BIOCHEMICAL OXYGEN DEMAND

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Contents

Summary

Biochemical oxygen demand (BOD) is a measure of the dissolved oxygen consumed by microorganisms during the oxidation of reduced substances in waters and wastes. Typical sources of BOD are readily biodegradable organic carbon (carbonaceous, CBOD) and ammonia (nitrogenous, NBOD). These compounds are common constituents or metabolic byproducts of plant and animal wastes and human activities (domestic and industrial wastewaters). The discharge of wastes with high levels of BOD can cause water quality problems such as severe dissolved oxygen depletion and fishkills in receiving water bodies. Standardized methods for the quantification of BOD in wastewaters have remained virtually unchanged for decades despite numerous shortcomings. Alternative techniques and estimation methods have been proposed. The kinetics of dissolved oxygen consumption resulting from BOD discharges have been formulated into several mathematical models for simulating surface water quality. The long history of the BOD test and its incorporation into many major water quality models ensures that it will continue to be measured for decades in the future.

1. Introduction

As the populations of many cities grew significantly larger during the late 19th Century due to industrial expansion, sewer systems were installed to transport domestic wastewater (from toilets, washing, etc.) and industrial wastewater to rivers or other surface waters for disposal with little or no treatment (see *Water Quality, Chemistry of Wastewater, Thermal Pollution of Water*). Primary wastewater treatment, that employed only sedimentation basins, removed large debris and readily settleable solids; however, the majority of the organic material was not removed because it was either dissolved or of low density so that it settled slowly. Thus, as human populations increased, so did the loading of organics to the nearby surface waters. The increased organic loading stimulated microbial decomposition that utilized dissolved oxygen (DO) in the surface water. This consumption of DO and attendant DO depletion in many cases led to the development of anaerobic conditions that could not support desired aquatic life, such as fish, and also caused aesthetic water quality problems (see *Eutrophication and Algal Blooms*). Advanced (secondary) wastewater treatment was then introduced to biologically remove the organic matter to alleviate this problem. The depletion of dissolved oxygen thus became a primary water quality concern after more important priorities such as disinfection (pathogen destruction) were addressed. During the period from 1950 to 1970 many industrialized nations passed legislation that aimed to reduce surface water pollution. As a result, wastewater treatment facilities were issued permits which established maximum allowable levels of oxygen demanding wastes (and other contaminants such as suspended solids) in their effluents (Figure 1).

Figure 1: Treated domestic wastewater being discharged into a stream

Biochemical oxygen demand (BOD) is also sometimes referred to as *biological* oxygen demand, but the latter term is considered inappropriate by many scientists and engineers. These terms are widely used to define the microbial use or consumption (i.e. *demand*) of oxygen during the aerobic oxidation of electron donors such as readily degradable organic carbon (e.g. sugars) and ammonia in waters as shown in the following simplified reactions:

$$C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O \quad (1)$$

$$NH_3 + 2\ O_2 \rightarrow NO_3^- + H_2O + H^+ \quad (2)$$

Natural sources of BOD in surface waters include organic material from decaying plants and animal wastes. Human sources of BOD include feces, urine, detergents, fats, oils and grease, etc. Proteins are produced by plants and utilized by animals. Through the microbial processes of proteolysis, deamination and ammonification proteins are degraded to a hydrocarbon skeleton and ammonia—the two primary chemical forms contributing to BOD as presented in the above equations. The subsequent biochemical oxidation of these reduced nitrogenous and carbonaceous compounds in water is mediated by a variety of microorganisms (primarily bacteria and protozoa).

Regarding wastewaters, BOD is often used as a measure of the *strength* of the waste—the greater the BOD, the more "concentrated" the waste. BOD is somewhat unique in that it measures an *impact* on the environment (mass of dissolved oxygen consumed per volume of water sample— $mgO_2\ L^{-1}$), rather than a concentration of any specific compound or family of compounds (e.g., total organic carbon or ammonia). Measurement of BOD in raw (influent) and treated (effluent) wastewaters is a standard practice to evaluate treatment facility performance. BOD is also one of the primary surface water quality parameters (see *Water Quality*, *Chemistry of Wastewater*).

2. Theory

A number of tests have been developed to quantify the BOD, as well as to estimate the rate of oxygen depletion in water or wastewater samples. This oxidation rate is commonly used in wastewater treatment and surface water quality models. Figure 2 diagrams the theoretical aspects of the biochemical oxygen demand of a wastewater sample as a function of time. Note that the oxygen demand (sometimes referred to as the BOD *exerted*) increases with time, asymptotically approaching an ultimate value. The inverse of the BOD exerted curve would represent the BOD (degradable organics) remaining in the sample, that exponentially approaches zero.

