CHEMISTRY OF WASTEWATER

Timothy G. Ellis
Department of Civil, Construction and Environmental Engineering, Iowa State University, Ames, Iowa, USA

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Summary

The chemistry of wastewater reflects human activities. Industrial, agricultural, and municipal activities are represented by the wastewater produced in each. Due to its value and scarcity, wastewater is treated, discharged to a receiving stream, and withdrawn for reuse by the downstream population. Consequently, the chemical and bacteriological composition must be monitored to ensure the public health. In addition, the oxygen consuming material in the wastewater must be minimized to protect the receiving stream from low dissolved oxygen conditions which can be deleterious to desirable aquatic species. Nutrients, such as nitrogen and phosphorus, should be removed to prevent eutrophication and siltation. Microbiological contaminants and other pollutants should be removed to protect downstream users, including contact users (e.g. boaters and swimmers). Typical municipal wastewater contains about 220 mg L^{-1} of both suspended solids and BOD. The organic composition of wastewater is approximately 50 percent proteins, 40 percent carbohydrates, 10 percent fats and oils, and trace amounts of priority pollutants and surfactants. The microbiological

composition of wastewater includes 10^5-10^8 CFU coliform organisms, 10^3-10^4 CFU fecal streptococci, 10^1-10^3 protozoan cysts, and 10^1-10^2 virus particles. This chapter discusses the water quality parameters concerning wastewater composition, generation, and treatment.

1. Introduction

Wastewater is the liquid end-product, or by-product, of municipal, agricultural, and industrial activity. As such, the chemical composition of wastewater naturally reflects the origin from which it came. In fact, the chemistry of wastewater reflects to a very high degree the chemistry of life. Just as wastewater chemistry reflects chemistry of human activities in life, so too, does wastewater microbiology reflect the microbiology of human activities in life. It is perhaps the microbiology of wastewater that presents the greatest concern to humanity from a public health standpoint.

The term 'wastewater,' however implies that it is a waste product to be discarded in an environmentally sound manner. This could not be farther from the truth. In fact, the world's available fresh water supply is about 3 percent of that total water supply. Only 20 percent of this amount is available for use in drinking water supplies. The remainder of the world water is salt water, which is costly to desalinate for drinking water purposes. Consequently, the water we use for drinking, washing, bathing, etc. ultimately ends up back in the stream, river, lake, or groundwater where it will be withdrawn, treated, and used again (see *Water Quality*). While it is not necessarily a positive mental image, the drinking water we are using today was the wastewater discharged by another community yesterday, or the day before, or the day before. Consequently, the chemical and microbiological composition of that wastewater must be monitored in order to safeguard downstream users. Current water use standards are enacted with this in mind. Table 1 provides a list of wastewater contaminants that are of concern, and the reasons that they are of concern.

Contaminants	**Reason for importance**
Oxygen consuming organic matter	Composed principally of proteins, carbohydrates, and fats, biodegradable organics are measured most commonly in terms of BOD (biochemical oxygen demand) and COD (chemical oxygen demand.) If discharged untreated to the environment, their biological stabilization can lead to the depletion of natural oxygen resources and to the development of septic conditions.
Suspended solids	Suspended solids can lead to the development of sludge deposits and anaerobic conditions when untreated wastewater is discharged in the aquatic environment.
Nutrients	Both nitrogen and phosphorus, along with carbon, are essential nutrients for growth. When discharged to the aquatic environment, these nutrients can lead to the growth of undesirable aquatic life. When

	discharged in excessive amounts on land, they can also lead to the pollution of groundwater.
Priority pollutants	Organic and inorganic compounds selected on the basis of their known or suspected carcinogenicity, mutagenicity, teratogenicity, or high acute toxicity. Many of these compounds are found in wastewater.
Refractory organics	These organics tend to resist conventional methods of wastewater treatment. Typical examples include surfactants, phenols, and agricultural pesticides.
Heavy metals	Heavy metals are usually added to wastewater from commercial and industrial activities and may have to be removed if the wastewater is to be reused.
Pathogens	Communicable diseases can be transmitted by the pathogenic organisms in wastewater.
Dissolved inorganics	Inorganic constituents such as calcium, sodium, and sulfate are added to the original domestic water supply as a result of water use and may have to be removed if the wastewater is to be reused.

