# BASIC CONCEPTS IN WATER POLLUTION CONTROL AND OVERVIEW OF WATER POLLUTION CONTROL METHODS*

By

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Water pollution may be defined as a change in water quality which causes an adverse effect on a beneficial use. The change itself cannot be considered pollution, since a change in the environment need not be harmful. The change can be considered harmful only if it alters something which is considered to be beneficial and desirable.

Among the many important concepts in water pollution control, the one that stands out is biochemical oxygen demand or BOD. The BOD is a measure of the amount of oxygen required by bacteria to oxidize waste aerobically to carbon dioxide and water.

If we were to introduce an amount of organic matter into some water and monitor its decomposition, we would observe that the amount of organic material remaining would decrease exponentially with time. The amount of BOD which remains after some period of time is proportional to the remaining organic material, which results in a curve as shown in Figure 1. The initial value of BOD will of course be the total oxygen requirement to oxidize the organic material. This quantity is called the ultimate BOD, of BOD.

Usually when curves of BOD versus time are drawn, they are actually made for BOD utilized and not BOD remaining. BOD utilized will be proportional to the amount of organic matter which has been oxidized and hence, will have the shape shown in Figure 2. This distinction between BOD utilized and BOD remaining can cause confusion and one must be aware of the difference.

A standard way to measure BOD is to determine the amount of oxygen required by the bacteria during the first 5 days of decomposition (at 20°C). This is the 5-day BOD called $BOD_5$ which is shown in Figure 2. The five-day BOD, measured at 20°C is the standard used for measuring the biochemical oxygen demand of wastewaters.

The importance of the concept of BOD in water quality management must be emphasized. Consider that normal domestic sewage may have a 5-day BOD of around 200 mg/1 and that industrial sew-

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age may have a BOD of several thousands of milligrams per liter. Compare these requirements for oxygen to the amounts actually dissolved in water (the saturation value at 20°C is only 9.2 mg. 1). It is thus easy to anticipate the quick depletion of oxygen in any receiving water unless the dilution factor is quite high. Depleting the water of oxygen will kill the fish and the anaerobic decay products will be extremely objectionable.

