BIOCHEMICAL OXYGEN DEMAND (BOD) – FACT OR FICTION?

Kevan Brian – AWT New Zealand Limited

ABSTRACT

Biochemical Oxygen Demand or BOD is one of the most widely used analytical tests used to assess the strength of wastewater. Most wastewater discharge consents in New Zealand, whether they are to land or to water, are likely to contain a limit for five day BOD either as an average, percentile or maximum value.

The design of wastewater processes such as pond systems, trickling filters and activated sludge plants is often undertaken using the BOD of influent wastewater to size aeration equipment, reactor volumes, pond surface areas and media requirements.

Given that BOD is such a widely used parameter in the industry, what does it measure, what interferences are there in the test and what are the fundamental biological processes behind it? What does BOD actually tell the regulator or designer about a particular wastewater or discharge and are there any alternatives that can be used?

This paper discusses the origins of the BOD test, what the test actually measures, the kinetics of the test and suggests some reasons why BOD is not always the most appropriate means for sizing treatment plants and assessing the impacts of wastewater discharges on the receiving environment.

KEYWORDS

Biochemical Oxygen Demand, Kinetics, Design, Regulation

1 INTRODUCTION

The Biochemical Oxygen Demand or BOD test was developed in Britain shortly after the turn of the twentieth century. The idea of the analysis was that in polluted water there is an oxygen demand caused by microorganisms and this was used to measure the extent of pollution.

The five day test duration was based on the assumption that most major surface waters in the United Kingdom take five days or less to reach the sea; hence the extent of pollution in these water bodies could be quantified. The test was developed to run at a temperature of 65^{o}F (about 18C) but has now been "standardized" to 20C.

Since its inception, the test has been modified by different countries to more accurately represent local conditions. For example, in France it is common practice to obtain both a five day BOD and a 21 day BOD and in Scandinavia the standard BOD duration is 7 days. In New Zealand, we have adopted the British standard and the majority of the tests conducted here are over a five day duration.

In its original form the BOD test could measure oxygen consumption of carbonaceous compounds only or a combination of these and the oxygen used to convert ammonium to nitrate. It has become reasonably common practice today to define if the test was used to measure conversion of ammonium by defining either BOD_5 or $cBOD_5$ (c referring to carbonaceous or nitrification inhibited tests).

2 THE TEST

The standard method for the BOD analysis is described in "Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF" and an overview is given below.

The test sample is mixed with pure aerated water and placed in a bottle such that there is no air above the liquid. The bottle is then placed in a temperature controlled environment at 20C. The test must be conducted in the dark such that no algal or other photosynthetic activity can contaminate the test by adding oxygen over time. The dissolved oxygen concentration at the start and end of the five day period is measured, and the initial dilution used to back calculate the oxygen demand of the original sample. The consumption of the dissolved oxygen in the sample must not be more than the theoretical saturation concentration (9.07mg/L at 20C) and should be conducted such that there is a residual dissolved oxygen concentration at the end of the test of at least 2.0 mg/L. Oxygen levels below this may inhibit the test and are likely to produce invalid data. Given that the dissolved oxygen range of the test is quite small, strong samples must be diluted to ensure that the resultant DO difference is not greater than the theoretical maximum of 7 mg/L. In a "standard" 300mL BOD bottle the maximum BOD mass that can be tested without dilution is 2.1mg or 7mgBOD/L.

In New Zealand the BOD of typical domestic strength wastewater (untreated) is usually in the range of 200-300mg/L. Hence a dilution of about 50 times (6mL of sample to 294mL of water) is required such that the DO range is not exceeded. If nitrification is not inhibited (by the addition of allythiourea (ATU)) then the dilution is likely to be larger such that there could be a significant oxygen demand for conversion of ammonium to nitrate.

As the BOD test relies on an oxygen demand by microorganisms, the test will not provide valid data if there is not a viable inoculum of organisms present in the sample. In raw untreated wastes this may not be an issue as there are often organisms present. In sterile wastewater, final effluent, and membrane filtered samples there is unlikely to be enough organisms present for the test to be valid. The Standard Method for BOD therefore includes the requirement of adding a "seed" of organisms to the test bottle. Generally this seed is obtained from the mixed liquor of an activated sludge plant, but in the case of industrial wastewater an acclimatized seed is needed. Standard Methods states that the oxygen demand of the seed should not be more than 0.6-1.0mgO_2/L over five days. Given that this is the case the minimum error associated with such a seed on the above example of typical raw domestic wastewater would be in the range of 30-50mgBOD/L.