Table 1. Important contaminants of concern in wastewater
Adapted from Metcalf and Eddy (1991) *Wastewater Engineering. Treatment Disposal Reuse*, G. Tchobanoglous and F.L. Burton (Eds.), 1820 pp. New York: McGraw-Hill.

2. Wastewater Analysis

Analysis of wastewater typically concentrates on the water quality parameters that affect the receiving stream. For instance, if the receiving stream for a wastewater discharge is a lake, the nutrients, nitrogen and phosphorus, in the wastewater may be the primary concern. Nutrients discharged to a lake or river can cause eutrophication, a condition that degrades water quality by increasing algae growth, depleting dissolved oxygen concentrations, and increasing sedimentation (see *Eutrophication and Algal Blooms*). If the receiving stream is a high quality river, the primary concern may be the oxygen consuming organics in the wastewater. Oxygen depletion in the river could lead to deterioration in the quality and diversity of fish species, and severe oxygen depletion will cause fish kills. The biochemical oxygen demand and chemical oxygen demand tests both measure the oxygen consuming organics in a wastewater sample. These tests do not identify individual components in the wastewater, but rather provide an indication of what effect the wastewater might have if discharged to a receiving stream where the dissolved oxygen concentration is impacted. Oxygen is sparingly soluble in water (e.g. at 25°C the equilibrium saturation concentration of oxygen in water is only 8.24 mg L^{-1}). The quality of the fish habitat begins to decrease when the dissolved oxygen concentration drops below 4 or 5 mg L^{-1}. Consequently, even if the receiving stream is at saturation, which is unlikely, that leaves only 3 or 4 mg L^{-1} of oxygen to be used for assimilation of the wastewater discharge.

2.1. Biochemical Oxygen Demand

In order to measure the extent to which a wastewater discharge will impact the dissolved oxygen concentration in a receiving stream (i.e. the body of water that the wastewater is discharged into), a measure of the oxygen consuming organic matter must be determined. One way to determine this is to measure the disappearance of oxygen from a bottle containing oxygen saturated water, a prescribed volume of the wastewater sample, a small amount of active biomass (primarily bacteria) seed, and any necessary nutrients for biomass growth. This is a direct measurement of the oxygen consuming capacity of the wastewater and is termed the biochemical oxygen demand (BOD) test (see *Biochemical Oxygen Demand*).

The general form of the equation for decomposition of organic matter during the BOD test is:

$$\text{organic matter} + \text{nutrients} + O_2 \xrightarrow{\text{biomass}} CO_2 + H_2O + \text{biomass} \qquad (1)$$

It should be noted that oxygen is consumed in the reaction and biomass is the catalyst for the reaction. Actually, the organic matter is the growth substrate (carbon and energy source) for the generation of new biomass, an end product of the reaction. Essential macro- and trace nutrients are also required for sustained growth of the microorganisms. Using glucose as an example (and ignoring the substrate being incorporated into biomass):

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \qquad (2)$$

The theoretical BOD of glucose can be calculated as:

$$\begin{aligned} \text{BOD} &= \frac{\text{grams of oxygen used}}{\text{grams of substrate used}} = \frac{6\times 32}{6\times 12 + 12 + 6\times 6} = \frac{192}{180} \\ &= \frac{1.067\,\text{gBOD}}{\text{grams of substrate utilized}} \end{aligned} \qquad (3)$$

As the biodegradation of organic matter proceeds, its remaining oxygen demand decreases. At any given time the rate of biodegradation can be modeled as a first order reaction (i.e. as a function of the remaining oxygen demand). A portion of the organic matter is also converted into cell material, or biomass, so its concentration is changing as well. If we were to look at all three events on the same plot of relative oxygen concentration versus time, it might look like that in Figure 1.

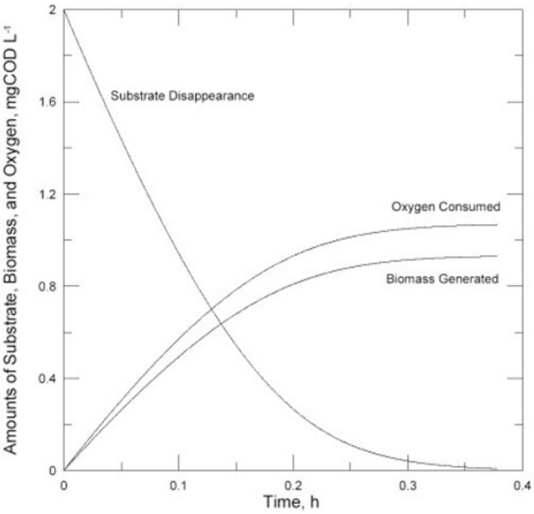

Figure 1. Theoretical plot of substrate disappearance, biomass growth, and oxygen consumption. Plot was generated with kinetic parameters similar to those typically measured for xenobiotic compounds and assumes a significant population of acclimated biomass.

