

# Industrial Wastewater Treatment

Performance of biological systems must be evaluated according to the chemical stoichiometry and kinetics of the process. Physical/chemical treatment should also be considered. In any case, the chemical engineer must not be constrained by traditional approaches.

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During treatment of wastewater by biological oxidation, microorganisms, principally bacteria, use organic carbon as an energy source and convert it into bacterial cells. Organic material must be in solution in order to be utilized. Although bacteria can dissolve particulate matter by enzyme hydrolysis, this step may be the limiting one in process kinetics.

Of course, particulate material and inorganic constituents can be removed by physical and/or chemical methods rather than bacterial action. Biological oxidation for removal of suspended or colloidal particles is neither necessary nor attractive from a process design standpoint.

Many industrial wastes contain little or no particulate material but have high concentrations of dissolved organic compounds. Designing a process for biological oxidation of these wastes requires the use of chemical stoichiometry and kinetics. This is true because the oxidation process for a particular waste can be described by a stoichiometric equation, and the oxidation rate of a particular waste is specific to the system.

## Design Parameters

It is important to differentiate between process and system performance. This will be seen when attempts are made to control and assess the performance of a wastewater treatment plant. Biological oxidation is simply a process for converting soluble organics to bacteria and should be evaluated on that basis. Poor effluent quality caused by solids overflow from a secondary clarifier affects system performance but does not reflect process performance.

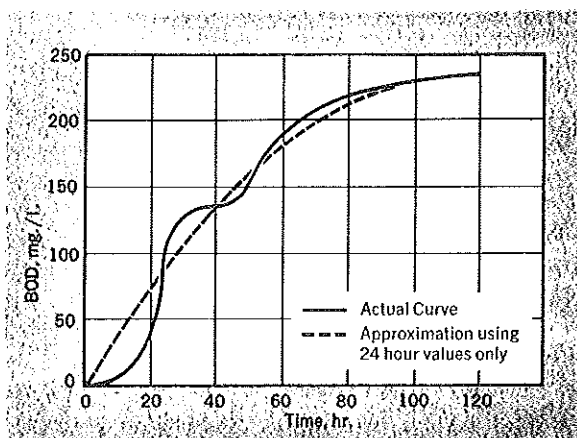
Biological oxidation generally is accomplished by a heterogeneous population of microorganisms. However, because some wastes contain complex organics that cannot be metabolized by all bacteria, populations that develop may sometimes approach a pure culture.

Design parameters should primarily involve the measurement of soluble substances. Soluble food is quickly converted into cell material: usually within 24 hours by

an adapted culture. Then oxygen uptake ceases for all practical purposes. One sharp decline in oxygen consumption occurs before reaching the theoretical oxygen requirement. A further increase in the oxygen uptake rate denotes secondary growth.

The progression of cumulative oxygen uptake by bacteria feeding on a single component soluble substrate exhibits a plateau that corresponds to the utilization of all primary substrate. Soluble substrate is defined as that amount of material which passes through a 0.45 micron filter. Data from a glucose solution in Fig. 1 show how a first order curve (with respect to unexerted biochemical oxygen demand) can be passed through values taken at 24-hour intervals. More frequent readings disclose the actual curve also indicated in the figure.

The plateau in Fig. 1 is highly reproducible, although it may be obscured if the sample contains a high fraction of bacterial predators. Filtering the seed through Whatman No. 2 paper minimizes this effect. A false plateau may also be observed if there is a nutrient limitation, for example, nitrogen.



TYPICAL OXYGEN uptake by bacteria feeding on glucose approximates first order reaction—Fig. 1.

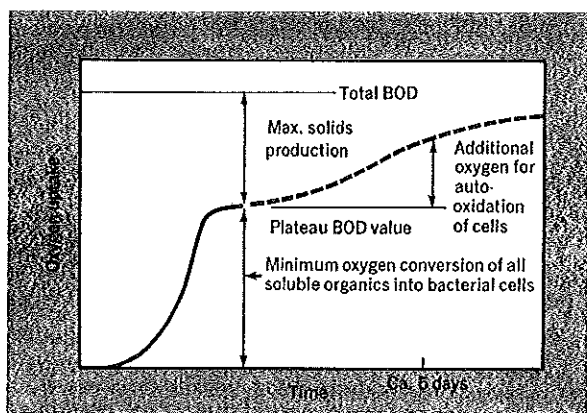
**Total BOD**

A schematic presentation of the total BOD concept is shown in Fig. 2. This is based on consumption of soluble substrates by microorganisms in a BOD bottle, which can be used to approximate the stoichiometry of engineered systems. Total BOD is defined in oxygen equivalents of biodegradable organic carbon. The relationship of carbon concentration to oxygen concentration is shown in Fig. 3.