As discussed above, the BOD can be tested with or without nitrification inhibitor. In New Zealand the standard nitrification inhibitor is allythiourea (ATU). This is added to the test bottle to inhibit the growth of nitrifying organisms that convert ammonium to nitrate. These organisms are not likely to be present in significant numbers in a raw wastewater sample, however if a seed is taken from the mixed liquor of an activated sludge process, then there is a much higher chance of nitrifiers being present.

The addition of a nitrification inhibitor can also affect the respiration rate of some of the organisms that oxidize carbonaceous compounds. If this occurs then the results of the test are likely to be invalid as the total mass of oxygen used in such a test would be reduced if this were to occur.

3 KINETICS OF THE BOD TEST

As discussed above the BOD test measures the oxygen consumption of a water or wastewater sample over time and this is then used to quantify the strength of the sample. The growth of microorganisms in the test can be described by typical chemical rate kinetics and these are described below.

The rate of "BOD" oxidation can be described based on the assumption that the amount of organic material remaining at time *t* is a first order function:

$$\frac{dBOD}{dt} = -kBODr$$

Integrating this equation from time $t=0$ to $t=t$ yields:

$$BODt = BODu(1-e^{-kt})$$

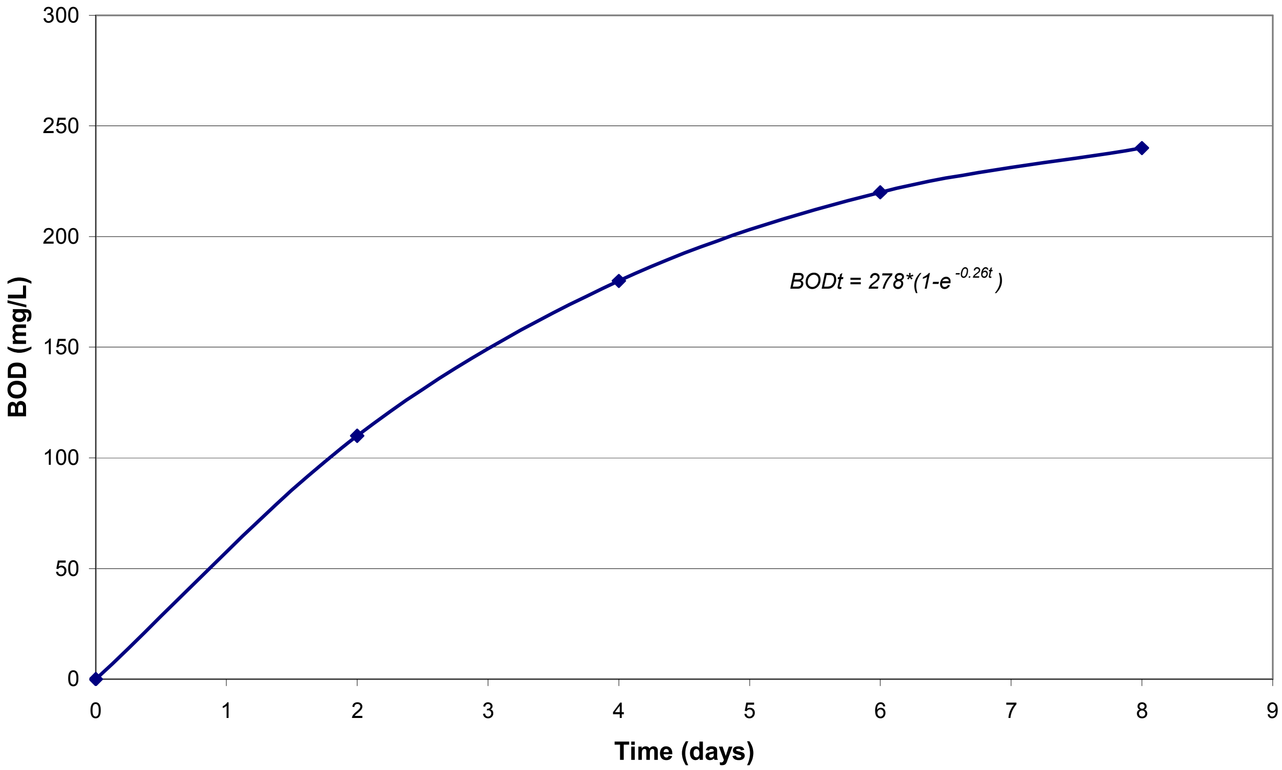
Where $BODt$ = BOD at time t (typically 5 days)

k = reaction rate constant (d^{-1})