The actual shape of plot will be determined by the experimental conditions at the beginning of the batch test (e.g. quantity of biomass seed, nature of substrate, acclimation of biomass, etc.). It should also be noted that, in this case, the initial oxygen demand of the substrate equals the sum of the oxygen consumed during the test and the concentration of biomass produced in oxygen units. In other words, one could perform a mass balance in terms of oxygen units. In practice, a mass balance on BOD is not very practical due to the high degree of variability in the BOD test.

In the laboratory procedure for determining the BOD concentration, the amount of biomass generated is considered negligible (or inconsequential), and only the two events (substrate depletion and oxygen consumption) are therefore considered. Depending on the biomass yield (milligrams of biomass formed per milligram of substrate utilized) and the experimental conditions, the actual measured concentration of BOD will vary. In fact, several measurements of the same sample (at the same dilution) are usually required to obtain reliable and reproducible results from the BOD test.

One of the potential difficulties in the BOD test is the interference of nitrification. The normal BOD test determines the carbonaceous BOD and excludes the effects of nitrification. Nitrification is the two-step process whereby ammonia is transformed to nitrate by autotrophic organisms (those that use an inorganic energy source and CO_2 for growth) as follows:

$$2NH_3 + 3O_2 \xrightarrow{\text{nitrosomonas}} 2NO_2^- + 2H^+ + 2H_2O \qquad (4)$$

$$2NO_2^- + 2H^+ + O_2 \xrightarrow{\text{nitrobacter}} 2NO_3^- + 2H^+ \qquad (5)$$

As can be seen from these two equations, the amount of oxygen required for nitrification is significant (and can actually exceed the amount of oxygen required to satisfy the BOD). Stoichiometrically, each milligram of nitrogen from ammonia (NH_3-N) requires 4.57 mg of oxygen to transform it biochemically to nitrate. If a wastewater contains 200 mg L^{-1} BOD_5 and 44 mg L^{-1} NH_3-N, the oxygen required for BOD removal and nitrification will be approximately the same. In practice, the total oxygen requirement is not realized since some of the ammonia is converted into new cell material, and the actual demand is usually closer to 4.3 mg O_2 per mg NH_3-N. In practice, however, the value of 4.57 mg O_2 per mg NH_3-N is often used as a conservative estimate.

In the BOD test, the carbonaceous BOD is usually the desired measurement since ammonia can be measured quickly and directly (e.g. using an ammonia probe). On the other hand, the BOD test is typically run for 5 days (designated as BOD_5). The reason for the 5-day BOD dates back to the early 19th Century in England where it was determined that it took approximately 5 days for wastewater to travel from London to the mouth of the Thames River. Thus, by the time the wastewater traveled to the mouth of the river, its 5-day oxygen demand had been realized, and the impact on the river could be accounted for. The five-day time period is also convenient since it usually takes the slow growing nitrifiers in the seed culture longer than five days to achieve significant numbers to impact the oxygen consumption noticeably. Nevertheless, Standard Methods published in 1998 recommend the use of a nitrification inhibitor during the BOD test so that only oxygen uptake associated with the oxidation of organic compounds (i.e. carbonaceous BOD or CBOD) is measured during the test. This inhibitor, allylthiourea, is not thought to significantly affect the growth of the heterotrophic organisms (those organisms that use the carbonaceous BOD as a carbon and energy source).

2.2. Chemical Oxygen Demand

An alternative to the BOD test for determining the oxygen consuming potential of a wastewater sample is the chemical oxygen demand (COD) test. As the name implies, the carbonaceous oxygen demand is oxidized chemically in the COD test. Like BOD, the units for COD are in milligrams of oxygen per liter (mg L^{-1}). The advantage of this test is that it is quick and reproducible. The disadvantage is that not all of the measured COD can be degraded biologically. Therefore, there is still a need to ascertain what the biodegradable portion of the oxygen demand is, since that is how the performance of biological wastewater treatment systems (e.g. activated sludge, trickling filters, anaerobic digesters, rotating biological contactors, oxidation ponds, and lagoons) will be evaluated. In addition, the BOD (not COD) is the component that is expected to induce an oxygen demand in the receiving stream. There are also some interferences in the COD test. For instance, low molecular weight fatty acids and aromatic hydrocarbons may not be well oxidized during the test and inorganic ions (chloride and nitrite for instance) may be oxidized. The addition of certain catalysts during the test can eliminate most of these interferences.

