The Many Intricacies of Biochemical Oxygen Demand

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Many engineers who are involved in effluent compliance, wastewater treatment and water quality assessment have heard of the term BOD or Biochemical Oxygen Demand. However, unless the engineer is from technically specific branches of engineering, many delicate intricacies involved with BOD may elude them.

In fact, the BOD_5 test (five days incubation at 20°C) which most engineers are familiar with is only the tip of the iceberg of a wider spectrum in relation to BOD. Thus, it is important for engineers to attain an adequate level of understanding of the components, kinetics and overall implication of the BOD test results not only for application in their daily work, but also in the interest of the environment.

Back to Basics

The history of the BOD_5 test dates back to 1908, when the Royal Commission on Sewage Disposal (UK) chose the parameter as an indicator for organic pollution in the Thames River, which in turn, has a nominal temperature of 20°C and retention time of five days at the tidal zone.

By definition, the BOD test should be reflective of the oxygen uptake of microorganisms during decomposition of readily biodegradable organic matter under aerobic conditions. The reaction path is shown in the following Equation [1].

$$C_nH_aO_bN_c + (n + \frac{a}{4} - \frac{b}{2} - \frac{3}{4}c)O_2 \rightarrow$$

$$nCO_2 + \left(\frac{a}{2} - \frac{3}{2}c\right)H_2O + cNH_3$$

$$+ \text{New Cells} \qquad (1)$$

This common definition is rather ambiguous as it makes no mention of complete decomposition occurring within five days at 20°C, thus inhibiting the oxygen uptake. However, it was later discovered that at the said temperature and time frame, most dissolved organic matter was stabilised, typically between 70%-80% in most sample tests.

However, there remained the question of the slowly biodegradable organic fraction, which takes longer to decompose, typically consisting of non-dissolved organics usually found in domestic sewage as well as more complex organic molecules from industry [2]. The hypothesis that most of the organic fraction is oxidised within five days thus becomes invalid for such cases.

BOD_5 Test and Ultimate BOD (uBOD)

We shall now examine the BOD_5 test itself. The oxygen uptake of microorganisms for the BOD_5 test is measured as the depletion in dissolved oxygen (DO) concentration between the first and the fifth day, ΔDO, in a 300ml BOD test bottle that can be mathematically expressed as[1];

$$BOD_5 = \Delta DO = \frac{DO_1 - DO_2}{P},$$

$$P = \frac{V}{300} \qquad (2)$$

Where DO_1 is the initial dissolved oxygen concentration (with and without dilution), and DO_2 is the residual DO measured after five days, with *P* as the dilution factor and *V* as the volume of sample. DO is typically measured via a pre-calibrated membrane probe or through the Winkler Titration method. The reaction kinetics that goes on during the five-day period is illustrated in Figure 1;

The above figure assumes that BOD_5 represents about 80% of the total BOD, or more commonly referred to as Ultimate BOD (uBOD). As discussed previously, this only holds true if certain conditions are met, where the uBOD value can be experimentally determined via a prolonged incubation time. *Standards Methods for the Examination of Water and Wastewater (21st Edition)* from the *American Public Health Association (APHA)* recommends an incubation time of 60 days [3]. Inherently, this is impractical for operational and regulatory purposes. However, since the reaction follows a first order rate kinetics pathway, the uBOD is correlated to BOD_5 through the following formulae [4];