$BODu$ = ultimate BOD concentration (mg/L)

The BOD ultimate value is the BOD that would be exerted at infinite time (about 100 days plus). Obviously this is difficult and time consuming to measure, and is usually found by constructing a curve of BOD versus time as shown in figure 1 below. This curve can also be used to find the reaction constant k that is required to fully describe the kinetics of the test.

Figure 1: Plot of BOD versus time

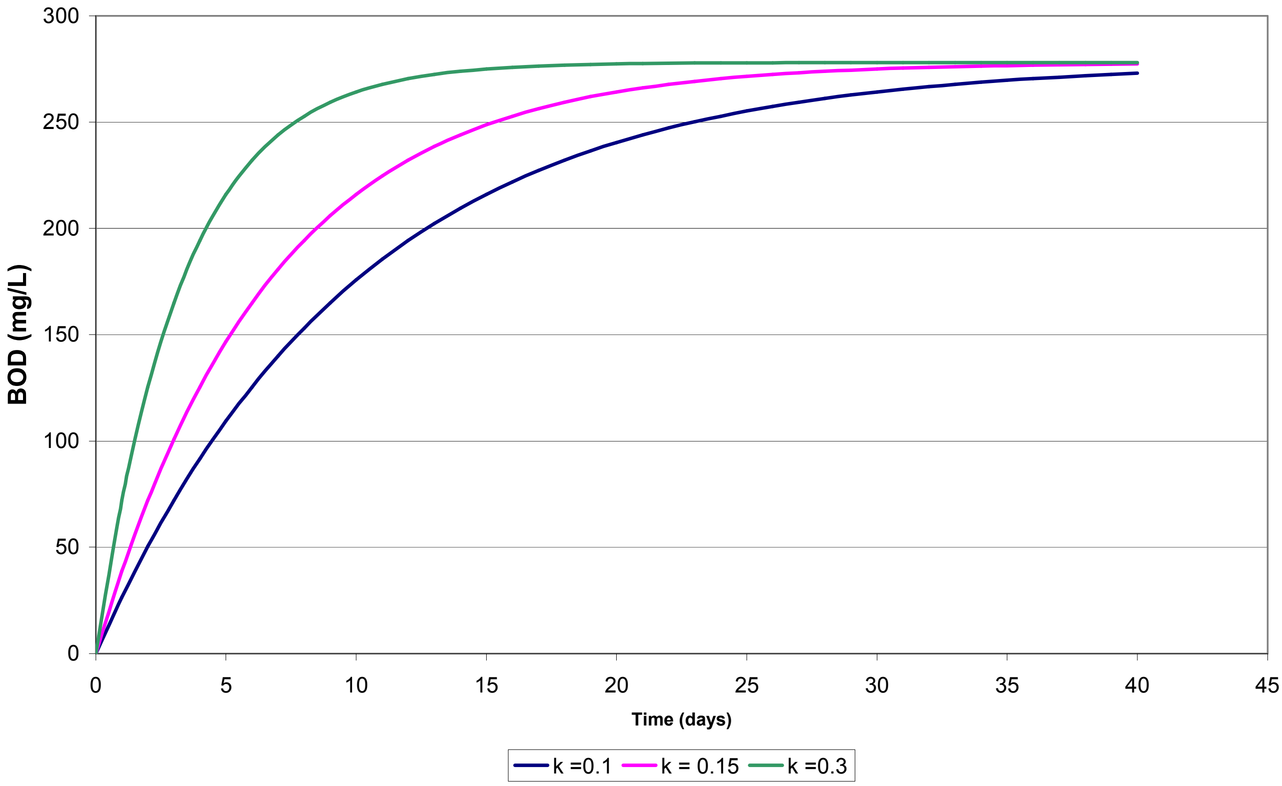


The rate constant fitted to the above set of data in this case was 0.26 $days^{-1}$. From this curve it should be possible to determine the oxygen demand of this particular sample at any point in time. For example, if this wastewater was discharged to a river catchment that had a long transit time from the discharge to the point where the effect of the discharge was critical, (for example 10 days) the oxygen demand on the receiving water would be 260mg/L.

