EVALUATION OF SHORT-TERM BOD METHODS

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ABSTRACT

Efforts have been made for decades to reduce the time required for measuring the 5-day biochemical oxygen demand (BOD_5) of wastewater and natural water samples (APHA, 1998). One of the earliest short-term BOD methods was to correlate dilution BOD_5 values to chemical oxygen demand (COD) or total organic carbon (TOC). Interest has been shown since the 1940's in using respirometers for making short-term BOD measurements. Generally, low-rate batch respirometric tests have provided about the same measure of BOD in two to three days as that obtained in the dilution BOD test in five days, thus there was not a substantial savings in test time. A number of research investigators have used high-rate respirometric tests in which a single dose of wastewater was added to mixed liquor from an activated sludge process as a basis for short-term BOD tests. In some cases, the net cumulative oxygen uptake is correlated to the dilution BOD_5 or is calibrated against an organic "standard" such as glucose-glutamic acid. A benefit of this method is that the reaction can be completed with a few hours instead of the standard five days. While these high-rate methods are very useful for operational control purposes, none has been accepted widely as a substitute for the standard 5-d dilution BOD.

Tests conducted by the authors and other researchers have shown a fundamental basis for using high-rate respirometric tests as a basis for measuring BOD on a short-term basis. In this case, the seed- and dilution-corrected oxygen uptake represents the oxygen required for synthesis of biodegradable wastewater constituents The method is sufficiently flexible that it can be conducted using a number of commercial respirometric instruments. The method can be used on a stand-alone basis or the short-term measurement can be correlated to standard 5-d dilution BOD values of wastewater samples or a standard organic substrate. This fundamentally defensible method for measuring BOD on a short-term basis should have valuable application as a substitute for the 5-d dilution BOD test.

KEY WORDS

BOD, Biochemical Oxygen Demand, respirometers, oxygen uptake, short-term BOD, wastewater characterization, OUR, oxygen uptake rate

INTRODUCTION

Efforts have been made for decades to reduce the time required for measuring the 5-day biochemical oxygen demand (BOD_5) of wastewater and natural water samples (APHA, 1998). Proposals for shortening the test time generally can be summarized as follows:

1. Correlate BOD_5 to chemical oxygen demand (COD), total organic carbon (TOC), or UV light absorbance,
2. Use a shorter incubation time for the standard dilution BOD method or conduct the test at 35^oC,
3. Correlate low-rate oxygen uptake measured by respirometers to dilution BOD_5,
4. Correlate instantaneous OUR or short-term oxygen uptake to standard dilution BOD_5, and
5. Use seed-corrected oxygen uptake from high-rate respirometer tests.

The objectives of this paper are 1) to review methods used to date for measuring BOD on a short-term basis, 2) to show the advantages and disadvantages of each method for its intended purposes, and 3) to present a proposed approach to unifying the methods.

REVIEW OF THE DILUTION BOD TEST

The standard dilution BOD test is a respirometric procedure in which both substrate and biomass concentrations are low but with initial COD/biomass (S_o/X_o) ratios generally ranging from 2 to 8 (Standard Methods, 2002). Its historical use, the test nomenclature, and many of the characteristics of the dilution BOD test set the stage for modern respirometer applications in environmental science and engineering. Of further significance are recent trends to use respirometers to provide a "short-term" BOD or an equivalent measure of dilution BOD_5.

BOD reactions typically consist of two major phases as illustrated in Figure 1. The first is a carbonaceous phase in which organic material is oxidized as follows:

$$\textbf{Organic matter} + O_2 \rightarrow CO_2 + H_2O + \textbf{biomass} \qquad (1)$$

The oxygen required for complete mineralization of organic material, that is, its conversion to inorganic end products, is defined as the ultimate carbonaceous oxygen demand ($CBOD_u$) and is roughly equal to the cumulative first-stage oxygen consumption after a 20- to 60-day (theoretically infinite) period of incubation (APHA, 1998). Because some organic material remains as nonbiodegradable cell residue and soluble microbial products (SMP), it is not possible biologically to oxidize all the organic material originally present in the sample.

Figure 2 illustrates some important features of carbonaceous BOD reactions that should be considered when relating BOD measurements to respirometric data.

Figure 1 – Schematic diagram showing two phases of the biochemical oxygen demand reaction.

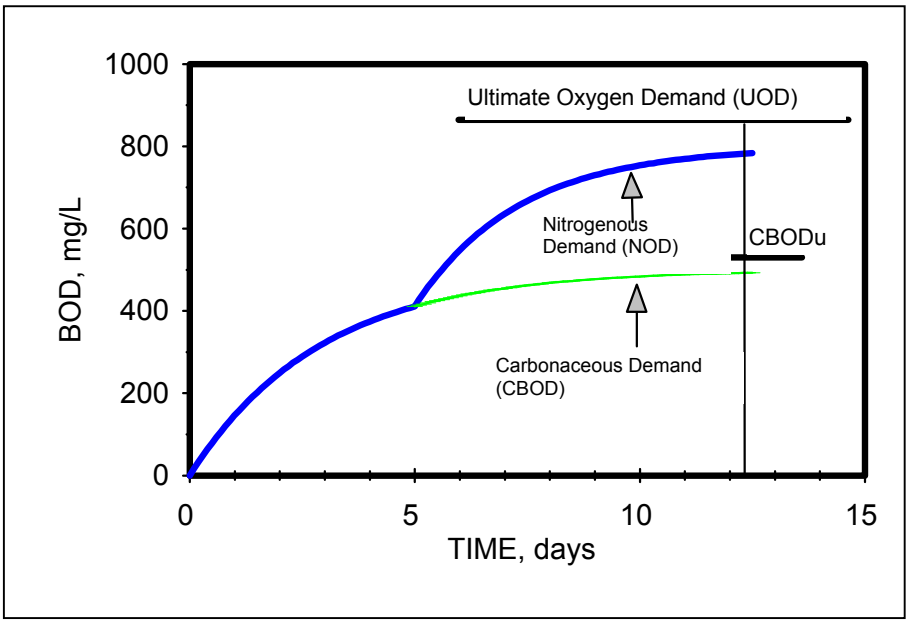
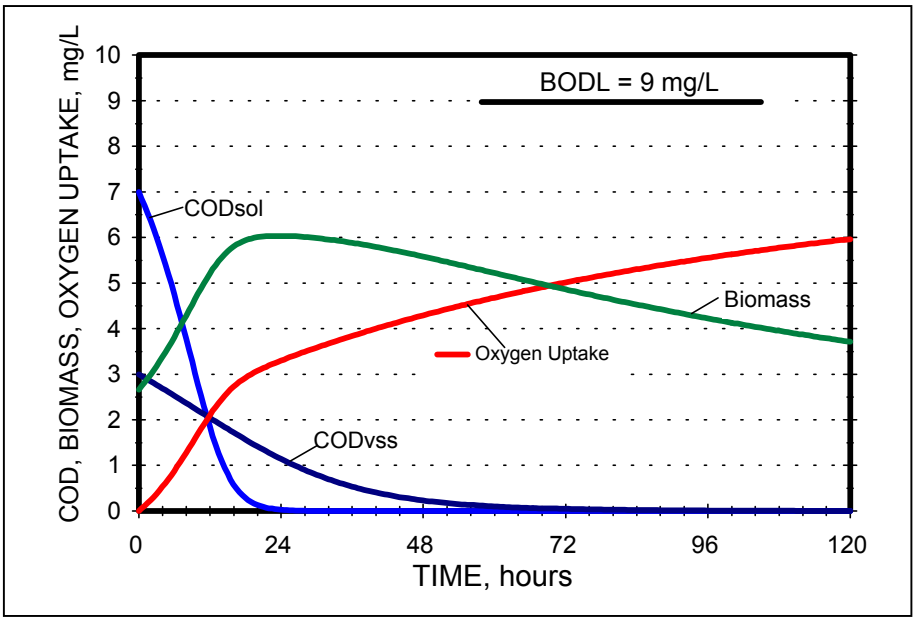