The real advantage of the COD test is that it is a measure of the energetics of the system. If one wants to keep track of a biological reaction, they must know what the energetics of the reaction are (i.e. what are the electron donors and electron acceptors for the system). Microorganisms degrade pollutants in biological treatment systems to our benefit, but also so that they can grow and reproduce. They require two major things: carbon and energy for growth. They also need lesser quantities of macro nutrients, nitrogen, phosphorus, and sulfur in addition to trace amounts of micronutrients. If we can keep track of the flow of carbon and the flow of energy in a system, we can understand the nature and extent of the biochemical reactions occurring. If we can keep track of, and manipulate, the biochemical reactions, we can engineer biological treatment systems to our advantage. The two main items to monitor are carbon and energy. Unfortunately, carbon is difficult to keep track of since upon mineralization of an organic compound, it is solubilized in water or released as a gas in the form of carbon dioxide (CO_2). The best way to track changes in carbon species is through ^{14}C labeling, but this obviously requires sophisticated laboratory procedures and equipment (e.g. radiolabeled carbon compounds and liquid scintillation counting). Energy equivalents, or specifically electrons, are much easier to measure. When we measure the amount of oxygen consumed in a reaction, we are in essence measuring the electrons transferred from the organic compound to the terminal electron acceptor (i.e. oxygen). Performing a mass balance on electrons is much simpler than on carbon, since all we need to do to balance electrons is measure the chemical oxygen demand of our starting and end products and measure the amount of oxygen consumed during the reaction (or methane produced if it is an anaerobic or methane producing reaction).

For instance, consider the reaction in Eq. (2) in which glucose is converted to carbon dioxide and water by a stoichiometric amount of oxygen (1.067 milligrams of oxygen per milligram of glucose). If we know the concentration of glucose both before and after biological treatment and calculate the biomass concentration before and after, we will know how much oxygen was consumed during the conversion of glucose to biomass and end products. This way we have a much better indication of what the reactions are than if we simply measure the total carbon concentration before and after treatment. In addition, the analysis of COD is much more practical than the analysis for specific pollutants.

The advantages of the COD test are that it is relatively fast and the results are reproducible. The disadvantage is that it measures everything, including non-biodegradable organic matter that can be oxidized by potassium dichromate. In addition, the test produces a small amount of hazardous waste that must be disposed of properly. Thus, the measured oxygen demand in the COD test may differ due to sampling and analytical error, and possible interferences in the COD procedure. The measured BOD may differ for the same reasons in addition to the fact that a portion of the compound will be incorporated into new biomass. A list of the theoretical oxygen demand of a variety of substances that can be found in municipal and industrial wastewater is provided in a book by Pitter and Chudoba published in 1990. The list of chemicals is organized by compound type (e.g. hydrocarbons, alcohols/phenols, aldehydes, ketones, quinones, organic and amino acids, esters, ethers, amines, amides, nitriles, halogen and nitro- derivatives, heterocyclic compounds, saccharides, alkyl benzene sulfonates and alkyl sulfates, dyes, and miscellaneous substances). From this extensive list of chemicals, two points should be noted. First, there is a large number of compounds that can be present in a wastewater samples. Second, the oxygen demand that could be exerted from a known quantity of a specific pollutant can be quickly determined.

2.3. Solids

Solids are an important constituent to measure in any wastewater sample. Solids in a wastewater effluent represent a pollutant load in addition to a potential sediment load on a receiving stream. There are two main categories of solids: suspended and dissolved. Typically, the division between the two is somewhat arbitrary. For instance, whatever is filtered out of a sample by a 0.45-1.2 µm filter is considered suspended solids. Dissolved solids are constituents that pass through the filter. Within the dissolved and suspended solids classification, the solids can be further characterized as volatile or fixed solids. Volatile solids will combust at a temperature of 550°C and fixed solids will not. The implication is that the volatile solids represent the organic portion of the solids. In a biological treatment system, the volatile solids are often associated with the biomass and can be used as a measure of the microorganism population. The difficulty with this assumption is that often the organic solids in the wastewater fed to the system are incorporated into total solids retained in the system. Determining the volatile portion of these solids does not guarantee that the solids are part of the active degrading population. Therefore, care must be exercised in correlating the volatile solids concentration with the microbial population.