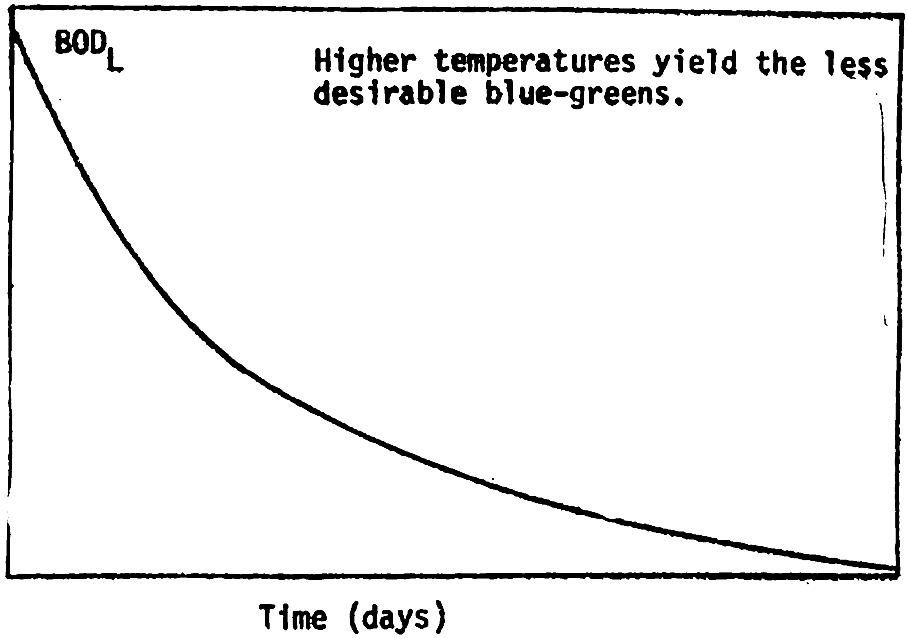


FIG. 1. *BOD remaining as a function of time with initial value BODL*

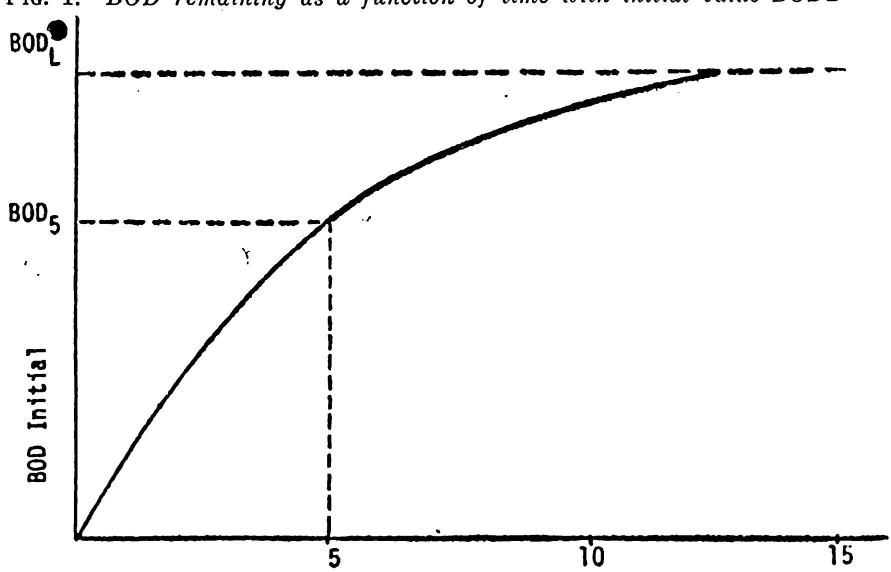


FIG. 2. *This is the usual curve for BOD, and is actually BOD utilized. Also shown is the 5 day BOD.*

It should be mentioned that there is a secondary effect which causes the demand for oxygen to suddenly increase after about 8-10 days. The organic nitrogen in the wastes in converted to ammonia during decomposition, and the subsequent oxidation of the ammonia to nitrite ($NO_2$) and then nitrate ($NO_3$) requires oxygen. This process of nitrification part of the nitrogen cycle

$$\underset{\text{ammonia}}{NH_3} \xrightarrow[\text{nitrite bacteria}]{0_2} \underset{\text{nitrite}}{NO_2} \xrightarrow[\text{nitrate bacteria}]{0_2} \underset{\text{nitrate}}{NO_3}$$

The total oxygen demand curve showing both the carbonaceous demand and the nitrification requirement is shown in Figure 3.

*THE OXYGEN SAG CURVE*

We have seen that when wastes are discharged into a body of water, the amount of dissolved oxygen will decrease to oxidation by bacteria. Opposing this drop is dissolved oxygen is reaeration which replaces oxygen through the surface, at a rate which is proportional to the depletion of oxygen below the saturation value. The simultaneous action of deoxygenation and reaeration produces what is called the oxygen sag curve, as shown in Figure 4. The DO curve initially drops as the wastes deplete the oxygen faster that it can be replaced. At the point where the DO is a minimum, the rate of reaeration becomes equal to the rate of oxygen utilization. Beyond that point the rate of reaeration exceeds the rate of utilization and the DO level eventually returns to normal. This sequence is referred to as the natural self-purification ability of water.

The horizontal axis of the oxygen sag curve may be either time or distance. If for example, a certain amount of waste is released all at one time into some impounded water, the DO level will be a function of time. If, however, there is a continuous discharge of wastes into a stream, then the oxygen sag curve will be a function of the distance downstream from the point of discharge.

As we move downstream from the point of discharge, and the dissolved oxygen begins to drop, there will be a corresponding change in the biota. Normal game fish will be replaced by fishes tolerant of the turbid, low DO waters. At the point downstream where the DO reaches its lowest value, conditions will be at their worst. If the stream goes anaerobic, there will be no fish and the only organisms present will be those able to obtain their oxygen from the surface, or those which are tolerant of low oxygen conditions.