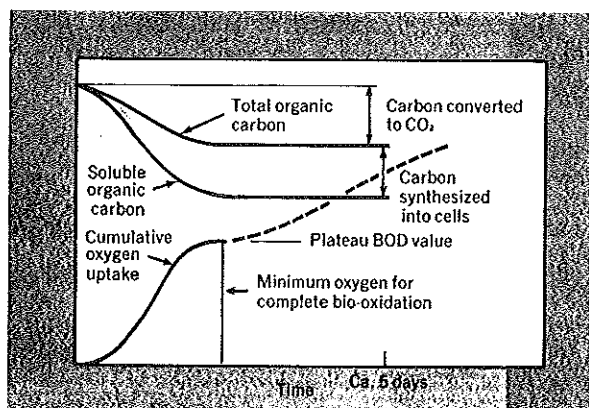
The sum of the oxygen used in reaching the curve's plateau and the oxygen equivalents of the cells produced is equal to the total biological oxygen demand. The total is also the theoretical stoichiometric oxygen requirement for complete conversion of the substrate to carbon dioxide and water. A detailed test procedure has been published.<sup>1,2,3</sup>

The bottle procedure is valuable as a conceptual tool, but is time consuming and mostly suited to quantitative research. The mass culture approach<sup>4</sup> is a quicker, simpler technique. As illustrated in Fig. 4, this method measures the change in organic content caused by bacterial oxidation rather than the amount of oxygen required to effect the change. It is performed as a batch reaction.

When the mass culture test is used for reactor design or process assessment, conditions should reflect those of the actual process. For example, initial solids and feed



**BOD BOTTLE TEST** measures total oxygen for complete conversion of organics to CO<sub>2</sub> and water—Fig. 2.



**CARBON** relationships in the BOD bottle test—Fig. 3.

concentration should be the same as in the process reactor. When these requirements are satisfied, the reaction time is defined as the point where the slope in Fig. 4 becomes zero. The change in soluble organics measured as oxygen equivalents is equal to the total biological oxygen demand and has been used effectively to characterize industrial wastes and in process design.<sup>5,7</sup>

A carbon analyzer can be used equally well in the mass culture test to determine total biologically available carbon. Hiser<sup>6</sup> describes methods using the carbon analyzer for process control.

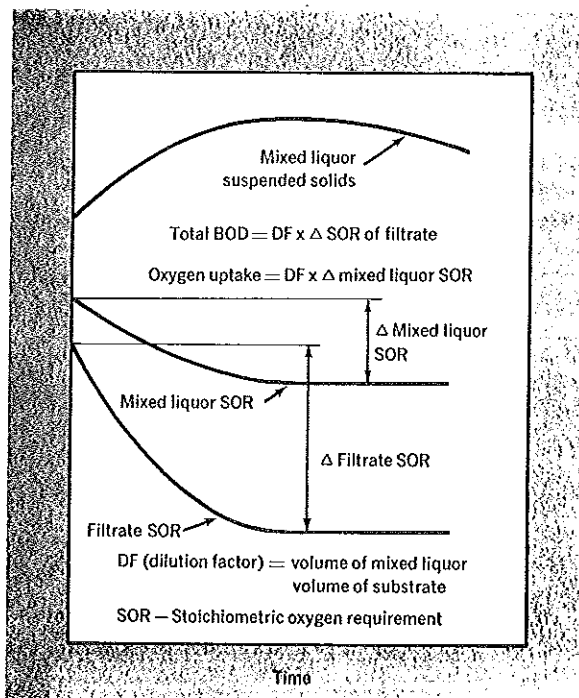
**BOD and Biodegradability**

The term "biodegradable" is specific to the system and refers to organic carbon converted to cells or carbon dioxide by biological metabolism. The amount of conversion depends on the microbial species, time and process conditions such as pH and temperature. Of course, essentially all soluble organic carbon will be eventually converted by microbial metabolism. The rate of conversion is the important factor to the engineer.