For the BOD test to be valid, all other tests with an ultimate BOD of 278mg/L (as in the graph above) should contain the same amount of substrate (here assumed to only be carbon) such that the ultimate strength of the carbonaceous matter in each sample is the same.

Figure 2 below shows a plot of three BOD curves all with the same ultimate BOD, but having different rate constants (k). As shown the oxygen demand of the sample follows a very different curve for each of the three cases and the oxygen demand at different points is quite different for each sample until the sample time is longer than 25 days.

Figure 2: *BOD versus time for different rate constants k*



The BOD_5 of each of these is summarized in table 1.

Table 1: *BOD_5 of Example BOD tests*

Rate constant (k)	Ultimate BOD (mg/L)	BOD_5
0.1	278	109
0.15	278	147
0.3	278	216

The range of BOD_5 values from table 1 is 109mg/L to 216mg/L, yet the samples are the same ultimate strength given that the ultimate BOD is the same in each case? Does this result mean that an activated sludge type process would require 50% more or less aeration for a wastewater that has been assumed to have the same total amount of carbon? Is the effect on a waterway from this discharge going to be the same at every point given that all three wastes contain the same amount of carbon based pollutants?

The above example illustrates that the BOD test does not tell the designer or regulator anything about the rate of degradability of the waste or its ultimate strength. This may mean that environmental effects or design of aeration equipment etc are over or under estimated. This is of particular importance to regulators as the rate of degradation of a waste will have an affect on how far downstream an environmental effect may be noticed and how quickly an oxygen deficit could occur in the environment.

3.1 OXYGEN CONSUMPTION FOR DEACY

The fundamentals of the BOD test as discussed above are to measure the oxygen consumed by microorganisms in a water or wastewater sample over time. This consumption of oxygen is usually a result of the growth of organisms on the carbon and oxygen in the sample. The organisms that do this are also subject to the same competition, decay and predation (maintenance) processes that they would be in the environment or in an activated sludge process. These maintenance processes consume oxygen, hence the requirement by standard methods that the seed consume no more than 1 mg/L of DO for the duration of the test. As the sample is degraded, the organisms in the seed will undergo a oxygen consuming decay process and those organisms grown during the test will also decay producing an additional oxygen demand that is not related to the original carbon content of the sample. The oxygen demand for decay of the seed can be described as shown below:

$\frac{dO}{dt} = -b(1-f)Xh$ integrating from $t=0$ to $t=t$

$$BOD = (1-f)Xh_{t=0}(1-e^{-bt})$$

Where $\frac{dO}{dt}$ = change in oxygen with time

$-b$ = decay constant

Xh = heterotrophic (carbon utilizing) organisms

f = fraction of organisms that is inert residue

This equation is based upon the initial concentration of organisms in the test being quantified. If the seed is taken from an activated sludge process it is very difficult to quantify the number of organisms present and even more difficult in the actual test (with dilution). Figure 3 below shows a plot of the BOD exerted by the seed organisms in a simulated BOD test at 50 times dilution with initial active organism concentrations of 1, 2 and 3mgCOD/L respectively.