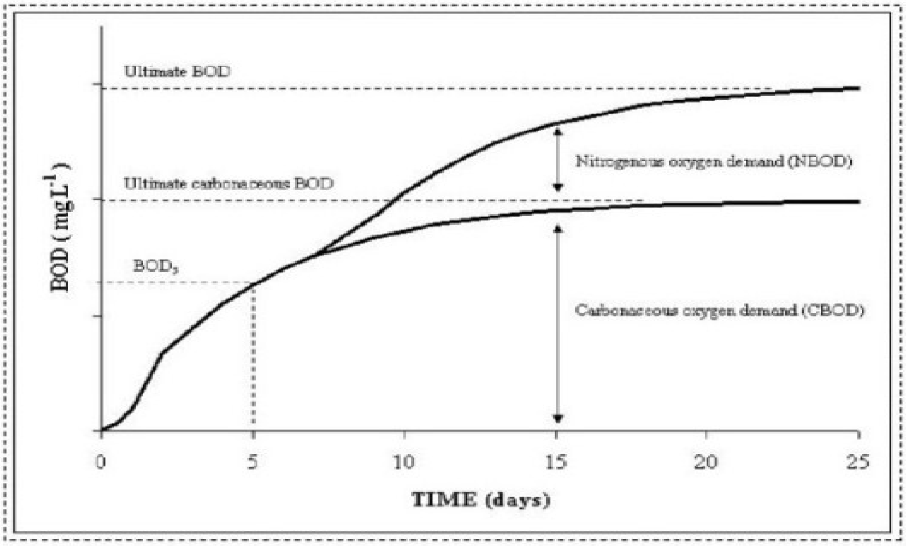

Figure 2: A theoretical representation of the biochemical oxygen demand of a wastewater as a function of time

2.1. Five-day BOD (BOD_5)

The BOD_5 test is a standardized test that provides information regarding the organic strength of wastewater. The amount of oxygen consumed in a sample within a five-day period is measured under carefully controlled and standardized conditions. Details of the test are described in Section 3. Generally the five-day period is not long enough for complete oxidation, but it provides sufficient time for microbial acclimation (*lag-phase* growth as seen during the first day in Figure 2) and for substantial (approximately 40 to 80 percent) oxidation. The five-day period has been widely retained, having its historical roots in early water quality studies when it was determined that no stream in England had a travel time of greater than five days to the ocean.

The $[BOD_5]$, expressed as $mgO_2\ L^{-1}$ (or equivalently as parts per million, ppm), is the difference between the initial dissolved oxygen ([DO]) measurement and the corresponding (final) measurement made on the fifth day of incubation.

$$[BOD_5]=[DO]_{final} - [DO]_{initial} \qquad (3)$$

Depending on the nature of the sample, it is either diluted or microbially seeded and additional nutrients are added. In these cases the equation is slightly modified (see Section 3). Since this test has been used for regulatory purposes for several decades, a wealth of information for a large number of effluent types is available (see Section 4). Unfortunately, little kinetic information can be derived from this test, and it provides little insight for modeling purposes.

2.2. Ultimate BOD (UBOD)

The ultimate biochemical oxygen demand ([UBOD]) is a parameter that quantifies the oxygen required for the total biochemical degradation of organic matter by aquatic microorganisms. [UBOD] and the rate of oxygen consumption are frequently used in mathematical models to predict the impact of an effluent on receiving bodies such as lakes and rivers. The rate of oxygen consumption is therefore often determined along with the [UBOD] value in the analytical test. A distinction is made between the carbonaceous oxygen demand ([CBOD]) and nitrogenous oxygen demand ([NBOD]) during the measurement as well as in many water quality models. Both CBOD and NBOD contribute to the overall UBOD, but the values and rates of oxidation differ (see *Water Quality*).

2.3. Carbonaceous Oxygen Demand (CBOD)

CBOD is the oxygen consumed during the oxidation of carbonaceous compounds to carbon dioxide (CO_2) and other oxidized end products. Reduced organic carbon ranges in form from labile (highly biodegradable, e.g., sugars) to almost refractory (e.g., cellulose) compounds. In reality, the oxidation of organic carbon consists of a series of biochemical reactions mediated by a variety of microorganisms feeding on either the substrate or other microorganisms involved in the oxidation process. Formulations of the CBOD breakdown, however, are described using simplified oxidation kinetics. The most common equation to describe the oxidation reaction is a first-order dependency on the CBOD concentration,

$$\frac{d[\mathrm{DO}]}{dt} = \frac{d[\mathrm{CBOD}]}{dt} = -k[\mathrm{CBOD}] \qquad (4)$$

where [CBOD] is carbonaceous biochemical oxygen demand remaining, usually in $mgO_2\ L^{-1}$, k is the first-order reaction rate constant, usually d^{-1}, and [DO] is dissolved oxygen concentration in $mgO_2\ L^{-1}$. This equation can be integrated resulting in the following:

$$[\mathrm{CBOD}] = [\mathrm{CBOD}]_0 \times e^{-kt} \qquad (5)$$

where $[\mathrm{CBOD}]_0$ is the initial CBOD concentration while t is time in days.