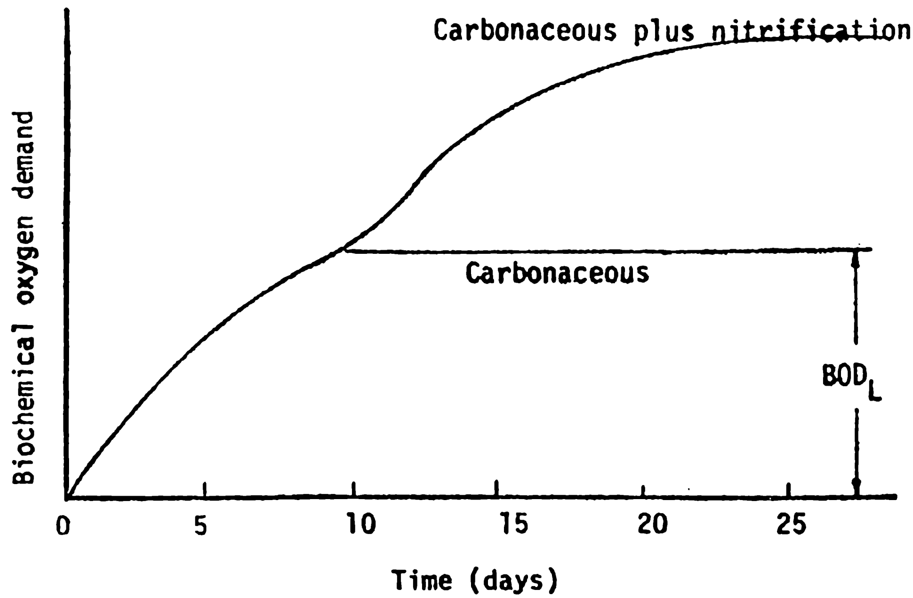


FIG. 3. *The complete BOD curve includes the carbonaceous and nitrification demands.*

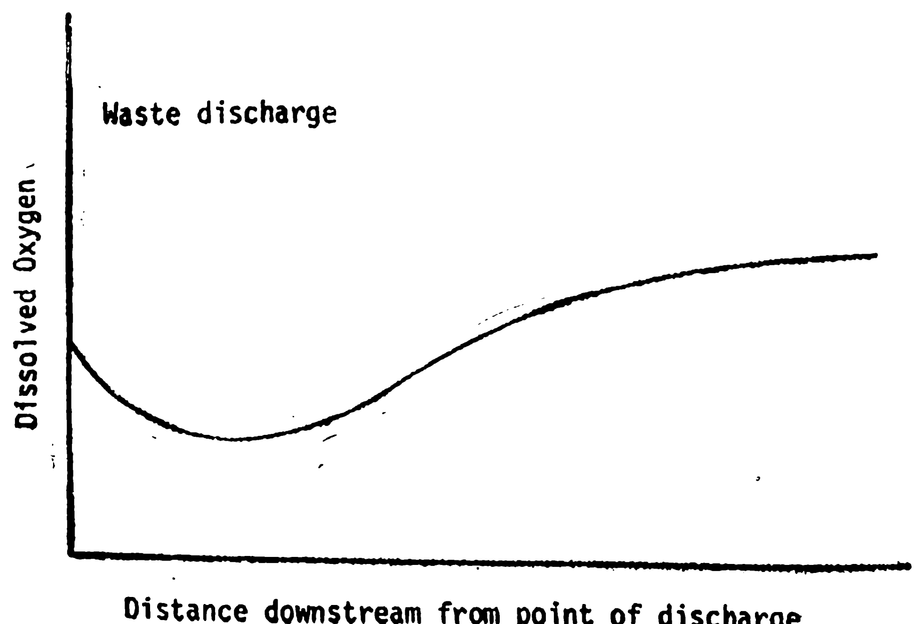


FIG. 4. *The oxygen sag curve.*

*TEMPERATURE*

Another important pollution parameter is temperature and its significance as far as possible environmental damage is concerned is not yet recognized by many people in industry.

Many of the deleterious effects to aquatic life associated with thermal pollution stem from the increased rate of metabolism that occurs as temperature increases. Generally, the metabolic rate doubles for every 10°C (18°F) rise in temperature. This causes an increased demand for oxygen by the organism. At the same time, the dissolved oxygen in the water decreases with increasing temperature. Thus, as the organism's demands for oxygen are increasing the amount available is decreasing.