Figure 3: BOD versus time for test seed

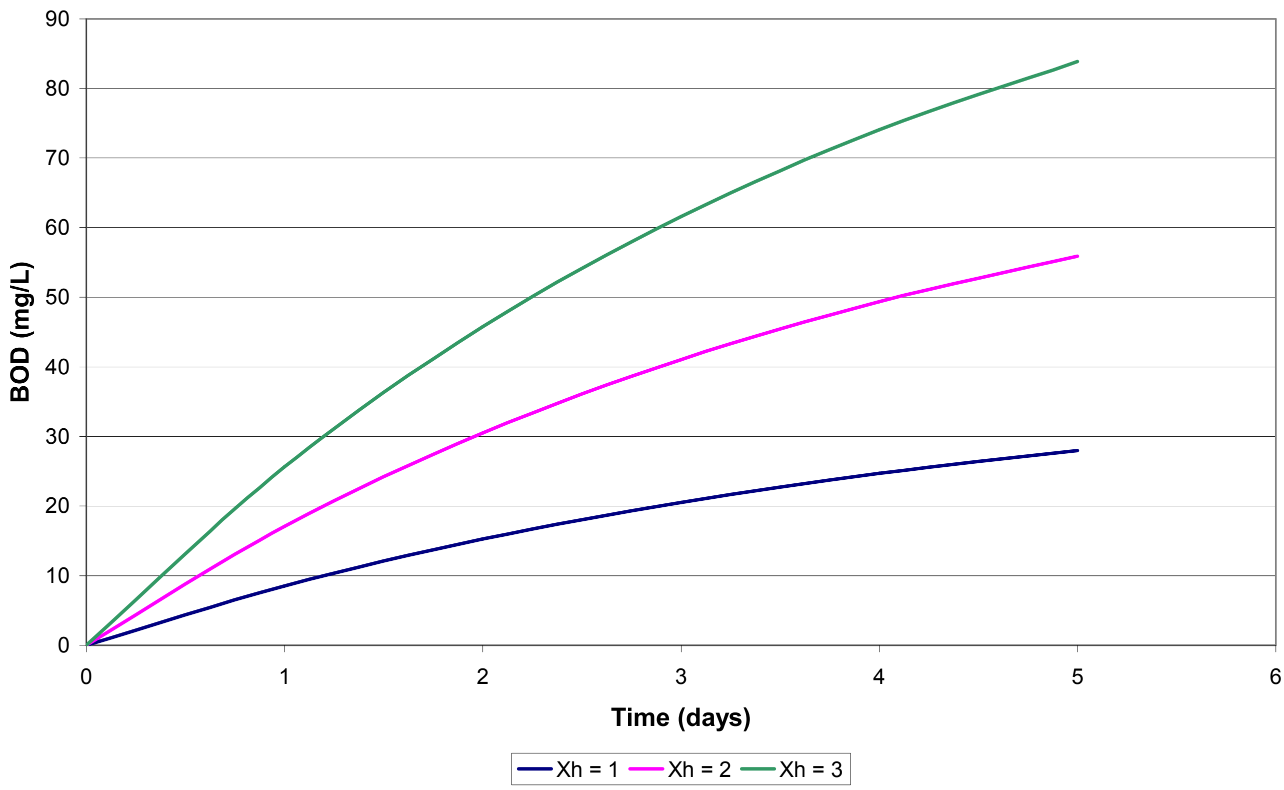


Figure 3 shows that for a typical raw domestic wastewater sample (BOD of about 300mg/L) the seed organisms could add a BOD to the sample of between 30 and 85 mgBOD/L over five days that is totally unrelated to the strength of the sample being tested and would have no relevance to the oxygen demand in the environment or in a wastewater treatment process. Note that the above example does not include the additional oxygen demand from the decay of organisms grown in the test which would add further demand.

