Pearson New International Edition

Introduction to Environmental Engineering and Science

Gilbert M. Masters Wendell P. Ela

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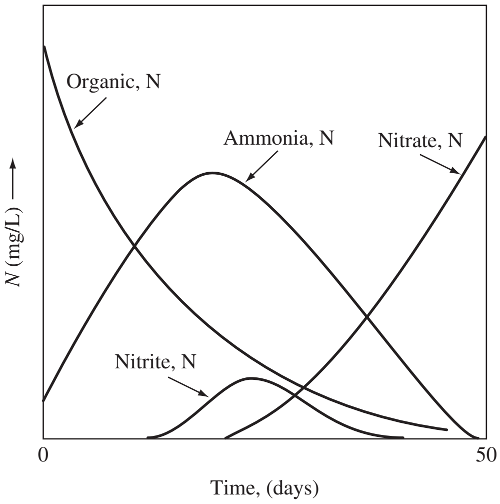

FIGURE 12 Changes in nitrogen forms in polluted water under aerobic conditions. (*Source:* Sawyer and McCarty, 1994. Reprinted by permission of McGraw-Hill, Inc.)

small but important fraction being nitrous oxide (N_2O). (Nitrous oxide is a greenhouse gas.) Nitrogen in the form of N_2 is unusable by plants and must first be transformed into either ammonia (NH_3) or nitrate (NO_3^-) in the process called *nitrogen fixation.* Nitrogen fixation occurs during electrical storms when N_2 oxidizes, combines with water, and is rained out as HNO_3. Certain bacteria and blue-green algae are also capable of fixing nitrogen. Under anaerobic conditions, certain denitrifying bacteria are capable of reducing NO_3^- back into NO_2 and N_2, completing the nitrogen cycle.

The entire nitrogen cycle obviously is important, but our concern in this section is with the nitrification process itself, in which organic-nitrogen in waste is converted to ammonia, ammonia to nitrite, and nitrite to nitrate. Figure 12 shows this sequential process, starting with all of the nitrogen bound up in organic form and weeks later ending with all of the nitrogen in the form of nitrate. Notice that the conversion of ammonia to nitrite does not begin right away, which means the nitrogenous biochemical oxygen demand does not begin to be exerted until a number of days have passed.

Figure 13 illustrates the carbonaceous and nitrogenous oxygen demands as they might be exerted for typical municipal wastes. Notice that the NBOD does not normally begin to exert itself for at least five to eight days, so most five-day tests are not affected by nitrification. In fact, the potential for nitrification to interfere with the standard measurement for CBOD was an important consideration in choosing the standard five-day period for BOD tests. To avoid further nitrification complications, it is now an accepted practice to modify wastes in a way that will inhibit nitrification during that five-day period.

A stoichiometric analysis of (15) and (16) allows us to quantify the oxygen demand associated with nitrification, as the following example illustrates.

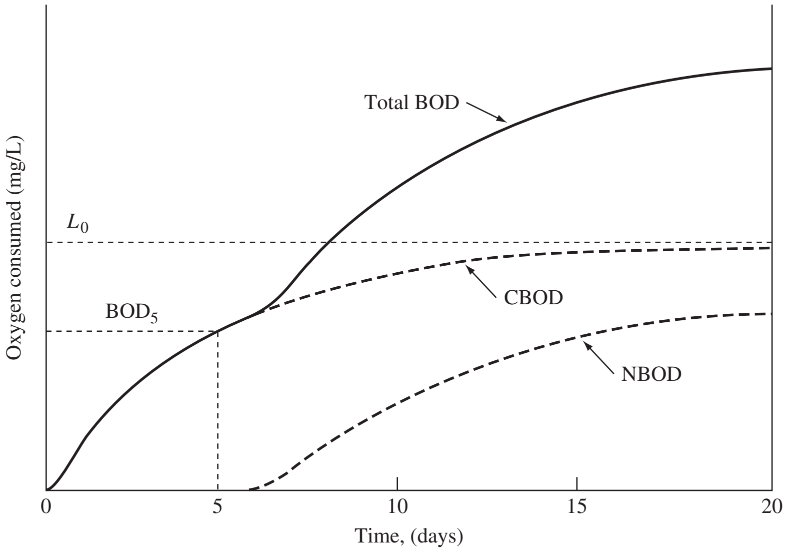

FIGURE 13 Illustrating the carbonaceous and nitrogenous biochemical oxygen demand. Total BOD is the sum of the two.