A second factor that decreases the dissolved oxygen is the increased rate of decomposition of wastes that occurs at higher temperatures. The faster the decomposition, the more oxygen will be required. This causes a lowering of the oxygen sag curve as a shown in Figure 5, which increases the probability that the minimum value of DO may drop below that required for survival of the fish. Thus, there is the possibility that a stream which previously might have been able to accept a certain sewage load (BOD) without deleterious effects, may, with the addition of a thermal load, no longer be viable.

Raising the water temperature causes many changes in the local community of organisms. For example, in Figure 6, the type of algae that predominates is shown to be very dependent on temperature. The blue-green algae, characteristic of higher temperatures, are in many respects the least desirable food organisms for aquatic life. They are the algae most responsible for taste and odor problems in water and they are even toxic to some organisms. Ecosystems, recall, are sensitive to changes in the food chain, so the shift represented here, at the bottom of the chain, can be very important.

There are more subtle effects which act to disrupt ecological communities subjected to temperature stresses. Organisms often can become acclimated to different temperatures providing the change in temperature is made slowly enough (e.g. a matter of several weeks). A rapid change in temperature can kill an organism, even if the same change, when made slowly, is not lethal. From this point of view, it is unfortunate that power plants sometimes not only have rapid daily changes in thermal output due to changing loads, but periodically they shut down altogether for maintenance, and, in the case of nuclear power plants, refueling. Thus it becomes difficult if not impossible, for flora and fauna to become acclimated to the temperature.

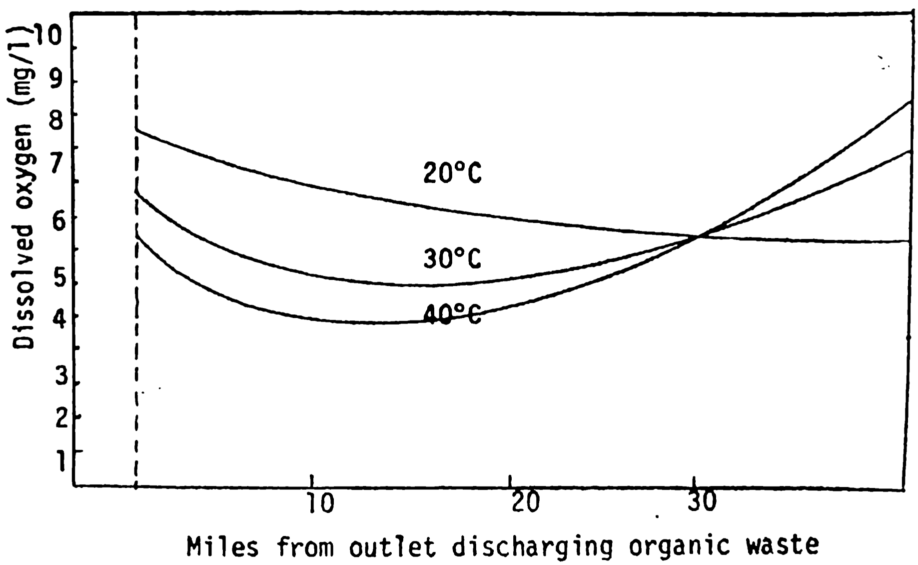


FIG. 5. *Relation between temperature and oxygen profile showing the minimum point is lower at higher temperatures.*