The ultimate CBOD can be estimated by running the experiment until all of the organic carbon is oxidized. However, this can take between 20-50 days or in some cases much longer. This method has several limitations that will be discussed later. Modifications of the test have been proposed to achieve results faster; two such methods are the Thomas Slope Method and an approximation using the BOD_5. The estimate based on the $[BOD_5]$ value is based upon the exponential (first-order) nature of oxygen demand. The ultimate carbonaceous oxygen demand is than

$$\textit{Ultimate-CBOD} = BOD_5 \times (1 - e^{-kt})^{-1} \qquad (6)$$

$$\text{Ultimate-[CBOD]} = [\mathrm{BOD}_5] \times (1 - e^{-kt})^{-1}$$

where $[BOD_5]$ is the biochemical oxygen demand that is exerted over the five day period.

The value of the reaction rate constant, k, is determined experimentally or from tabulated values. Readily degradable wastes (e.g., domestic wastewater) will have higher (faster) coefficients (0.3 to 0.7 d^{-1}) whereas less readily degradable sources (e.g., river water) will have lower rates (0.1 to 0.2 d^{-1}). An assumption when estimating the ultimate CBOD value is that nitrogenous compounds are inhibited and do not contribute to the overall oxygen consumption.

2.4. Nitrogenous Oxygen Demand (NBOD)

NBOD is the oxygen consumed during the oxidation of nitrogenous compounds (mainly NH_3) to nitrate with nitrite being an unstable intermediate. Different from CBOD, only two classes of bacteria are believed to be responsible for the oxidization of reduced nitrogen. These bacteria (nitrifiers) are surface-based (associated with suspended solids), and therefore are usually only present in the water in low concentrations. In Figure 2, the NBOD does not become discernable until approximately 7 days of incubation have occurred. This is not uncommon as the nitrifiers typically have slower growth rates and do not flourish until the food supply for the heterotrophic (CBOD consuming) microbes has diminished (i.e., as [BOD] exerted approaches the ultimate [CBOD] and the [CBOD] remaining approaches zero). The standard analytical test may result in incorrect results because the growth of nitrifiers on the surface of the sample bottle, known as bottle effects, can artificially enhance the nitrification. For this reason, a short-term measurement (1 to 3 days) is suggested to estimate [NBOD]. An accurate method to measure [NBOD], is to track the ammonia (or total Kjeldahl nitrogen, TKN, as a surrogate) concentration over a 1 to 3 day period. [NBOD] (and rate of oxygen consumption) is estimated using the stoichiometric value of 4.57, although a lower value has also been used since some of the nitrogen is consumed for cell maintenance. The rate of oxygen demand in samples can thus be calculated:

$$\frac{d[\mathrm{DO}]}{dt} = 4.57 \times \frac{d[\mathrm{NH_3}]}{dt} = 4.57 \times k_{\mathrm{n}}[\mathrm{NH_3}] \qquad (7)$$

where k_{n} is nitrification rate (typically d^{-1}). Integrating and solving the above equation results in

$$[\mathrm{NH_3}] = [\mathrm{NH_3}]_0 \times e^{-k_{\mathrm{n}} t}. \qquad (8)$$

Attempts have been made to measure the [CBOD] and [NBOD] rates simultaneously, but this often results in an incorrect *BOD* value due to bottle effects (see Section 3.2). The *UBOD* value should rather be expressed and calculated as the sum of the [NBOD] and [CBOD]:

$$\frac{d[\mathrm{DO}]}{dt} = \frac{d[\mathrm{UBOD}]}{dt} = 4.57 \times k_{\mathrm{n}}[\mathrm{NH_3}] + k[\mathrm{CBOD}]. \qquad (9)$$

This equation in many forms is commonly used in dissolved oxygen components of wastewater, lake and river models.

3. Measurement

The [BOD] of a water or wastewater sample is measured using a *bioassay*--a test in which organisms (biota) are used to determine (assess) the amount of a target substance. In the case of a BOD test microorganisms are used to degrade/oxidize many different compounds in the sample. The term BOD is often used ambiguously when referring to CBOD—it is important to specify between CBOD and BOD (recall that [BOD] is the sum of [CBOD] and [NBOD]). The following description of the BOD test methodology summarizes the detailed method outlined in *Standard Methods for the Examination of Water and Wastewater* which is published and frequently revised by the American Public Health Association, the American Water Works Association and the Water Environment Federation. Other biodegradability tests can be found in the Organization for Economic Cooperation and Development (OECD) *Set of Guidelines for Testing of Chemicals*. In general, the BOD test determines the difference between the initial and final dissolved oxygen measurements of a sample over time.

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Biographical Sketches

Michael R. Penn is an Associate Professor of Civil and Environmental Engineering at the University of Wisconsin-Platteville. He received an M.S. in Environmental Engineering from the University of Michigan and a Ph.D. from Michigan Technological University. He is a coauthor of the *Fundamentals of Environmental Engineering* (*Fundamentos de Ingenieria Ambiental*) textbook by Mihelcic et al. published by John Wiley and Sons. His research focuses on providing undergraduate students opportunities to study nonpoint water pollution and sediment-water interactions. His teaching interests are wastewater treatment, and contaminant fate and transport. He is a registered Professional Engineer in the State of Wisconsin.

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