EXAMPLE 5 Nitrogenous Oxygen Demand

Some domestic wastewater has 30 mg/L of nitrogen in the form of either organic nitrogen or ammonia. Assuming that very few new cells of bacteria are formed during the nitrification of the waste (that is, the oxygen demand can be found from a simple stoichiometric analysis of the nitrification reactions given above), find

a. The ultimate nitrogenous oxygen demand
b. The ratio of the ultimate NBOD to the concentration of nitrogen in the waste.

Solution

a. Combining the two nitrification reactions (15) and (16) yields

$$NH_3 + 2O_2 \rightarrow NO_3^- + H^+ + H_2O \tag{17}$$

The molecular weight of NH_3 is 17, and the molecular weight of O_2 is 32. The foregoing reaction indicates that 1 g-mol of NH_3 (17 g) requires 2 g-mole of O_2 ($2 \times 32 = 64$ g). Since 17 g of NH_3 contains 14 g of N, and the concentration of N is 30 mg/L, we can find the final, or ultimate, NBOD:

$$\text{NBOD} = 30 \text{ mg N/L} \times \frac{17\text{g NH}_3}{14 \text{ g N}} \times \frac{64 \text{ g O}_2}{17 \text{ g NH}_3} = 137 \text{ mg O}_2\text{/L}$$

b. The oxygen demand due to nitrification divided by the concentration of nitrogen in the waste is

$$\frac{137 \text{ mg O}_2\text{/L}}{30 \text{ mg N/L}} = 4.57 \text{ mg O}_2\text{/mg N}$$

The total concentration of organic and ammonia nitrogen in wastewater is known as the *total Kjeldahl nitrogen* (TKN). As was demonstrated in the preceding example, the nitrogenous oxygen demand can be estimated by multiplying the TKN by 4.57. This is a result worth noting:

$$\text{Ultimate NBOD} \approx 4.57 \times \text{TKN} \tag{18}$$

Since untreated domestic wastewaters typically contain approximately 15–50 mg/L of TKN, the oxygen demand caused by nitrification is considerable, ranging from roughly 70 to 230 mg/L. For comparison, typical raw sewage has an ultimate carbonaceous oxygen demand of 250–350 mg/L.

Other Measures of Oxygen Demand

In addition to the CBOD and NBOD measures already presented, two other indicators are sometimes used to describe the oxygen demand of wastes. These are the *theoretical oxygen demand* (ThOD) and the *chemical oxygen demand* (COD).

The theoretical oxygen demand is the amount of oxygen required to oxidize completely a particular organic substance, as calculated from simple stoichiometric considerations. Stoichiometric analysis, however, for both the carbonaceous and nitrogenous components, tends to overestimate the amount of oxygen actually consumed during decomposition. The explanation for this discrepancy is based on a more careful understanding of how microorganisms actually decompose waste. While there is plenty of food for bacteria, they rapidly consume waste, and in the process, convert some of it to cell tissue. As the amount of remaining wastes diminishes, bacteria begin to draw on their own tissue for the energy they need to survive, a process called endogenous respiration. Eventually, as bacteria die, they become the food supply for other bacteria; all the while, protozoa act as predators, consuming both living and dead bacteria. Throughout this sequence, more and more of the original waste is consumed until finally all that remains is some organic matter, called humus, that stubbornly resists degradation. The discrepancy between theoretical and actual oxygen demands is explained by carbon still bound up in humus. The calculation of theoretical oxygen demand is of limited usefulness in practice because it presupposes a particular, single pollutant with a known chemical formula. Even if that is the case, the demand is overestimated.