Figure 2 – Schematic diagram showing the relationship of BOD to concentrations of soluble and particulate substrate and biomass.



1. Readily biodegradable – usually soluble – substrates (COD_{sol}) are converted rapidly to metabolic intermediates or biomass,
2. Particulate solids and slowly degraded organic materials (COD_{vss}) are oxidized more slowly,
3. After about 24 to 48 hours, carbonaceous oxygen uptake is due almost entirely to endogenous respiration of the seed culture plus biomass synthesized during the biodegradation reaction, and
4. The five-day BOD is approximately two-thirds of the ultimate BOD.

In the second, or nitrogenous, phase of the BOD reaction, ammonia and nitrite are converted to nitrate through autotrophic nitrification as follows:

$$\text{a. } \mathbf{NH_3 + 1.5\ O_2 \xrightarrow{\textit{Nitrosomonas, Nitrospira}} HNO_2 + H_2O} \qquad \mathbf{(2a)}$$

$$\text{b. } \mathbf{HNO_2 + 0.5\ O_2 \xrightarrow{\textit{Nitrobacter}} HNO_3} \qquad \mathbf{(2b)}$$

$$\text{Net: } \mathbf{NH_3 + 2\ O_2 \longrightarrow HNO_3 + H_2O} \qquad \mathbf{(2)}$$

Theoretically, if the nitrogenous reactions in Equation 2 are carried to completion, 3.43 g of molecular oxygen are used per gram of ammonia nitrogen oxidized to nitrite, and 1.14 g of oxygen are used for each gram of nitrite converted to nitrate. However, some of the reduced nitrogen is assimilated as cell material by the nitrifying organisms, which reduces the amount of oxygen theoretically needed for nitrification. For most purposes, the factors of 3.22 g O_2/g NH_3-N and 1.11 g O_2/g NO_2^--N are sufficient for estimating the actual oxygen consumption during nitrification (Wezernak and Gannon, 1968). Therefore, if ammonia nitrogen exists in wastewaters in appreciable amounts, a significant part of the potential oxygen demand can be attributed to nitrification. For this reason, a nitrification-specific inhibitor must be used in BOD and other respirometer tests to provide a measure of true carbonaceous BOD. Two inhibitors are available. Allylthiourea (ATU) is used widely in European countries to inhibit nitrification and BOD and other respirometric tests (CEN, 1989). In the US, 2-chloro-6-trichloromethyl pyridine (TCMP) is the preferred inhibitor (Young, 1973: APHA, 1998). ATU is moderately biodegradable and its effect disappears after a few days. The biodegradation rate is higher in high-rate tests having high biomass concentrations. TCMP has a longer effective life, but also can be degraded in long-term tests (Haffely and Johnson, 1994).

The carbonaceous BOD reaction traditionally has been modeled mathematically by assuming that the rate of removal of oxygen-demanding material is first order with respect to the concentration of un-oxidized material, L, remaining at any time, t, or:

$$\mathbf{dL/dt = - k L} \qquad \mathbf{(5)}$$

where $L = BOD_u - BOD_t$. Integrating Eq. 5 with boundary conditions of $L = BOD_u$ at $t = 0$ and $L = BOD_t$ at $t = t$, and converting from natural logarithms to base 10 gives

$$BOD_t = BOD_u \ (1 - 10^{-k_{10}t}) \qquad (6)$$

where k_{10} is a first-order rate coefficient (base 10).

The first-order equation represents an empirical description of the carbonaceous BOD reaction, which is a complex series of reactions between multiple substrates and a diverse consortia of microorganisms. If the individual biodegradation reactions could be distinguished, each no doubt would have its individual and different reaction rate. The first-order equation then fits BOD test data reasonably well only because of the averaging effect of simultaneous biological reactions. The entrenched use of the first-order reaction for describing BOD tests often is carried over into other respirometric tests. There is a risk in this carry-over of dilution BOD methodology to respirometer tests, and high-rate tests require more rigorous modeling techniques to describe the biological reactions (Spangers et al., 1994).

Historically, k_{10} values for domestic sewage (as measured by the dilution BOD method) have been considered to average ~ 0.1/day at 20°C. In this case, the carbonaceous BOD_u would be 1.5 times the five-day 20°C BOD. However, as far back as 1946, the National Research Council (1946) concluded that "In a certain way the variability of k invalidates the usual assumption that the 5-day BOD is directly proportional to the strength of the sewage." In spite of this warning, the 5-day BOD is still assumed to represent a valid measure the total amount of biodegradable organic material in wastewaters. Assuming that BOD_u = 1.5 times the 5-day BOD can lead to significant errors in estimating ultimate BODs for wastewaters that contain slowly degrading organic materials (Young and Baumann, 1976: Lee and Oswald, 1954).

There also is no reason to assume that k_{10} values should be the same for all wastewater samples. When cell synthesis is the predominant reaction, as it would be for readily degradable soluble chemicals, k_{10} can be greater than 0.20/d and can vary greatly depending on the type of organic materials present, the freshness of the sample, and the history of sampling and sample storage. If cell respiration predominates, k_{10} averages closer to 0.15/d. Nitrification occurring a day or two after the beginning of a BOD test can cause the overall k_{10} to appear to be lower than 0.10/d. This situation occurs because the nitrification reaction spreads the total oxygen uptake over a longer period of time, thereby giving a false indication of the individual rates for the major oxygen-demanding reactions (Young, 1984). In general, this latter problem is more severe with stream waters and treatment plant effluents than with specific chemicals or raw wastewaters (Ruchhoft et al., 1948).

The 20°C temperature for BOD tests is accepted worldwide as standard. The first order rate coefficient is widely considered to change with temperature according to the Arrhenius equation where

$$k_T = k_{20} \, \theta^{T-20} \qquad (7)$$

where θ generally is considered to be 1.05 for temperatures between 15 and 35°C. However, other equations have been used (Young, 1984), and conducting dilution BOD tests at 35°C has

been shown to reduce the time to equivalent 5-d 20°C BOD to 2.5 days (Young and Clark, 1965). Short-term BOD methods would be expected to be affected similarly by temperature changes.