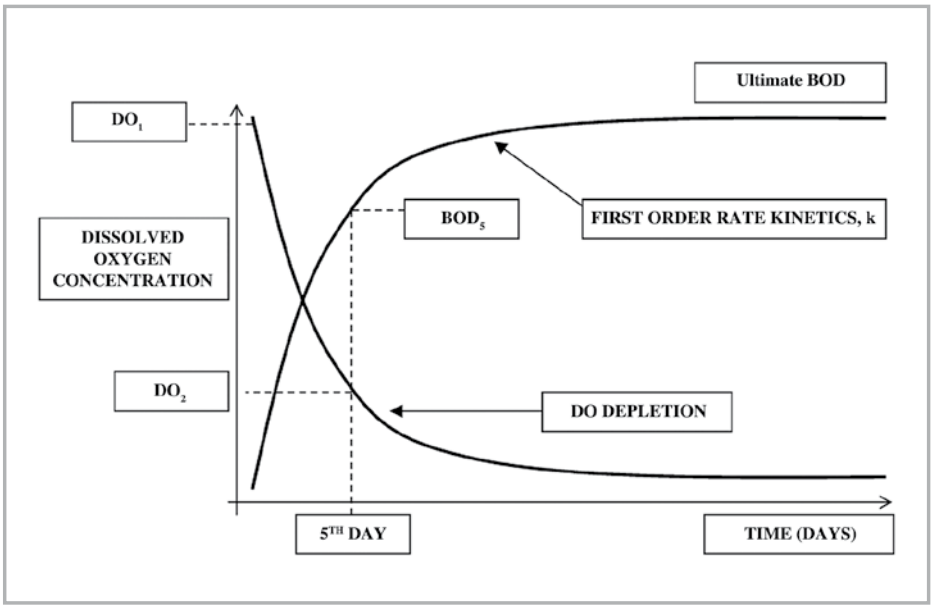

Figure 1: Graphical illustration of DO-BOD kinetics

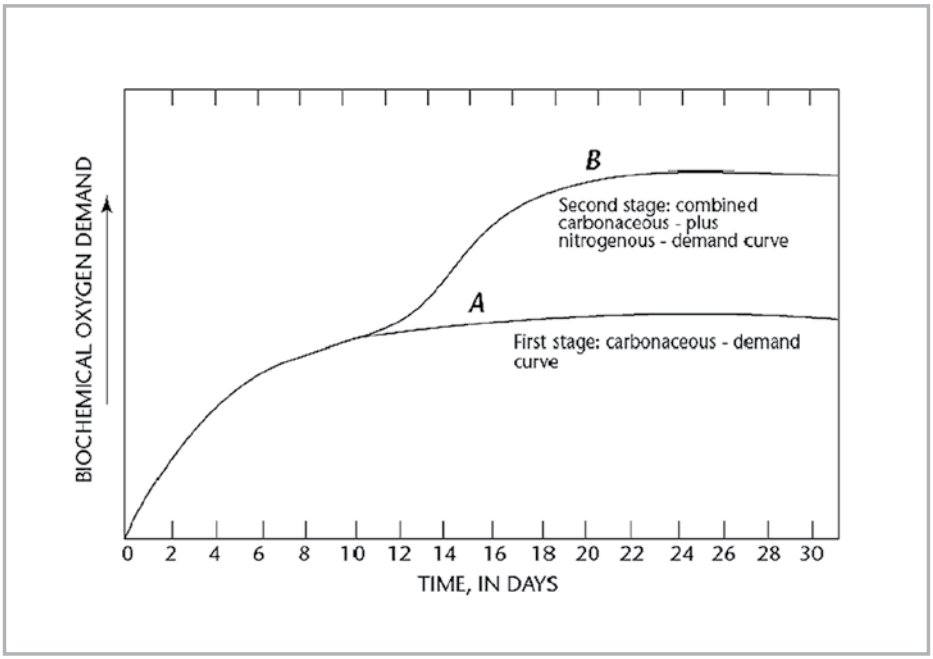

Figure 2: Carbonaceous and nitrogenous BOD[1]

$$BOD_5 = uBOD(1 - e^{-5k}) \quad (3)$$

Where k is the first order rate constant determined from experiment for various types of water samples (available from literary sources). This k value governs the rate of reaction in the correlation, which in turn, is independent of the amount of BOD_5 representing uBOD. In other words, regardless of where the final BOD_5 value is located in Figure 1, through utilisation of the k value, the uBOD and, thus, the actual organic pollution strength can be estimated.

Why is this important to consider? The answer lies in the travel time of the receiving main stream or tributaries of rivers to its downstream segment. If the travel time of the organic pollutant is more than five days and consists mainly of the *slowly biodegradable fraction*, an underestimation of the organic pollution strength may occur, particularly in Malaysia where the primary pollution load contribution are from sewage sources. Moreover, tropical temperatures actually heighten microbial activity and may incur higher BOD in a shorter timeframe.

A reconciliation of this paradox is done through the regulation of COD or Chemical Oxygen Demand. Since the COD test utilises a synthetic oxidising agent to replicate the BOD oxidation process, the *slowly biodegradable fraction* is also instantaneously oxidised. This measure of control is prudent towards water quality preservation.

Chapra *et al.* (2005)[4], however, suggests for BOD to be differentiated to two specific categories; fast-BOD and slow-BOD, where the former would represent the readily biodegradable fraction, and the latter, the slowly biodegradable fraction. This method of distinction was further reaffirmed when it was incorporated into the *United States' Environmental Protection Agency's* widely used water quality model, QUAL2K.