Some organic matter, such as cellulose, phenols, benzene, and tannic acid, resist biodegradation. Other types of organic matter, such as pesticides and various industrial chemicals, are nonbiodegradable because they are toxic to microorganisms. The chemical oxygen demand (COD) is a measured quantity that does not depend either on the ability of microorganisms to degrade the waste or on knowledge of the particular substances in question. In a COD test, a strong chemical oxidizing agent is used to oxidize the organics rather than relying on microorganisms to do the job. The COD test is much quicker than a BOD test, taking only a matter of hours. However, it does not distinguish between the oxygen demand that will actually be felt in a natural environment due to biodegradation and the chemical oxidation of inert organic matter. It also does not provide any information on the rate at which actual biodegradation will take place. The measured value of COD is higher than BOD, though for easily biodegradable matter, the two will be similar. In fact, the COD test is sometimes used as a way to estimate the ultimate BOD.

6 The Effect of Oxygen-Demanding Wastes on Rivers

The amount of dissolved oxygen in water is one of the most commonly used indicators of a river's health. As DO drops below 4 or 5 mg/L, the forms of life that can survive begin to be reduced. In the extreme case, when anaerobic conditions exist, most higher forms of life are killed or driven off. Noxious conditions then prevail, including floating sludges; bubbling, odorous gases; and slimy fungal growths.

A number of factors affect the amount of DO available in a river. Oxygen-demanding wastes remove DO; photosynthesis adds DO during the day, but those plants remove oxygen at night; and the respiration of organisms living in the water as well as in sediments removes oxygen. In addition, tributaries bring their own oxygen supplies, which mix with those of the main river. In the summer, rising temperatures reduce the solubility of oxygen, while lower flows reduce the rate at which oxygen enters the water from the atmosphere. In the winter, ice may form, blocking access to new atmospheric oxygen. To model properly all of these effects and their interactions is a difficult task. A simple analysis, however, can provide insight into the most important parameters that affect DO. We should remember, however, that our results are only a first approximation to reality.

The simplest model of the oxygen resources in a river focuses on two key processes: the removal of oxygen by microorganisms during biodegradation, and the replenishment of oxygen through reaeration at the interface between the river and the atmosphere. In this simple model, it is assumed that there is a continuous discharge of waste at a given location on the river. As the water and wastes flow downriver, it is assumed that they are uniformly mixed at any given cross section of river, and it is assumed that there is no dispersion of wastes in the direction of flow. These assumptions are part of what is referred to as the *point-source, plug flow* model, illustrated in Figure 14.

Deoxygenation

The rate of deoxygenation at any point in the river is assumed to be proportional to the BOD remaining at that point. That is,

$$\text{Rate of deoxygenation} = k_d L_t \tag{19}$$

where

k_d = the deoxygenation rate constant (day^{-1})
L_t = the BOD remaining t (days) after the wastes enter the river, (mg/L)

The deoxygenation rate constant k_d is often assumed to be the same as the (temperature adjusted) BOD rate constant k obtained in a standard laboratory BOD test. For deep, slowly moving rivers, this seems to be a reasonable approximation, but for turbulent, shallow, rapidly moving streams, the approximation is less valid. Such streams have deoxygenation constants that can be significantly higher than the values determined in the laboratory.

Substituting (9), which gives BOD remaining after time t, into (19) gives

$$\text{Rate of deoxygenation} = k_d L_0 e^{-k_d t} \tag{20}$$

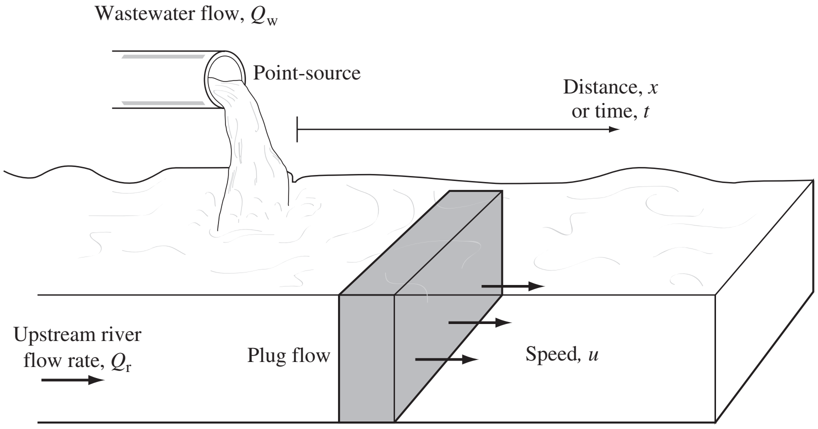

FIGURE 14 The point-source, plug flow model for dissolved-oxygen calculations.