REVIEW OF METHODS FOR SHORT-TERM BOD MEASUREMENT

A satisfactory short-term BOD test generally would be expected to 1) accurately reflect the factors known to affect the dilution BOD_5 test – seed concentration, temperature, pH, etc., 2) provide a reasonably repeatable correlation with dilution BOD_5, and 3) provide acceptable results in minutes to hours rather than the five days required for the standard test. A major question relative to short-term BOD tests is whether the resulting measurement must provide a value equivalent to the 5-d 20°C dilution BOD, or should be correlated to the dilution BOD_5, or should be used as a stand-alone measurement that reflects biodegradation characteristics of an environmental sample. The acceptance of short-term BOD methods is contingent upon the answer to these questions and the willingness of the environmental community to accept changes in BOD measuring methodology.

Approaches that have been used to provide short-term estimates of the dilution 5-day BOD are discussed below.

Correlation of 5-d BOD to Chemical Parameters

One of the earliest short-term BOD methods was to correlate dilution BOD_5 values to chemical oxygen demand (COD) or total organic carbon (TOC) (Ford, 1968; Shriver and Young, 1972; Le Blanc, 1974; Young, 1984). Also, some instrument manufacturers claim that UV absorbance provides a credible indication of BOD_5 (Strategic Diagnostics, 2002). Generally, there has been a rather weak correlation between chemical organic parameters and dilution BOD_5 and the correlation changes with wastewater type and among points within a treatment plant (Ford, 1968). Since these methods are not biologically based, they do not reflect biodegradability of the test constituents and hence are not considered to provide acceptable measures of 5-d or short-term BOD.

Reduced Time of Incubation for Standard Method

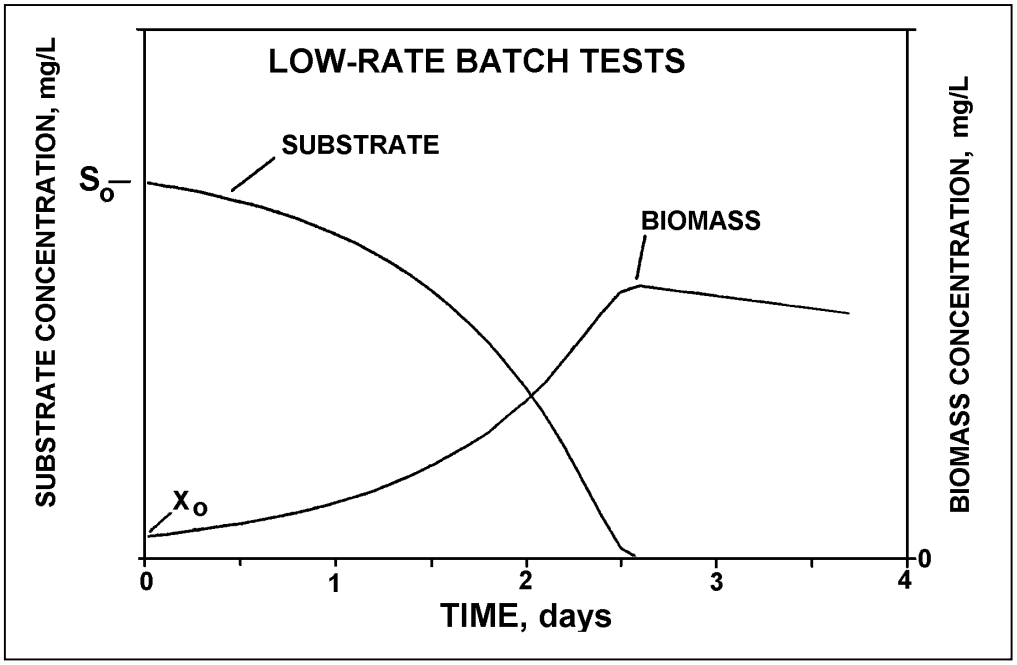
Numerous reports have been published of attempts to measure BOD by simply reducing the time of incubation in the standard dilution method (LeBlanc, 1974). These tests have shown good correlation of 2 and 3-day oxygen uptake with the 5-d dilution BOD_5. Correlations deteriorated substantially at 1-d incubation times. Young and Clark (1965) reported that increasing the test temperature to 35°C produced the same oxygen uptake in 2.5 days as was measured in 5 days at 20°C. Busch (1961) proposed using the plateau that typically occurs around 24 hours in the dilution BOD test as a substitute for the dilution BOD test. This point usually represents the end of biodegradation of organic constituents and synthesis of biomass and represents around 50% of the 5-d dilution BOD or one-third of the ultimate BOD. While these reduced times provide short-term BODs that are useful for diagnostic purposes, none has been accepted as a substitute for or equivalent to the 5-d, 20°C dilution BOD.

Correlation of Low-Rate Respirometric Tests to Dilution BOD_5

Aerobic batch respirometer tests are conducted by dosing a microbial culture with a defined amount of organic chemical or wastewater followed by monitoring the reactions through measurement of oxygen uptake. Batch respirometer tests are therefore transient, non-steady-state reactions in which both substrate and biomass concentrations change throughout the biodegradation reaction.

Batch respirometer procedures fall into two classifications: low rate and high rate. Low-rate batch tests involve the addition of test substrates to a growth medium containing a small amount of active seed organisms (Brown et al., 1990; Mulchandani and Luong, 1989; Young and Baumann, 1976). In this case, the initial substrate COD to biomass (S_o/X_o) ratio ranges from around 10:1 to greater than 50:1. The residual substrate, oxygen uptake, and in some cases biomass concentrations, are measured at frequent intervals throughout a relatively long period of time (typically 24 to 96+ hours) or until the reaction is complete (Figure 3). While applicable to any batch culture environment, low rate tests have been used primarily for determining biodegradation characteristics of wastewater constituents and intrinsic kinetic parameters for organic chemicals (Rozich and Gaudy, 1992; Brown et al., 1990; Smets et al., 1996; Grady and Magbanua, 1998). A significant disadvantage of low-rate batch tests is that they do not represent the response that would be seen in a treatment process where the wastewater constituents are combined at low concentrations with the mixed liquor microorganisms. However, low-rate tests – including the standard 5-d dilution BOD test – are useful for diagnosing the factors affecting substrate conversion reactions such as acclimation, toxicity, and sequential substrate utilization.

Figure 3 – Schematic illustration of the changes in substrate and biomass concentrations during low-rate respirometer tests.



Early attempts to use respirometers for BOD measurements involved correlation of low-rate respirometric data to dilution BOD_5 measurements (APHA, 1955, 1959; Orford and Matusky, 1959; Young and Baumann, 1976). Both laboratory and field applications of these procedures have shown that respirometers gave more precise measurements in one to two days of incubation that is claimed for the dilution BOD test in five days (Young and Baumann, 1976; Logan and Patnaik, 1997). Typical correlations for such tests are shown in Table 1. While this lower incubation time represents an improvement over five days, the reduction in time has not been sufficient to justify using low-rate respirometric measurements as an equivalent of the standard five-day BOD.