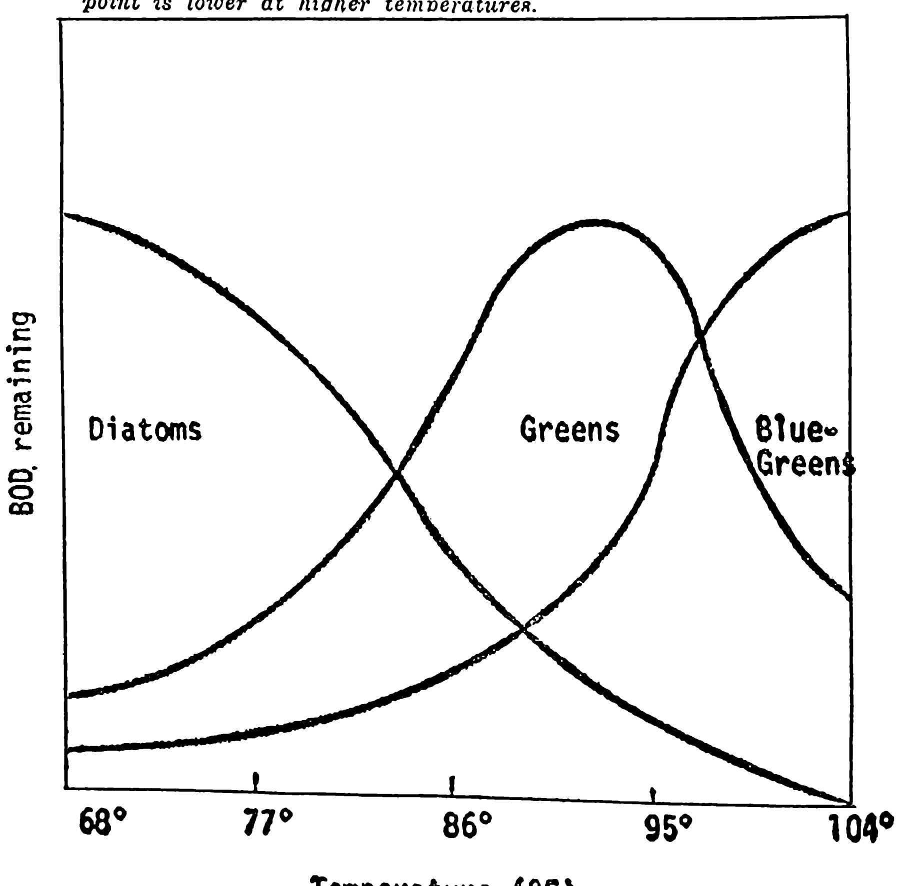


FIG. 6. *Effect of temperature on types phytoplankton.*

*Floating, Suspend, Settleable, and Dissolved Solids*

A third parameter which is also of great significance in wastewater treatment and pollution abatement is the presence of solids in the wastewater.

The presence of floating materials in rivers or lakes is objectionable even if they do not harm marine organisms because they are unsightly. Settleable solids, on the other hand, coat the bottom of these waterways and prevent the growth of bottom-living organisms.

Fine suspended solids cause turbidity or interference of transmitted light. Silt and sediment are the principal causes of turbidity, but sewage and some industrial wastes—like effluents from ceramic industries—also contribute significantly to the concentration of suspended particles in rivers and lakes.

Silting and sedimentation rates are highly variable. They depend on the amount of rainfall, the kinds of rocks and soil, the amount of plant cover and land use. Rapid use of forests for timber contributes significantly to the silting of rivers. Construction of residential areas, shopping centers, highways and other facilities associated with urbanization expose and reshape soil material. During rainstreams, sediment is washed into stream from these areas where soil is exposed.

The ability to exist by some fixed organisms, such as the oyster, is adversely affected by the presence of fine suspended solids and sediments. In addition, these solids affect the photosynthetic activity of marine plants on which some aquatic animals feed on.

Industrial effluents containing large amounts of dissolved solids or salts can adversely affect the quality of rivers which are used for irrigation purposes. In addition, a drastic change in the salinity of a river causes an adverse affect on fresh water aquatic life.

*Tainting Substances*

A fourth parameter may be classified under the general term *tainting substances.* Tainting substances are those that, while not causing death of an organism, render it unfit for its previous use. Small quantities of some chemicals like phenols and petroleum products such as the aromatics will render fish inedible because of the production of offensive or objectionable tastes in the flesh of the animal.

Pathogenic bacteria and viruses discharged with human wastes can be accumulated in an organism such as the oyster, which is not in itself harmed but because of the accumulation is made unfit for human consumption.

Synthetic detergents discharged into water streams cause foaming and frothing, and detergent wastes retained in treated water supplies cause taste and odor problems.

Detergents were developed as cleaning agents to overcome the disadvantages of ordinary soap in hard water. While ordinary soap loses much of its cleaning power in hard water due to the formation of insoluble particles or scum, detergents, on the other hand, maintain their effectiveness and do not produce scum.

Synthetic detergent contain a chemical called alkyl benzene sulfonate of ABS. It is this chemical that causes foaming in water streams. Alkyl benzene sulfonate is a highly stable compound. It is not biodegradable and it can travel long distances in rivers and through the soil without losing its chemical identity.