where L_0 is the BOD of the mixture of streamwater and wastewater at the point of discharge. Assuming complete and instantaneous mixing,

$$L_0 = \frac{Q_w L_w + Q_r L_r}{Q_w + Q_r} \tag{21}$$

where

L_0 = ultimate BOD of the mixture of streamwater and wastewater (mg/L)
L_r = ultimate BOD of the river just upstream of the point of discharge (mg/L)
L_w = ultimate BOD of the wastewater (mg/L)
Q_r = volumetric flow rate of the river just upstream of the discharge point (m^3/s)
Q_w = volumetric flow rate of wastewater (m^3/s)

EXAMPLE 6 Downstream BOD

A wastewater treatment plant serving a city of 200,000 discharges 1.10 m^3/s of treated effluent having an ultimate BOD of 50.0 mg/L into a stream that has a flow of 8.70 m^3/s and a BOD of its own equal to 6.0 mg/L. The deoxygenation constant, k_d, is 0.20/day.

a. Assuming complete and instantaneous mixing, estimate the ultimate BOD of the river just downstream from the outfall.
b. If the stream has a constant cross section, so that it flows at a fixed speed equal to 0.30 m/s, estimate the BOD remaining in the stream at a distance 30,000 m downstream.

Solution

a. The BOD of the mixture of effluent and streamwater can be found using (21):

$$L_0 = \frac{1.10\ m^3/s \times 50.0\ mg/L + 8.70\ m^3/s \times 6.0\ mg/L}{(1.10 + 8.70)\ m^3/s} = 10.9\ mg/L$$

b. At a speed of 0.30 m/s, the time required for the waste to reach a distance 30,000 m downstream would be

$$t = \frac{30{,}000\text{ m}}{0.30\text{ m/s}} \times \frac{\text{hr}}{3600\text{ s}} \times \frac{\text{day}}{24\text{ hr}} = 1.16\text{ days}$$

So the BOD remaining at that point, 30 km downstream, would be

$$L_t = L_0 e^{-k_d t} = 10.9\, e^{-(0.2/\text{d} \times 1.16\text{d})} = 8.7\text{ mg/L}$$

Reaeration

The rate at which oxygen is replenished is assumed to be proportional to the difference between the actual DO in the river at any given location and the saturated value of dissolved oxygen. This difference is called the oxygen deficit, D:

$$\text{Rate of reaeration} = k_r D \tag{22}$$

where

k_r = reaeration constant (time^{-1})
D = dissolved oxygen deficit = $(\text{DO}_s - \text{DO})$ (23)
DO_s = saturated value of dissolved oxygen
DO = actual dissolved oxygen at a given location downstream

The reaeration constant, k_r, is very much dependent on the particular conditions in the river. A fast-moving, whitewater river will have a much higher reaeration constant than a sluggish stream or a pond. Many attempts have been made empirically to relate key stream parameters to the reaeration constant, with one of the most commonly used formulations being the following (O'Connor and Dobbins, 1958):

$$k_r = \frac{3.9\, u^{1/2}}{H^{3/2}} \tag{24}$$

where

k_r = reaeration coefficient at 20°C (day^{-1})
u = average stream velocity (m/s)
H = average stream depth (m)

Typical values of the reaeration constant k_r for various bodies of water are given in Table 9. Adjustments to the reaeration rate constant for temperatures other than 20°C can be made using (14) but with a temperature coefficient θ equal to 1.024.

The saturated value of dissolved oxygen varies with temperature, atmospheric pressure, and salinity. Table 10 gives representative values of the solubility of oxygen in water at various temperatures and chloride concentrations.

Both the wastewater that is being discharged into a stream and the stream itself are likely to have some oxygen deficit. If we assume complete mixing of the two, we can calculate the initial deficit of the polluted river using a weighted average based on their individual concentrations of dissolved oxygen:

$$D_0 = \text{DO}_s - \frac{Q_w\, \text{DO}_w + Q_r\, \text{DO}_r}{Q_w + Q_r} \tag{25}$$