Table 1 – Typical correlations between dilution BOD_5 and low-rate batch respirometric oxygen uptake measurements (from Young, 1984).

Comparison (Y:X)	Type of Sample	Correlation (Y = a + bX) a	b	(R, %)	N	Reference
Dilution BOD_5: 18-hr Warburg BOD	Glucose	–	1.59	0.91	28	Dillingham and Jose, 1960
Dilution BOD_5: 18-hr Warburg BOD	River water + glucose	–	0.84	0.83	85	Dillingham and Jose, 1960
Dilution BOD_5: 24-hr Warburg BOD	Domestic Sewage	13.6	1.27	0.97	10	Caldwell and Langelier, 1948
Dilution BOD_5: 24-hr Warburg BOD	Industrial Wastes	-48.0	1.57	0.98	10	Caldwell and Langelier, 1948
Dilution BOD_5: Warburg BOD_5	Pure Chemicals	30.7	0.82	0.97	6	Gellman and Heukelekian, 1951
Dilution BOD_5: Warburg BOD_5	Domestic Sewage	- 4.5	0.91	0.92	11	Lee and Oswald, 1954
Dilution BOD_5: electrolytic BOD_5	Domestic Sewage					
	Plant A:	- 6.7	0.85	0.98	74	Young and Baumann, 1976
	Plant M:	-17.4	0.94	0.92	61	Young and Baumann, 1976
	Plant D:	-12.8	0.86	0.98	20	Young and Baumann, 1974
Dilution BOD_5: Headspace gas $HBOD_1$	Domestic Sewage	–	2.0	~ 7% Cv	6	Logan and Wagenseller, 1993
Dilution BOD_5: Headspace gas $HBOD_3$	Domestic Sewage	–	1.02	~ 5% Cv		Logan and Patnaik, 1997

One difficulty of using respirometers to provide short-term estimates of the dilution BOD_5 is that the amount of seed affects the results substantially. This effect is illustrated in Figure 4 when using mixed liquor from an activated sludge plant in volumes ranging from 0.5 to 20% of the wastewater sample. Ethanol at 300 mg COD/L was the organic substrate; TCMP was added to inhibit nitrification. The resulting S_o/X_o ratio ranged from approximately 0.3 to 5.0. The end of the OUR curve – the point at which the OUR returns to endogenous levels – represents the point at which all readily biodegradable organic constituents were degraded. These data show clearly that the reaction was completed more rapidly as the seed dose was increased. The data also show that large amounts of seed provided the same seed-corrected oxygen uptake in as little as six hours of incubation. Therefore, various amounts of seed provided the same measure of BOD_{st} but at different times.

High-Rate Respirometer Tests as a Short-Term BOD Measure

The data shown in Figure 4 indicate that high-rate respirometer tests – tests using relative large seed concentrations – provide a sound basis for a short-term BOD procedure. In high-rate batch tests, the ratio of initial substrate COD to seed VSS (essentially a food:microorganism ratio) for assessment of reactions in a wastewater treatment environment typically is less than 2:1 (Pollard et al., 1998; Chudoba et al., 1992). In this manner, high-rate tests simulate more closely those reactions that occur in wastewater treatment processes, and are the basis for extant kinetic tests (Ellis et al, 1996). The substrate concentration decreases relatively rapidly from an initial high to essentially zero over a short period of incubation (Figure 5). While biomass growth and decay occur throughout the reaction, the changes in biomass concentration are small. This rapid response minimizes the likelihood of shifts in microbial population dynamics during the test. The principle advantage of high-rate batch methods is that the tests are simple to perform and the biological reactions are completed in a relatively short incubation time – generally a few minutes to hours – and the method is adaptable to a number of commercial respirometers.

Figure 4 – Example of short-term BODs as measured by differential oxygen uptake rate for seven seed concentrations.

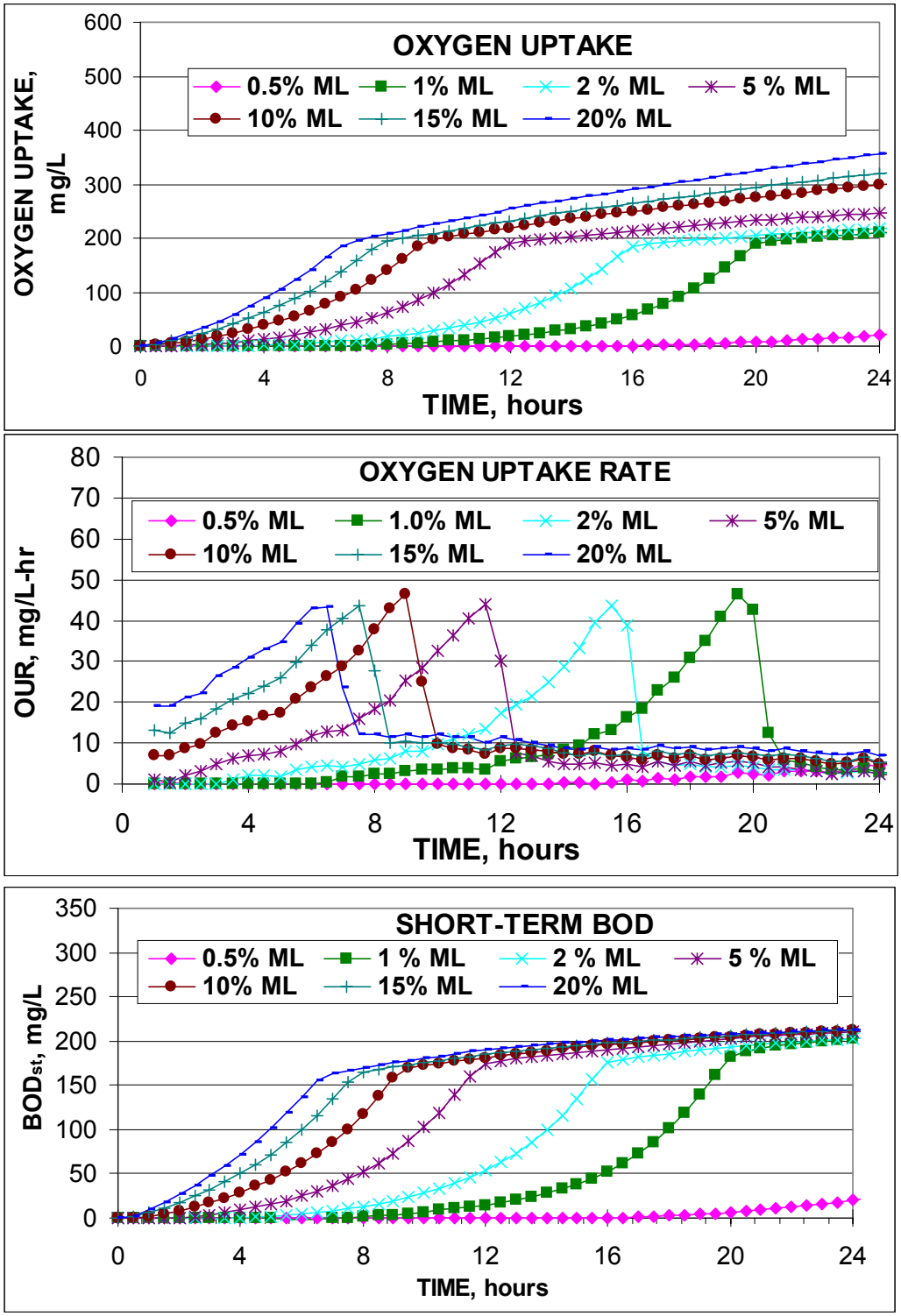
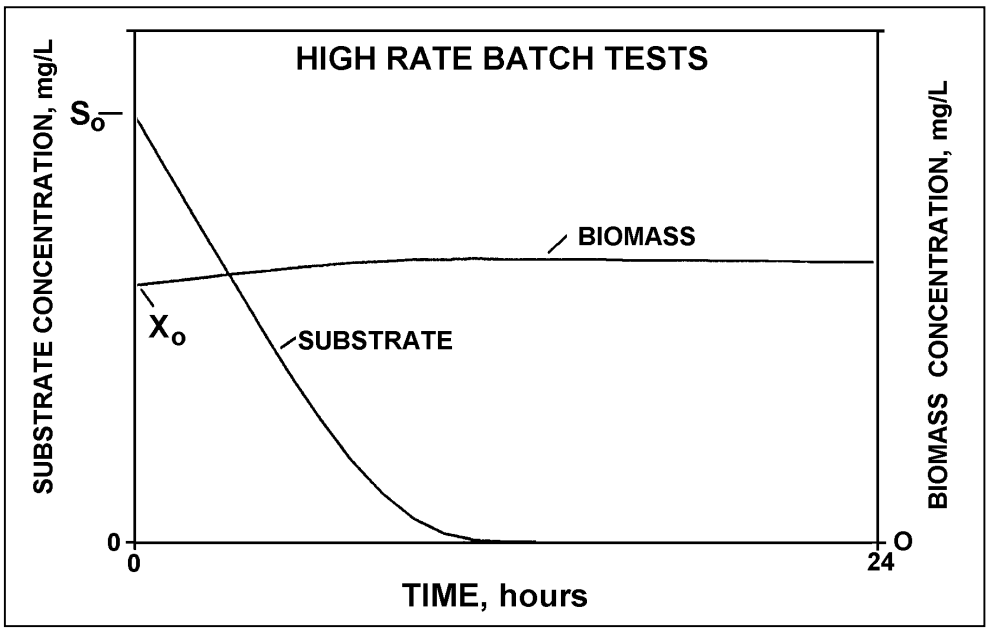