This type of pollution is widespread and, indeed, is one of the major water polution problems now encountered.

*Toxic Substances*

A fifth and final grouping of important water pollution parameters fall under the general substances. Toxic substances are those that directly affect living organisms present in the water. Acid and alkaline wastes are examples of those that directly kill living organisms. Other substances are toxic even at very low concentrations. These are: mercury, silver, arsenic, copper, chromium, zinc, and cyanides. Of these substances, mercury pollution is the most dangerous.

The most common sources of mercury pollution are caustic soda-chlorine plants employing the electrolytic method and pulp and paper mills using mercury compounds as biocides. Mercury is usually discharged into the environment as inorganic divalent mercury, elemental mercury, phenyl mercury, or an alkoxy-alkyl mercury. In any case, once mercury reaches the lake or river, it tends to be converted to methyl mercury which is highly toxic. This chemical conversion can happen before or after the mercury is taken in by the fish. For example, pike has been found with mercury concentrations up to 3,000 times more than that of the water in which they swim.

Once ingested by man, mercury, like lead, accumulates in the body, specifically in the liver, kidneys, and the brain. According to some studies, neurological symptoms begin to show up when the mercury concentration in the brain reaches about 20 ppm. Acute and chronic poisoning can cause: numbness and tingling lips, hands, and feets; inability to coordinate voluntary muscular movements; impairment of speech, vision, and hearing; emotional disturbances and death. When pregnant women eat mercury-contaminated fish, the mercury compound can accumulate in the fetus' neurological tissues, resulting in cerebral palsy or mental retardation.

Other poisonous substances like DDT, aldrin, dieldrin, endrin, heptaclor and toxamphene can also be ingested by minute aquatic organisms and vengers. Fish feed on these poisoned organisms and build concentrations of these toxic substances and their visceral fat. Metal factories and chemical plants throughout the world discharge trillions of gallons of wastewater containing these toxic substances into rivers, lakes and waterways until they finally end up in the oceans where they can remain poisonous for at least 20 years.

## WASTEWATER TREATMENT METHODS

There are two ways of classifying wastewater treatment methods. One way is to classify them according to the degree of treatment or purification attainable. With this classification, treatment methods are referred to as primary, secondary, or tertiary treatment processes. The second way is to classify them according to the mechanisms involved in treatment process. Hence, treatment methods may be classified as physical, chemical, or biological.

### *Physical Methods*

Physical treatment methods involve only physical operations and they can be used for the primary, secondary, or tertiary treatment of industrial wastes. These operations involve the physical removal of solids from the wastewater and they are classified as primary because the resulting effluent usually requires additional treatment before it can be safely discharged into a watercourse.

Secondary physical methods include filtration and foam separation while the physical methods used for the tertiary treatment of water include activated carbon adsorption, distillation, and reverse osmosis.

### *Chemical Methods*

Chemical ranging from ordinary limestone to complex polyelectrolytes are used in wastewater treatment. Chemical treatment methods include the neutralization of acidic or alkaline wastes; oxidation, reduction and precipitation of color, odor, and heavy metals; the coagulation and flocculation of colloidal solids and oil emulsions.

Chlorine, as liquid chlorine or as hypochlorite salts, is the most common chemical oxidant used in wastewater treatment. The treatment of sulfides from refining wastes and chemical plants and the destruction of highly toxic cyanides from the wastewaters of the metal plating industries are two of the most common uses of chlorine for wastewater oxidation. Chlorine reacts with sulfides according to the following reactions:

$$CI_2 + H_2S = S + 2\ HCI$$
$$3\ CI_2 + H_2S + 2H_2O = 6\ HCI + SO_2$$

For cyanides the chemical reactions are:

$$CN + CI_2 + H_2O = CNO^- + 2\ HCI$$

$$2\ CN^- + 5\ CI_2 + 4\ H_2O = 8\ HCI + 2\ CO_2 + N_2 + 2\ CI^-$$

Notice that in all of the above reactions, HCI is produced thereby requiring the neutralization of the acid.