The dissolved solids in the sample include the organic pollutants in solution (carbohydrates, proteins, fats, oils, surfactants, volatile acids, urea, ammonia, trace pollutants) as well as inorganic compounds, some of which were present in the source drinking water. Table 2 shows the relationship between suspended, dissolved, fixed, and volatile solids.

Total Solids (TS)	Total Suspended Solids (TSS)	Total Dissolved Solids (TDS)
Total Volatile Solids (TVS)	Volatile Suspended Solids (VSS)	Volatile Dissolved Solids (VDS)
Total Fixed Solids (TFS)	Fixed Suspended Solids (FSS)	Fixed Dissolved Solids (FDS)

Table 2. Solids matrix showing the relationship between volatile, fixed, dissolved, and suspended solids. Rows can be added from the bottom to get the constituents on the top (e.g. FSS+VSS=TSS) and analogously columns can be added from the right (e.g. TDS+TSS=TS).

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Bibliography

Csuros M., Csuros C. (1999). *Microbiological Examination of Water and Wastewater*, 324 pp. Boca Raton, Florida, USA: CRC Press. [This text provides a brief but comprehensive description of some of the microbiological characteristics of natural water sources.]

Ellis T.G., Eliosov B. (2002). *Field Validation of Biokinetic Coefficients for Predicting Degradation of Organic Compounds*, Project 98-CTS-3 final report submitted to the Water Environment Research Foundation, 160 pp. Alexandria, Virginia, USA. [This report provides details on predicting the removal efficiencies and effluent concentrations of individual contaminants in wastewater treatment plants.]

Metcalf and Eddy (1991). *Wastewater Engineering. Treatment Disposal Reuse.* G. Tchobanoglous, F.L. Burton (Eds.), pp. 1820. New York: McGraw-Hill. [This is an indispensable volume on the design of wastewater treatment systems.]

Pitter P., Chudoba J. (1990). *Biodegradability of Organic Substances in the Aquatic Environment,* 306 pp. Boca Raton, Florida, USA: CRC Press. [This is a unique book that compiles biodegradation rate data for an extensive list of organic compounds.]

Standard Methods for the Examination of Water and Wastewater (1998) American Public Health Association, American Water Works Association, and Water Environment Federation, 20th Edition, 1220 pp. Washington, D.C. [This is an essential handbook describing the analytical methods used for water and wastewater.]

Biographical Sketch

Timothy Ellis has been teaching in the Department of Civil, Construction, and Environmental Engineering at Iowa State University since 1995. Currently he is an Associate Professor of Environmental Engineering. He received his Ph.D. in environmental systems engineering in 1995 at Clemson University with Professor Les Grady where he furthered the development of respirometric techniques for measuring biodegradation rates of xenobiotic organic compounds. He received his M.Sc. degree in environmental engineering in 1988 at Georgia Tech with Dr. Fred Pohland where he studied the biodegradation of consumer polymer products in simulated landfill environments. In addition to his graduate studies, he has worked for Parsons Engineering Science in Fairfax, Virginia and in Abu Dhabi, United Arab Emirates where he was involved in the process design of water and wastewater treatment facilities, including a 10 million gallons per day (MGD) sequencing batch reactor (SBR) facility for the City of Abu Dhabi. Prior to his masters degree, he worked for the City of Baltimore at the Back River Wastewater Treatment Plant in process control, design, and start-up.

At Iowa State University Dr. Ellis has been involved in teaching and research in biological processes for the treatment of wastewater and residuals. His recent research involves several new technologies, including the static granular bed reactor (SGBR), an anaerobic process that takes advantage of anaerobic bacteria’s propensity to form dense granules. He is also involved in research to provide early warning detection of toxic or inhibitory compounds in water and wastewater. He is active in committees with the American Society of Civil Engineers, Water Environment Research Foundation, and Water Environment Federation. He has authored or co-authored over 50 publications appearing in international journals and conference proceedings. He has been the major professor for over 20 MS and PhD students. In addition, he holds a patent for the SGBR (U.S. Patent 6,709,591).