Figure 5 – Schematic illustration of the changes in substrate and biomass during high-rate respirometer tests.



Examples when using high-rate respirometer tests for measuring BOD_{st} are shown in Figures 6 and 7 for two wastewater samples – one from a chemical process industry and one from a pharmaceutical industry. In both cases, wastewater was added to return activated sludge (RAS) in ratios normally received daily at the plant so that the S_o/X_o ratio was less than 1:1. The chemical process wastewater showed completion of the biodegradation reaction in about six hours while the pharmaceutical wastewater sample required 10 hours of incubation.

The oxygen uptake rate curve from high-rate respirometer tests typically is called a "respirogram". OUR respirograms – also called OUR fingerprints – have been used widely as a means for assessing biodegradation characteristics of various types of wastewaters and as a means for making operating decisions for activated sludge processes (Spanjers et al., 1994; Young, 1999). A significant feature of OUR respirograms is that the seed- and dilution-corrected cumulative oxygen uptake when the OUR returns to endogenous levels, in effect the BOD_{st}, represents the oxygen required to synthesize the biodegradable wastewater constituents (Chudoba et al, 1992). For biomass yield coefficients (Y_o) of 0.5 g VSS/g $COD_{removed}$ (0.67 g COD_{vss}/g COD_r), the BOD_{st} represents approximately one-third of the theoretical oxygen demand of the sample ($1 - Y_o = 0.33$) and approximately one half the 5-d dilution BOD (assuming a k_{10} of 0.10/d).

Expressing the data in terms of oxygen uptake rate (OUR) versus time provides a useful means for assessing the end of the biodegradation reaction. In this case, the reaction can be considered complete when the total oxygen uptake rate (seed biomass plus sample) returns to the endogenous OUR of the seed biomass only. A unique feature of this approach is that the incubation time for short-term BOD is expressed in terms of the state of the reaction rather than a

Figure 6 – Example of oxygen uptake and short-term BOD for a wastewater from a chemical processing facility.