3.2 ORGANISM YEILD

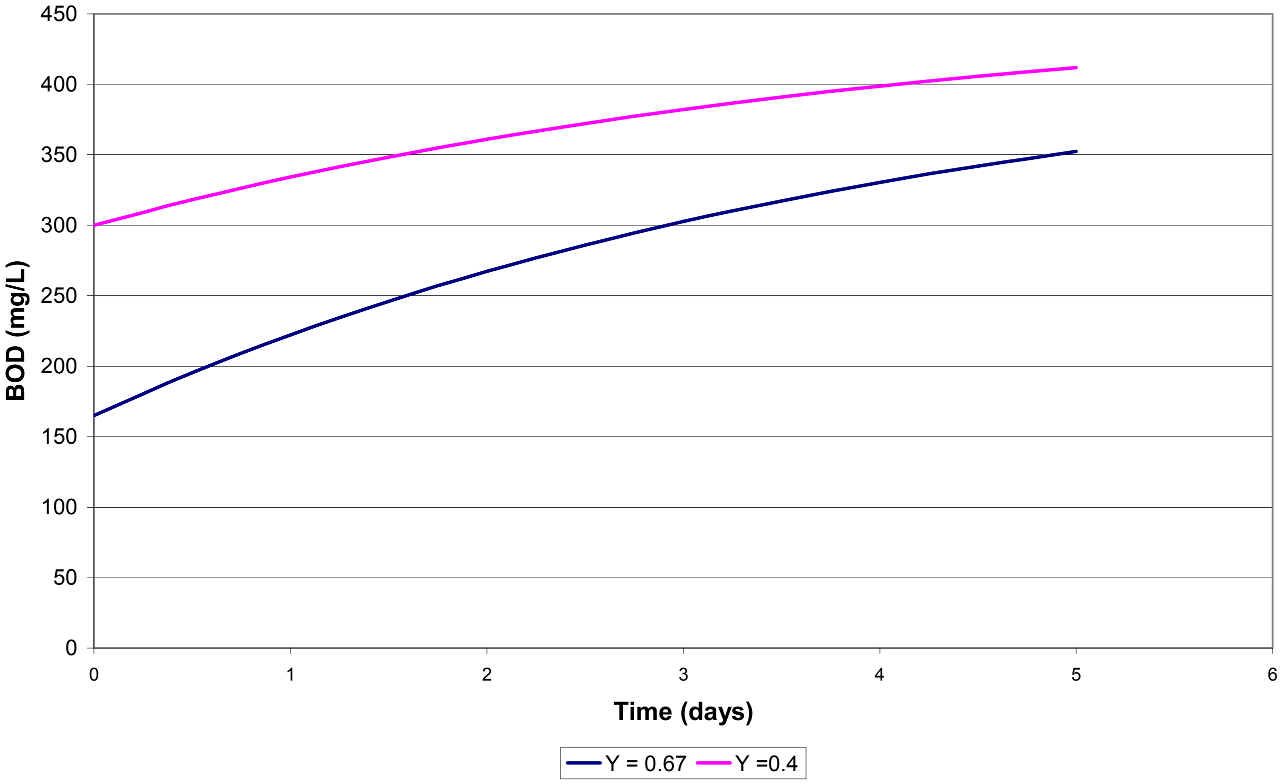
Heterotrophic organisms in an aerobic environment use organic carbon compounds for both energy and growth. The substrate used as an energy source is given off as CO_2 while the carbon used for growth increases the cell mass and number of organisms present. As discussed above new organisms grown on organic carbon undergo decay and maintenance processes and this also gives off CO_2.

The ratio of the mass of carbon that is used for growth versus that used for energy is called the organism yield. In most circumstances this ratio is less than one unless a large amount of intracellular storage is occurring (for example in biological phosphorus removal processes).

For the BOD test the organism yield is critical as only the carbon used as an energy source will exert a BOD. The rest will be used to grow new organisms. The rate of decay and subsequent use of oxygen is usually very much slower than that for growth, hence over five days, all of the carbon that is “lost” to cellular growth will not be measured in the test. For typical domestic/municipal wastewater without significant industrial input the yield ratio is about 0.67kg/kg, however many substances such as methanol, acetic acid and complex compounds that may be found in industrial wastewater have yields that are very different from this value. For example under aerobic conditions the yield of acetate is about 0.4kg/kg.

Figure 4 shows a plot of the simulated BOD for a “test” where the total Chemical Oxygen Demand (COD) of the wastewater sample is 500mg/L with acetate and “normal” COD from wastewater. Note that both simulated tests assume 100% readily degradable substrate and the same seed concentration of organisms.

Figure 4: *BOD versus time different organism yield*



This makes mass balances using BOD impossible as it is impossible to tell how much carbon was used for each process.

The above example illustrates the potential error in the BOD test from one group of organisms with varying yield on different substrates. It should also be noted that yield can be different between different organism groups and well as between substrates. This is not likely to be a major problem for municipal wastewater but it can be a major issue in industries such as pulp and paper where the type of substrate and possibly the type of organisms using this substrate can vary with time.

3.3 ACCLIMATIZATION OF SEED

The above simulated BOD tests all assume that the organisms used as a seed are acclimatized to the substrate being tested. This will most likely always be the case where the sample and seed come from the same plant, but is very unlikely if a standard seed is used for an industrial wastewater or the sample contains compounds that are degraded by a specialist group of organisms. In this case the BOD measurement could be completely false as the seed may take a significant amount of the five days of the test to acclimatize or to reach sufficient numbers to utilize the substrate.

4 OTHER SOURCES OF ERROR

The determination of the BOD in a test sample of water or wastewater assumes that the oxygen consumed during the test period was the result of a source of pollution (e.g. sewage). In some wastewater treatment systems there can be instances where the treatment system itself contributes to the oxygen demand.