The treatment of toxic chromate ion ($CrO_4^=$), which is present in the wastewaters of the metal finishing industry, usually requires the use of a reducing agent like sulfur dioxide. In this treatment process, the chromate ion is reduced to trivalent chrome which can later be precipitated as solid metal hydrate. The chemical reaction proceeds as follows:

$$Na_2Cr_2O_7 + 3SO_2 + 2H_2SO_4 = Cr_2\ (SO_4)_3 + Na_2SO_4 + H_2O$$

Other common wastewater reducing agents include ferrous chloride, sodium metabisulfite, and hydrogen sulfide.

Fluoride ion from glass manufacture and cupola wastewater is usually removed by precipitation to calcium fluoride, $CaF_2$, using $Ca(OH)_2$ as the precipitating agent. Other precipitation reactions in wastewaters are the removal of aluminate from aluminum etching and anodizing plants, sulfide from chemical plants, and phosphate from domestic sewage and fertilizer plants. In the case of phosphates, the reactions are:

$$2PO_4^{-3} + AI_2(SO_4)3 = 2AIPO_4 + 3SO_4^=$$
$$PO_4^{-3} + FeCI_3 = FePO_4 + 3CI^-$$

The removal of suspended and colloidal solids from water can be enhanced by coagulation and flocculation. Coagulation differs from flocculation in that the former is an electrochemical process while the latter is physico-chemical in nature. The stability of a colloidal suspension is due to the presence of electrostatic repulsive forces between particles. These electrostatic repulsive forces are brought about by the absorption of similarly charged ions on the surface of the colloidal solids: A measure of the magnitude of these electrostatic forces is the zeta potential. By adding inorganic salts like NaCI, $CaCI_2$, etc. the zeta potential between suspended particles is lowered thereby allowing van der Waals attractive forces between particles to predominate. This results in particle-to-particle attachment or coagulation. On the other hand, flocculation is achieved by the addition of long-chain organic polyelectrolytes (4, 5, 6). The aggregation is achieved by a two-step process: (1) As the polyelectrolytes are added, some segments adsorb into the particles surface while the rest remain extended from the surface; (2) the extended segments are then absorbed into the surface of the other particles or get entangled with the other extended segments producing "bridges" which interconnect several particles. The flocs that are produced are, therefore, large, loose, and easier to settle than the coagulation produced during coagulation. Typical flocculants are polyacrylamides and poyamines with molecular weights ranging from 100,000 to 6,000,000.

With the exception of neutralization, most chemical methods are used for secondary or tertiary treatment of wastewater.

*Biological Treatment*

Biological wastewater treatment is nothing but a duplication of nature's self-purification process under contained, concentrated, and controlled conditions. This treatment method may be classified as aerobic or anaerobic. Under aerobic conditions, microorganisms use the dissolved oxygen present in water to convert organic wastes to carbon and water. Under anaerobic conditions, dissolved oxygen is absent. Anaerobic microorganisms use bound oxygen in compounds such as nitrates, to convert dissolved organics into organics acids and alcohols. Further decomposition yields carbon dioxide and methane.

Most biological treatment processes like the use of stabilization ponds, aerated lagoon, activated sludge process, and trickling filters and classified as secondary treatment processes. Tertiary biological treatment methods include aerobic denitrification and algae harvesting.

Aerobic denitrification is specially suited for treating wastewater that is already low in organic waste content but still high in nitrates. In this method, an organic chemical like methanol or acetic acid is added as a source of carbon. The waste is then placed in an anaerobic environment during which the nitrate is reduced to nitrogen gas by denitrifying bacteria. With methanol, the biochem cal reaction is:

$$6H^+ + 6NO_3^- + 5CH_3OH \overset{\text{bacteria}}{=} 5CO_2 + 3N_2 + 13H_2O$$

The most common method employed in the treatment of industrial effluents high in bio-degradable organic content—such as distillery wastes from the production of ethyl alcohol from molasses—is the activated sludge process. Depending upon several operating variables but particularly the B.O.D. loading and the ratio of the B.O.D. to the mixed liquor suspended solids (BOD/MLSS), activated sludge processes may be classified an extended, conventional, and high rate. The conventional activated sludge process, which is the most commonly used type, represents the best compromise between costs and degrees of purification attainable. While the extended aeration type of activated sludge is capable of more than 95% BOD removal, compared to 90% in the conventional type, the land area requirement for the former could be as high as three times the land area needed for the latter. On the other hand, high rate activated sludge is capable of only 50% to 70% BOD removal.