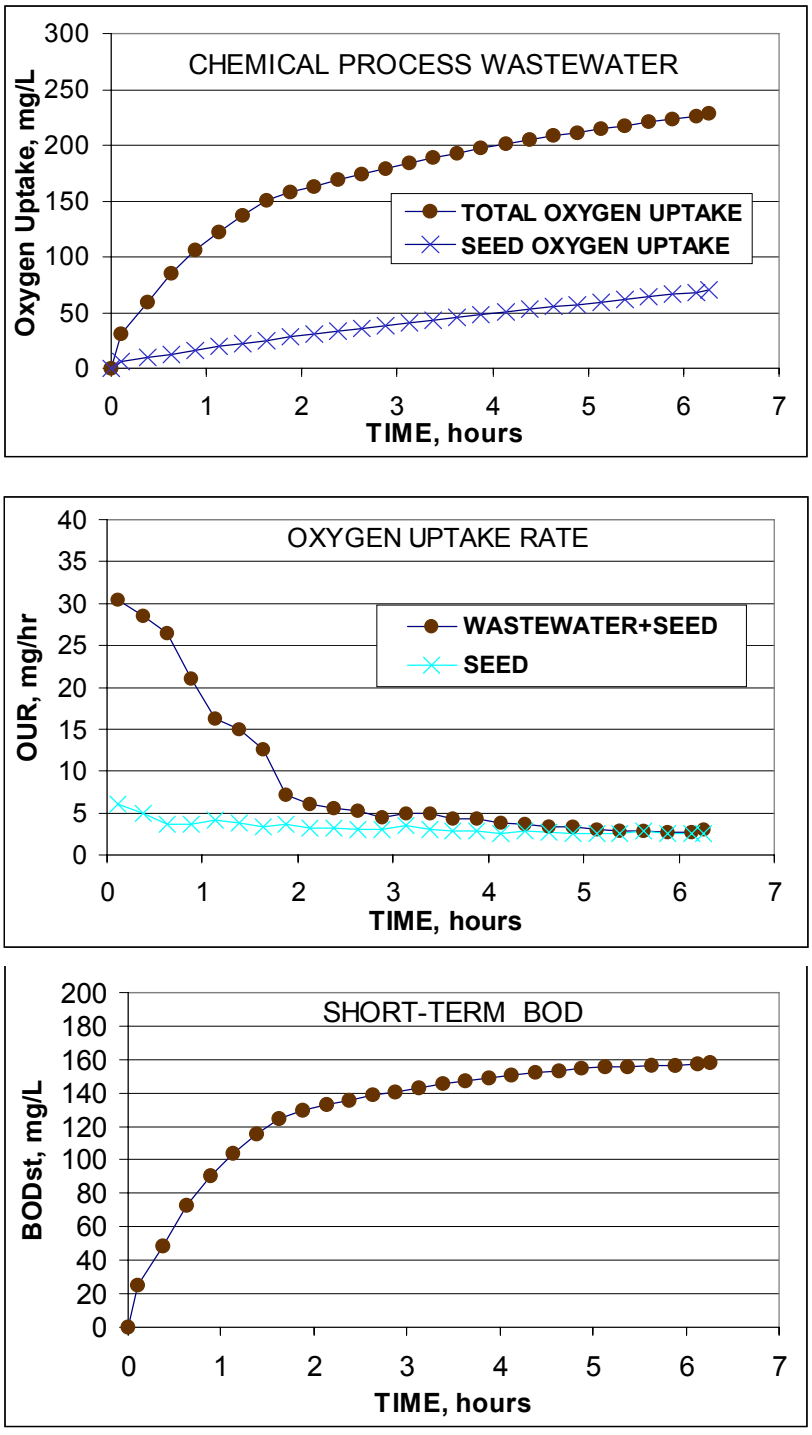
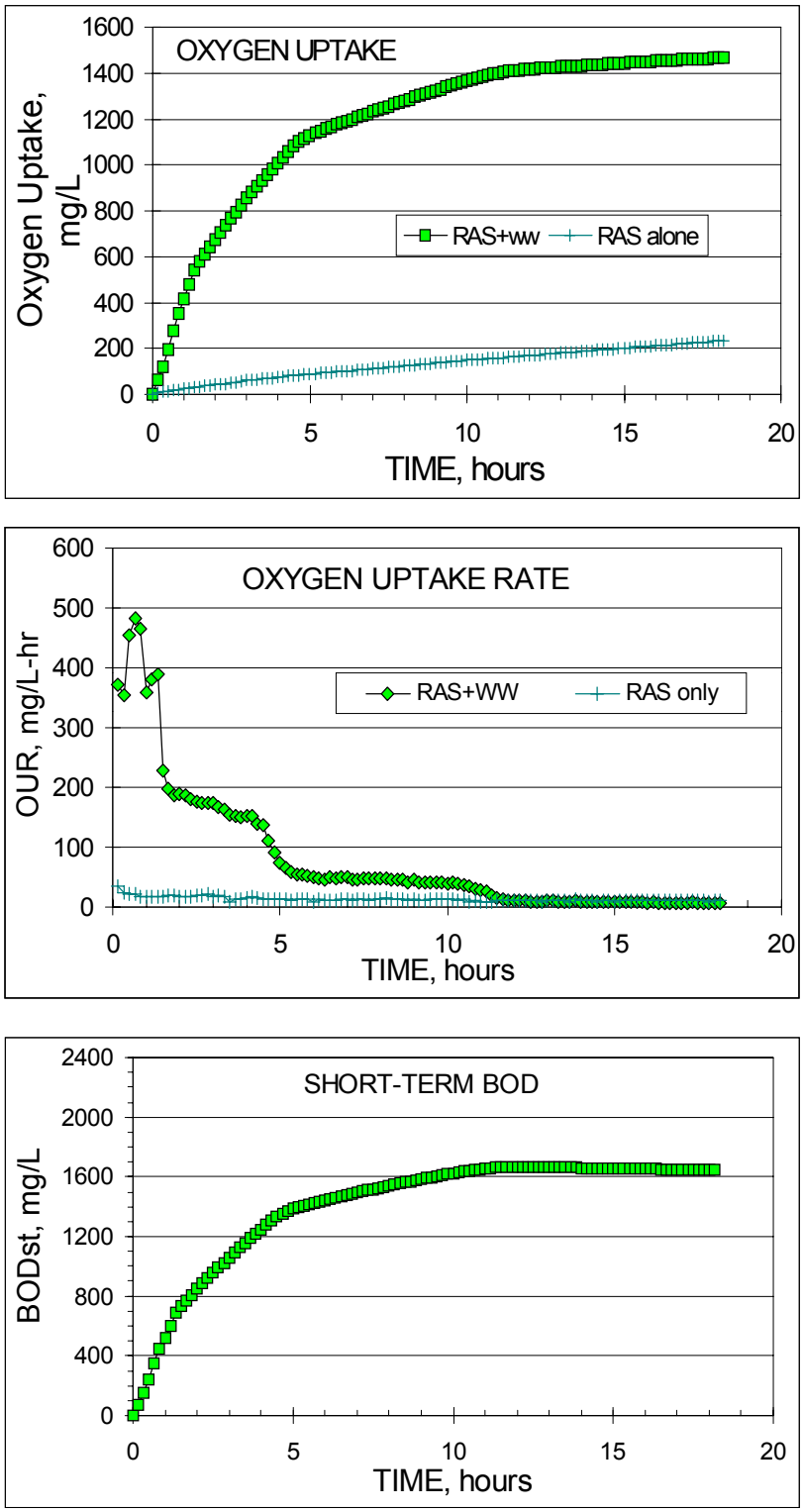


Figure 7 – Example of oxygen uptake and short-term BOD for a wastewater from a pharmaceutical plant.



set time. In fact, setting a specific time would introduce greater variability in the test results and remove much valuable information about the test sample. A second important feature of this reaction is that the net oxygen uptake (total minus endogenous) represents only the oxygen uptake associated with biodegradation of wastewater constituents and synthesis of new biomass. Since the initial biomass concentration is high, there is little contribution to the oxygen uptake reaction from endogenous metabolism of the biomass that is synthesized during the biodegradation reaction. Tests not reaching an OUR that is less than 110% of the endogenous OUR after 12 hours show the existence of slowly degraded polymeric materials or the S_o/X_o ratio was so high that endogenous respiration of the biomass synthesized during the biodegradation reaction presents a significant contribution to the endogenous respiration of the seed culture. Ideally, and in most cases, the OUR will return to endogenous rates, but a 10% margin is suggested to account for some test variability and differences in the manner in which the substrates are degraded.

High-rate OUR respirograms (fingerprints) also show important information about the manner in which wastewater constituents are degraded. The fingerprint for the chemical process wastewater shown in Figure 6 shows two readily biodegradable constituents that are completely degraded within two hours. The low OUR rate between 2 and 5 hours represents oxidation of biopolymers formed during the first two hours or a slowly degrading wastewater constituent.

The OUR fingerprint shown in Figure 7 shows two peaks within the first two hours that represent oxidation of readily biodegradable substrates. The declining OUR between two and five hours represents oxidation of a substance that likely is hydrolysis controlled. The low OUR between five and ten hours represents oxidation of slowly degraded substances – possibly suspended solids – or reactions like nitrification that have low competent biomass concentration and a low half-saturation coefficient. Addition of a nitrification inhibitor would have helped to identify the source of this low OUR section of the fingerprint.