Pond systems are a very common method of treating wastewater in New Zealand and these rely on the settlement of organics and the action of algae to promote oxygenation of wastewater. The algae use CO_2 from the atmosphere, with sunlight, to produce oxygen and new cellular material. New algae cells contain carbonaceous compounds that will exert a BOD once released from the cell during decay or predation. This oxygen demand may be measured in the effluent to a pond system, however the carbon that is utilized during the BOD test would have been fixed from atmospheric (dissolved) CO_2 and would have nothing what so ever to do with the strength of the waste that the pond was treating. Using effluent BOD data from a pond therefore to quantify the performance of a pond system may not be valid if the measured oxygen demand did not originate from the influent wastewater. This would be a large issue in summer where the population of algae cells is higher than in the winter.

5 PROCESS MASS BALANCES FOR DESIGN

Biochemical oxygen demand is very widely used not only in the regulation and operation of treatment plants, but also in their design. Sizing of aeration basins, sludge processing facilities and aeration systems are undertaken using BOD data. The design fundamentals for process design with BOD are typically based on empirical values or loading rates such as:

- Areal loading rates of pond systems (old Ministry of Works design guideline of 84kgBOD/ha/day)
- Trickling filter media loading rates (kgBOD/m^3 of media)
- Activated sludge processes (food to microorganism ratio (F to M) kgBOD/kgMLVSS.d)
- Sludge production from an activated sludge process (kgTSS/kgBOD.d)

These loading rates are usually based on long term operational data where the influent BOD concentration has been correlated to the plant performance. The empirical approach does not provide any information on how the process is actually working, how sludge production changes with time or the kinetics of the processes involved in treating the waste. These issues may not be important from an operational point of view provided the empirical data can be used to optimize and run the plant properly. In complex systems such as nitrogen removal and biological phosphorus removal, and the digestion of biosolids, the empirical approach is limited as the designer knows nothing about rates of reaction, affinity to different substrates and sludge production, all of which are needed to size and manage these complex systems more efficiently and effectively.

Biochemical Oxygen Demand data has limited value in the design of complex systems as mass balances cannot be closed using this data. As discussed above, the "strength" of the wastewater measured by the BOD test does not actually relate to the total amount of carbon in the waste, therefore sludge production cannot be properly quantified and therefore prediction of mixed liquor and sludge quantities cannot be predicted without empirical relationships such as those outlined above. Processes such as biological phosphorus removal cannot be designed on a BOD basis as the carbon cannot be properly traced throughout the system.

Possibly the most significant design issue related to BOD is the sizing of aeration equipment. As the BOD test includes endogenous respiration (see above) double accounting of the oxygen needed for this and carbon oxidation will occur as the designer has no way of telling how much BOD was related to the sample, how much was endogenous activity and how much of the oxygen demand is related to the specific yield of the substrate being treated. This is particularly difficult in a nitrogen removal process where nitrate essentially replaces oxygen for the electron transfer process. If cellular yield is not included in this analysis, aeration equipment will be oversized and may operate very inefficiently.

The above issues are the primary reason why activated sludge models (ASM models) do not use BOD at all in their calculations or model structure. Mass balances over a process are not possible with BOD and therefore the process simulation models cannot be designed around this parameter. Most models use or back calculate BOD as this is what users expect to see rather than this actually being used in the models themselves.

Designers need to be aware of the limitations of the BOD test when undertaking design and the implications it has for over or underestimating the amount of capital expenditure (concrete and mechanical equipment) that is needed to treat a particular wastewater.

6 CONCLUSIONS

The BOD test is the probably the most commonly used test in the wastewater industry for measuring the strength of wastewater. It was developed as an empirical measure to determine the oxygen depleting potential of water or wastewater, but does not measure the carbon content of the wastewater that is critical in the design of complex wastewater treatment systems.

The five day duration of the test is not always the best indicator of the polluting effect of a discharge and is based upon the history of the test rather than any fundamental scientific principle. Many other countries use a different time basis for the BOD test to better reflect local conditions and this may be necessary in some cases in New Zealand.

Wastewater plant regulators, operators and designers should all be aware of what the BOD test actually is and take it limitations and advantages into account when using BOD based data.

REFERENCES

Metcalf and Eddy "*Wastewater Engineering, Treatment and Reuse*", Mc Graw Hill, 2003

"Standard Methods for the Examination of Water and Wastewater", 21st Edition, APHA, AWWA, WEF,2005

Henze, M; Harremoes, P; la Cour Jansen, J and Arivin, E "*Wastewater Treatment, Biological and Chemical Processes",* Springer, 1991.