read form relative humidity gauge [%]

O_n = oxygen concentration of sample measured on day n [%].

$O_{0,n}$ = oxygen concentration in a blank tube sealed on day 0 but analyzed on day n [%].

T_o = the temperature of air on day 0 [°C]

V_T = the total volume of empty HBOD tube [ml]

V_L = the volume of liquid wastewater sample put into HBOD tube [ml]

DO = saturation dissolved oxygen concentration in water at 760 mmHg (1 atm) in water-saturated air at temperature To from a reference table [mg/l]

Results

The BOD_5 was compared to daily HBOD measurements made using a primary effluent sample obtained from the Penn State University Wastewater Treatment Plants. The BOD_5 for the sample was 191 ± 29 mg/L, while the average 2-day HBOD ($HBOD_2$) was 168 ± 12 mg/L (Figure 1). By the third day, the $HBOD_3$ had increased to 212 ± 2. Thus, we can see that HBOD values similar to the BOD_5 were reached much sooner (after only 2.5 days) due to the higher concentration of microorganisms and biodegradable organic matter in the sample. The comparison of the BOD and HBOD data also demonstrates the greater precision of the HBOD test. The standard deviation was only 2-12 mg/L, or 1-7% of the averages for the HBOD test, while it was 29 mg/L, or 15% for the BOD_5 test.

Because the HBOD and BOD_5 tests do not produce exactly the same values, the $HBOD_2$ or $HBOD_3$ test must be multiplied by some constant to achieve a value identical to the BOD_5. To determine an average ration of the HBOD taken on days 2 and 3 to the BOD_5, several tests were made using wastewater samples from the UAJA Wastewater Treatment Plant. These data are shown in Figure 2. The solid line on the graph indicates the average of all $HBOD_3$ data, while the upper and lower dotted lines indicate the standard deviation of the samples. All individual measurements are shown with an average and standard deviation. The average $HBOD_2$ values were within 60 ± 11% of the BOD_5 values (data not shown), and $HBOD_3$ values were within 76 ± 22% of the BOD_5 (Figure 2).

Discussion

The use of an HBOD test can allow more rapid, and more precise measurement of the biodegradable organic matter in a wastewater. The HBOD and BOD tests are both batch tests, but the oxygen demand in a BOD test is exerted much more slowly than in the HBOD test because a wastewater sample must be diluted for BOD analysis. Dilution of the sample reduces both the concentration of the organic matter and the microbes, causing the test to run much more slowly. It was shown here that an oxygen demand of a non-diluted sample was exerted in the HBOD test in about half the time (after 2.5 days) versus that in the BOD test after 5 days. The more rapid exertion of the HBOD test than the BOD test affords the

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wastewater treatment plant an earlier measurement of wastewater strength allowing operational changes to be made in the plant if necessary.

Two of the most frustrating aspects of the BOD tests are measurements that fall outside of the BOD dilution range, and a lack of precision in test results. It was shown here that the precision of the HBOD tests was larger than for BOD tests. Our experience has been that the HBOD precision is generally in the range of a 5% variation between samples, but almost always <10%. This is much less than the typical bottle-to-bottle variation in the BOD test of 10-20%. It has also been shown in an earlier study (Logan and Patnaik 1997) that a single HBOD test has a very large range of oxygen demand. This means that HBOD values are much less likely to fall outside of the analysis range than BOD tests.

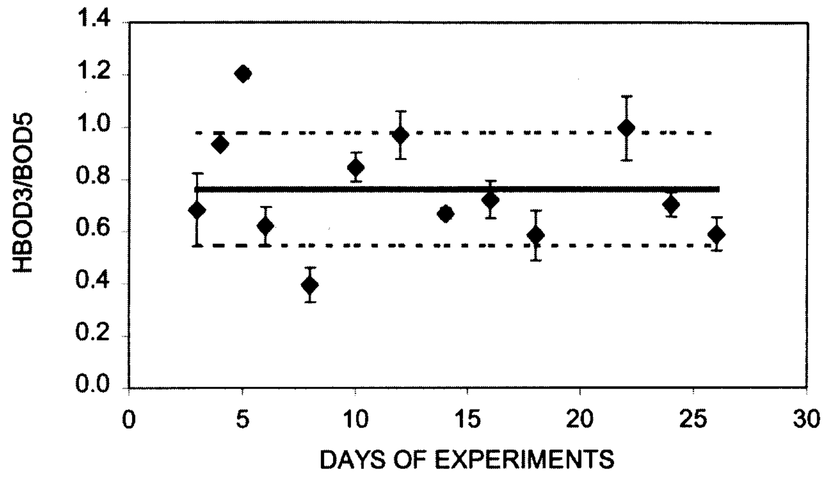

Figure 2. Comparison of HBOD and BOD_5 data expressed as a ration of the three-day ($HBOD_3$) and BOD_5 values. Samples are primary clarifier effluent from the UAJA Wastewater Treatment Plant.

In conclusion, we have found that the HBOD probe can be used to measure oxygen rapidly in HBOD tests. From our analysis on wastewater samples from the Penn State University and UAJA plants, we have found that the HBOD test is a potentially useful alternative method to the BOD test. The HBOD test also has the advantages of reducing the test time and labor required to prepare and analyze wastewater samples. The HBOD test is relatively easy, and therefore laboratory technicians can easily learn how to conduct the HBOD test based on their experience with the BOD test. It is hoped that rapid respirometric tests, such as the HBOD test, will find greater applications for wastewater treatment plants. ■

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