A third feature of the high-rate respirometric approach is that it is adaptable to a variety of commercial respirometer systems including dissolved oxygen depletion units (Spanjers, et al., 1998), headspace gas respirometers (Young, 1999), and a number of on-line respirometers (Young, 1998. Spanjers et al. (1994) also presented methods for using data from continuous respirometers for estimating short-term BODs.

As with all BOD tests, an inhibitor can be added to suppress nitrification if desired.

Correlation of Oxygen Uptake Rate to BOD_5

In some cases, the net oxygen uptake rate – total OUR corrected for the endogenous OUR of the seed culture and dilution – as measured by continuously-fed on-line respirometers, is used as a measure of short-term BOD (LAR, 1997; Zermeño et al., 2002). In some cases, the differential oxygen uptake rate is correlated to the dilution BOD_5 for wastewater samples or is calibrated against an organic ”standard” such as glucose-glutamic acid. An example is shown in Figure 8. A benefit of this method is that the reaction can be measured continuously thereby giving an almost instantaneous measure of BOD_5. This approach has merit as a short-term BOD test only

if the biological reaction is completed within the hydraulic retention time in the reaction vessel. In this case, the short-term BOD should be the same as observed in high-rate batch tests.

Dilution BOD_5 values also have been correlated with high-rate cumulative oxygen uptake after only four hours of incubation (Arthur and Hursta, 1968). This correlation usually is rather weak, changes from point to point within a treatment process, is highly variable among waste sources, and varies between points within a treatment plant.

Measuring Short-Term BOD by Flow-Through Respirometers

In other respirometric methods, wastewater is passed through vessels that contain immobilized cultures (STIP, 1991; Zermeño et al., 2002). In these cases, the change in dissolved oxygen between inlet and outlet of the reaction vessel is correlated to the dilution BOD_5 (Figure 9). The hydraulic retention time in the reaction vessel ranges from three to fifteen minutes depending on the commercial apparatus, so that the test is conducted under low S_o/X_o conditions. One difficulty with this method is that the oxygen uptake reaction may represent only partial oxidation of slowly degraded organic constituents of the wastewater and, therefore, may not include a measure of all materials that contribute to BOD_5. Oxygen transfer limits also can occur if the substrate concentration is allowed to get too high. Further research is needed to establish the equivalency of this method for measuring BOD_{st} to that for high-rate batch tests.

Figure 8 – Example correlation between short-term BOD and 5-d BOD when using seed- and dilution-corrected oxygen uptake rate from high-rate continuous respirometers (from LAR commercial literature).

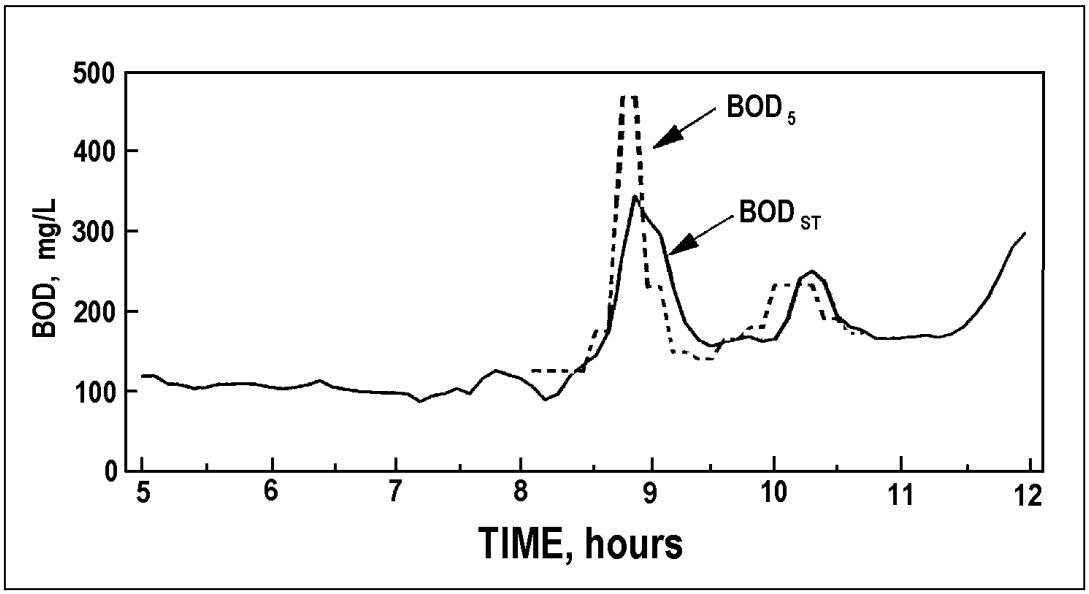
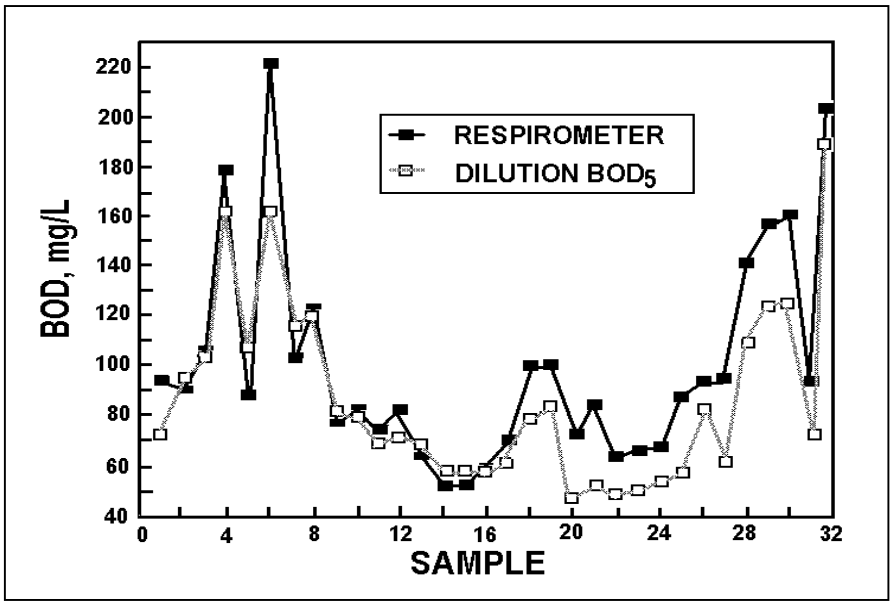


Figure 9 – Example of short-term BOD versus standard dilution BOD_5 as measured by immobilized culture respirometer (Data from STIP instrument bulletin, 1991)

