Example 8.2

A sample treatment plant effluent begins to clarify after 13 days. What percent of the original BOD remains unsatisfied?

From table 8.3, the relative stability is 95%. Therefore, only 5% of the initial BOD remains unsatisfied.

D. CHEMICAL OXYGEN DEMAND

Unlike BOD, which is a measure of oxygen removed by biological organisms, chemical oxygen demand (COD) is a measure of maximum oxidizable substances. Therefore, COD is an excellent measure of *effluent strength*.

COD testing is required in environments of chemical pollution. In such environments, the organisms necessary to metabolize organic compounds may not exist. Furthermore, the toxicity of the water may make the standard BOD test impossible to carry out. The COD test also produces results faster than the BOD test. COD test results are usually available in a matter of hours.

If the toxicity is low, BOD and COD test results can be correlated. The BOD_s/COD ratio typically varies from 0.4 to 0.8. This is a wide range, but for any given treatment plant and waste type, the correlation is essentially constant. The correlation can, however, vary along the treatment path.

E. CHLORINE DEMAND

Chlorination destroys bacteria, hydrogen sulfide, and other noxious substances. For example, hydrogen sulfide is oxidized according to equation 8.13.

$$H_2S + 4H_2O + 4Cl_2 \rightarrow H_2SO_4 + 8HCl \qquad 8.13$$

Chlorine demand is the amount of chlorine (or its chloramine or hypochlorite equivalent) required to give a 0.5 mg/l residual after 15 minutes of contact time. 15 minutes is the recommended contact and mixing time prior to discharge since this period will kill nearly all pathogenic bacteria in the water. Typical doses for wastewater effluent are given in table 8.4.

Table 8.4
Typical Chlorine Doses

final process	dose (mg/l)
no treatment (straight discharge)	10–30
secondary sand filter	2–6
secondary activated sludge	2–8
secondary trickling filter	3–15
primary sedimentation	5–25

In actuality, the chlorine dose needs to be determined by careful monitoring of coliform counts and free residuals, since there are several ways that chlorine can be used up without producing significant disinfection. Only after uncombined (free) chlorine starts showing up is it assumed that all chemical reactions and disinfection are complete.[5]

Because of their reactivity, chlorine is initially used up in the neutralization of hydrogen sulfide and the rare ferrous and manganous (Fe^{++} and Mn^{++}) ions. The resulting HCl, $FeCl_2$, and $MnCl_2$ ions do not contribute to disinfection. They are known as *unavailable combined residuals*.

Plants and animals use nitrogen. Bacterial decomposition and the hydrolysis of urea produces ammonia, NH_3. This ammonia, once it enters the wastewater stream, forms ammonium ion, NH_4^+, also known as *ammonia nitrogen*.

Ammonia nitrogen combines with chlorine to form the family of *chloramines*. Depending on the water pH, *monochloramines* (NH_2Cl), *dichloramines* ($NHCl_2$), or *trichloramines* (nitrogen trichloride, NCl_3) may form.[6] Chloramines have long-term disinfection capabilities, and chloramines are therefore known as *available combined residuals*. Equation 8.14 is a typical chloramine formation reaction.

$$NH_4^+ + HOCl \rightleftharpoons NH_2Cl + H_2O + H^+ \qquad 8.14$$

The continued addition of chlorine after chloramine formation changes the pH, and *chloramine destruction* begins. Chloramines are converted to nitrogen gas (N_2) and nitrous oxide (N_2O). The destruction of chloramines continues with the continued application of chlorine, until no ammonia remains in the water. The point at which all ammonia has been removed is known as the *breakpoint*. Equation 8.15 is a typical chloramine destruction reaction.

$$2NH_2Cl + HOCl \rightleftharpoons N_2 + 3HCl + H_2O \qquad 8.15$$

In the *breakpoint chlorination* method, additional chlorine is added after the breakpoint in order to obtain free chlorine residuals. The free residuals have a high disinfection capacity. Typical free residuals are free chlorine (Cl_2), hypochlorous acid (HOCl), and hypochlorite ions. Equations 8.16 and 8.17 illustrate the formation of these free residuals.

$$Cl_2 + H_2O \rightarrow HCl + HOCl \qquad 8.16$$

$$HOCl \rightarrow H^+ + ClO^- \qquad 8.17$$

5 Chlorine kills most bacteria, but many viruses are resistant.

6 Lower pH favors the formation of di- and trichloramines.