Fast-BOD is determined via removal of suspended organics through filtration. Slow-BOD is then determined as a product of the unfiltered sample versus the filtered sample [4]. It is recommended, however, that some nitrogenous inhibitation be done to capture only the carbonaceous fraction (cBOD).

Carbonaceous and Nitrogenous BOD (cBOD and nBOD)

The preceding discussions only covered BOD_5 and uBOD without consideration for oxygen demand exhibited by nitrifying microorganisms. Typically, for the BOD_5 test, this is not a cause for concern as this type of oxygen demand only occurs after a prolonged duration, after most of the carbonaceous organic matter has been stabilised.

However, APHA still recommends the use of an inhibiting agent such as TCMP (2-chloro-6-(trichloro methyl) pyridine) [3]. This is because, for low level BOD water that contains minute amount of carbonaceous matter or high amount of ammonia nitrogen, nitrification may occur at an earlier stage inside the test bottle. In addition, to be representative of flowing river conditions where nitrification does not usually occur, the use of an inhibiting agent would prove advantageous.

Nitrification is the transformation process of ammonia nitrogen to nitrite and nitrate by microorganisms from the *nitrosomonas* and *nitrobacter* genus [1]. Since ammonia nitrogen is a by-product of organic decomposition, the probability of nitrification occurring and affecting the BOD results increase as more time pass (i.e. incubation time).

Sampling Requirements

A water sample due for BOD analysis must be kept at 4°C onsite and analysed within 24 hours. This can be achieved through the utilisation of a cooler box and some ice cubes or cooling gel packs. Microbial activity shall be kept to a minimum with this procedure, thus reducing the amount of organics stabilised during transit. Bubbles and air pockets should also be eradicated from the sample bottle to ensure no oxygen transfer occurs [5].

A common misconception is that BOD is a suitable parameter of assessment for all types of water. This is not true, especially for water with above normal saline concentration such as brackish water and seawater. The high chloride content disrupts microbial activity through protoplasmic degradation (osmosis). This is one of the reasons why the Interim Marine Water Quality Standards (IMWQS) for Malaysia does not prescribe BOD as a parameter of provision. Total Organic Carbon (TOC) is a more suitable parameter for such conditions in substitute of BOD in determining organic pollution.

Other Considerations

For the test results to hold water (pun intended), several conditions have to be met, one of which is that the residual DO_2 (on the fifth day) cannot be less than 2mg/l, otherwise the sample would

simply be rejected. This is because such low oxygen levels would induce stress to microorganisms stabilising the organic matter and likely cause anaerobic respiration. However, APHA has since reviewed this number and the latest edition of Standard Methods state that DO_2 must be more than 1mg/l.

In addition, APHA also states that for the BOD_5 results to hold any meaning; a minimum of 2mg/l oxygen depletion must be met. In other words, the detection limit for BOD should be set at 2mg/l [3]. One reason behind this guideline is to ensure that the indicated results are actually from microbial respiration instead of external influences.

Finally, the analyser needs to determine whether seeding is necessary. Under typical circumstances, the microbial population present within a water sample is usually enough to incur oxygen demand. However, there are instances when induced seeding of these microorganisms is required. Seeding ensures homogeneity of the microorganisms stabilising the organic matter, thus ensuring more accurate results.

Conclusion

Details pertaining to BOD have been thoroughly explained. It is hoped that the reader would now have a better understanding and appreciation of the many intricacies involved pertaining to BOD and be able to utilise the knowledge gained in their daily engineering practices for the interest of the environment. ■

REFERENCES

[1] C. N. Sawyer, P. L. McCarty and G. F. Parkin, 'Chemistry for Environmental Engineering and Science: Fifth Edition', In : Chapter 23 : Biochemical Oxygen Demand, McGraw-Hill Professional., USA, 2003, pp. 604 - 621.

[2] S. C. Chapra, 'Surface Water-Quality Modeling', Prentice Hall, USA, 1997.

[3] American Public Health Association (APHA), American Water Works Association (AWWA) and Water Environment Federation (WEF), 'Standard Methods For The Examination of Water and Wastewater : 21st Edition', APHA, AWWA and WEF, 2005.

[4] S. C. Chapra, G. Pelletier and H. Tao, QUAL2K: A Modeling Framework for Simulating River and Stream Water Quality, Version 2.04: Documentation and Users Manual, Civil and Environmental Engineering Dept., Tufts University, Medford, MA., 2005.

[5] Recommended Holding Time and Preservatives (Catalog), ALS Technichem (M) Sdn. Bhd., Bukit Jelutong, Shah Alam, Malaysia.