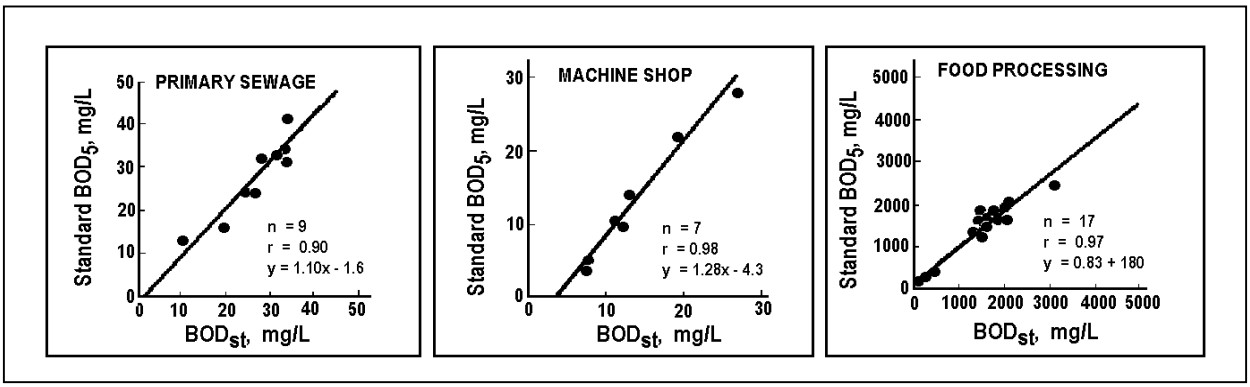


In yet another immobilized-culture method, wastewater is contacted with a culture that is confined between two oxygen-permeable membranes or encapsulated in a porous matrix (CKC, 1994; Garg and Mathur, 1997; Liu and Mattiasson, 2002). Soluble wastewater constituents diffuse into the membrane, thereby consuming oxygen and causing a dissolved oxygen differential across the encapsulated culture. This DO differential is correlated to dilution BOD_5 values for wastewater samples or standard substrates such as the glucose-glutamic acid to provide a short-term BOD measure. Examples of correlations from such measurements are shown in Figure 10. One disadvantage of this method is that oxygen uptake is measured only for readily biodegradable and soluble organic compounds. One version of an immobilized membrane BOD monitor was approved in Japan in 1990 as a standard for short-term BOD measurement for industrial wastewaters (JSA, 1990).

DISCUSSION

Of the many methods proposed as short-term BOD measures, none has been accepted as an equivalent or substitute for the 5-d, 20°C, dilution BOD. Short-term BOD measurements – whether by reduced time of incubation of the dilution method, by low-rate respirometer tests, or by high-rate respirometer tests – generally have shown poor correlation to 5-day, 20°C, dilution BOD data. Also the relationship between methods changes with type of wastewater and even among sampling points within a given treatment plant.

Figure 10 – Examples of estimated five-day BOD by correlating the ΔDO across an immobilized culture to standard dilution BOD_5 values (data from CKC Corp, 1990).



The authors are of the opinion that the seed- and dilution-corrected oxygen uptake from high-rate respirometer tests provides the most defensible procedure for assessing short-term BOD. This approach has the following advantages: 1) it is truly short-term, with reactions being completed within minutes to hours, 2) it is adaptable to a number of commercial respirometers, 3) it is subject to variables normally affecting biological reactions – pH, temperature, wastewater characteristics, kinetics, etc., 4) mathematical models are not needed to determine the BOD_{st} value that would be used for documentation purposes, and 5) the same data can be used to estimate extant kinetic parameters for the biodegradation reactions (Young, 1999). The method has a sound fundamental basis so that the resulting measurement represents the oxygen uptake associated with biodegradation and synthesis of organic matter in an environmental sample. It is possible, although not yet proven, that the method is not temperature dependent because the oxygen uptake for synthesis is not related to temperature. However, the rate at which the reaction proceeds, and the time for the OUR to return to endogenous, would increase with increases in temperature. While the method can be used with low-BOD samples, it is less applicable to monitoring of BOD of treated effluents and natural environmental samples because 1) the rate of biodegradation of the residual organic solids is low, 2) some of the BOD of effluents and natural samples is associated with suspended solids, and 3) the difference between seed+sample and seed alone is small. Further research is needed to establish the limits of usng high-rate respirometric methods for testing low-BOD samples on a short-term basis.

Specific steps for a "standardized" short-term BOD procedure would include the following:

1. A biomass sample would be selected from a source that can degrade the wastewater constituents. Typically this source would be the mixed liquor from an activated sludge process or biomass removed from fixed-film reactors. Its concentration must be sufficiently high to support high-rate biological reactions (MLVSS ~ 1,000 to 4,000 mg/L).
2. The biomass sample should be dosed with test sample to give S_o/X_o ratios (g COD/g VSS) between 0.01 and 0.5. In some cases, a range of S_o/X_o should be used to assess potential toxic impacts. The restriction of a maximum S_o/X_o ratio of 0.5:1 helps to eliminate concern

for oxygen uptake due to decay of the biomass synthesized during the biodegradation reaction.

3. Nutrients and trace minerals should be added in sufficient concentration to satisfy biological growth requirements. A buffer should be used to maintain the pH between 6.8 and 7.2.
4. The biological reaction should be allowed to proceed until the total oxygen uptake rate (biomass + sample) returns to the endogenous oxygen uptake rate of the seed biomass alone.
5. The seed- and dilution-corrected oxygen uptake at the point when the OUR returns to endogenous (or 110% of endogenous) is defined as the BOD_{st} for the sample being tested.

A unique feature of this method is that the incubation time is not time-dependent but is reaction dependent. That is, the reaction is allowed to proceed until the biodegradation reaction is complete. Tests requiring greater than 6 hours for completion likely are conducted at S_o/X_o ratios that are too high or the biodegradation rate of one or more wastewater constituents is very slow. This approach requires the use of a respirometer system that can provide accurate oxygen uptake measurements under the test conditions. A number of commercial respirometers can meet these conditions so the method is not limited to any one instrument type or brand.

The authors further feel that short-term BOD provided by high-rate respirometric procedures should be used as a stand-alone parameter. That is, there should be no need to correlate the short-term BOD measurements to the 5-d dilution BOD of the same sample. This approach removes much of the work needed for application. The single most important quality control parameter is that the user demonstrate that the biodegradation reaction actually goes to completion within the reaction vessel during the time of sample confinement. Further research may be needed to establish this control point for some commercial respirometers. While not required for calibration purposes, glucose-glutamic acid or similar substrates can be used to validate the test procedure or as a basis for comparing various types of respirometers. More complex substrate mixtures would be needed for high-rate respirometer tests to insure that the method measures the impact of slowly degraded substances.

CONCLUSIONS

The above review illustrates methods previously proposed as “short-term BOD” tests and shows a significant divergence in approach that adds substantial variability to the chemical and instrumental options. At the time of this writing, no standardized approach to measuring BOD_{st} has been widely accepted. However, each method has its own advantages and unique applications. Tests conducted by the authors have shown a fundamental basis for the high rate cumulative oxygen uptake approach, which is more defensible and subject to fewer interferences than are other methods. This measure represents the oxygen uptake due to synthesis only, and therefore is relatively independent of seed concentration. And the method is sufficiently flexible that it can be conducted using a number of commercial respirometric instruments. A fundamentally defensible method for measuring BOD on a short-term basis should have valuable application to the design and operation of biological wastewater treatment processes.

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