The five-day test for biological oxygen demand is intended to serve four purposes:<sup>7</sup>

- Measure the biodegradable carbon content of wastewater in oxygen equivalents.
- Predict oxygen requirements for biological oxidation.
- Define process performance.
- Provide rate data for process design and determination of effluent effect in the receiving stream.

There is nothing wrong with using oxygen equivalents to measure biodegradable carbon, and the advantages with respect to predicting oxygen needs are obvious. A common error, however, is in failing to distinguish be-



**MASS CULTURE** method for measuring total BOD—Fig. 4.

tween oxygen for carbon conversion to cells and carbon dioxide, and that for auto-oxidation of cells. Because of his error, predicted oxygen requirements based on BOD<sub>5</sub> are unnecessarily high.

BOD<sub>5</sub> is inadequate for judging process performance for reasons relating to biodegradability. Wastewater treatment that involves only hours of contact cannot be assessed by a test that takes five days. During this extended period, the microbial population may shift with the result that some compounds not attacked in the reactor may degrade. Also, substances that degrade slowly can exert an oxygen demand over five days much greater than that imposed in the process in a few hours. The result is that performance is likely to be judged unsatisfactory by a long-term test not compatible with the reaction environment.

Rate data from a BOD<sub>5</sub> test should not be used because the quiescent conditions in the bottle produce a diffusion-limited system. (This is a probable explanation for many first order reaction models.) Also, rate data from a system with high initial ratio of food to microorganisms are not applicable to an activated sludge process, which has a low initial ratio and is food limited.

### Oxygen Requirements

The use of oxygen equivalents to measure biodegradable carbon implies that this is the quantity of oxygen required to remove the carbon from solution. Because the oxygen utilized reduces the total stoichiometric oxygen requirement of the system, oxygen uptake is conveniently measured as the change in oxygen requirement for the mixed liquor (Fig. 4). The important point is that dissolved oxygen measurements are not necessary to determine oxygen needs or uptake rates.

The effect of mixing on oxygen demand can be considered on two scales: the macro and the micro. Macro-scale mixing promotes uniformity and provides contact between reactants. This means that solids are kept in suspension and all reactants are dispersed uniformly across a given cross section.

Mixing on the microscale affects molecular diffusion since shear intensity influences the film thickness through which molecules must migrate. The mathematical description of molecular diffusion can be used for eddy diffusion within the random turbulent eddies produced by mixing.

In biological treatment plants that handle rapidly degradable organics, the rate of degradation is limited by the mass transfer of oxygen and organics to the microorganisms. Obviously, an increase in the power/volume ratio will increase turbulence in the system and promote mass transfer.

On a microscale the system can be visualized as consisting of a large number of biological flocs, each surrounded by a boundary layer the size of a characteristic eddy.<sup>10</sup> Increased turbulence decreases eddy size and, through higher shear, increases the surface area of the floc. The change in the mass transfer coefficient,  $k_L a$ , for various power inputs is listed in Table I.<sup>11</sup> Of course, if the mixing equipment also provides oxygen transfer, this will further enhance the overall reaction rate.

Effect of Turbulence—Table I

	Power hp/1,000 cu. ft.	Eddy Size Dia. in Microns	Increase in $k_L a$
Aerated lagoon	0.1	280	0.3
Activated sludge process	0.5	180	0.8
	1.0	160	1.0
Industrial fermentations	2.0	134	1.4
	5.0	106	2.3
	10.0	90	3.2

### Pure Oxygen Helps

Recently, there has been a resurgence of interest in the use of pure oxygen for biological treatment. Technology is available for full scale systems and several large treatment plants of this type are under construction.

Aerobic biological treatment processes traditionally operate above a critical dissolved oxygen concentration in the mixed liquor of 0.2 to 0.5 mg./l.<sup>17</sup> Below the critical concentration, the rate of bacterial respiration is dependent on dissolved oxygen concentration and the rate of waste assimilation decreases. However, too high a dissolved oxygen concentration is also not desirable because the rate of mass transfer from the gas to liquid phase will be reduced according to the following equation:

$$N = dc/dt = k_L a(C^* - C)$$

where:

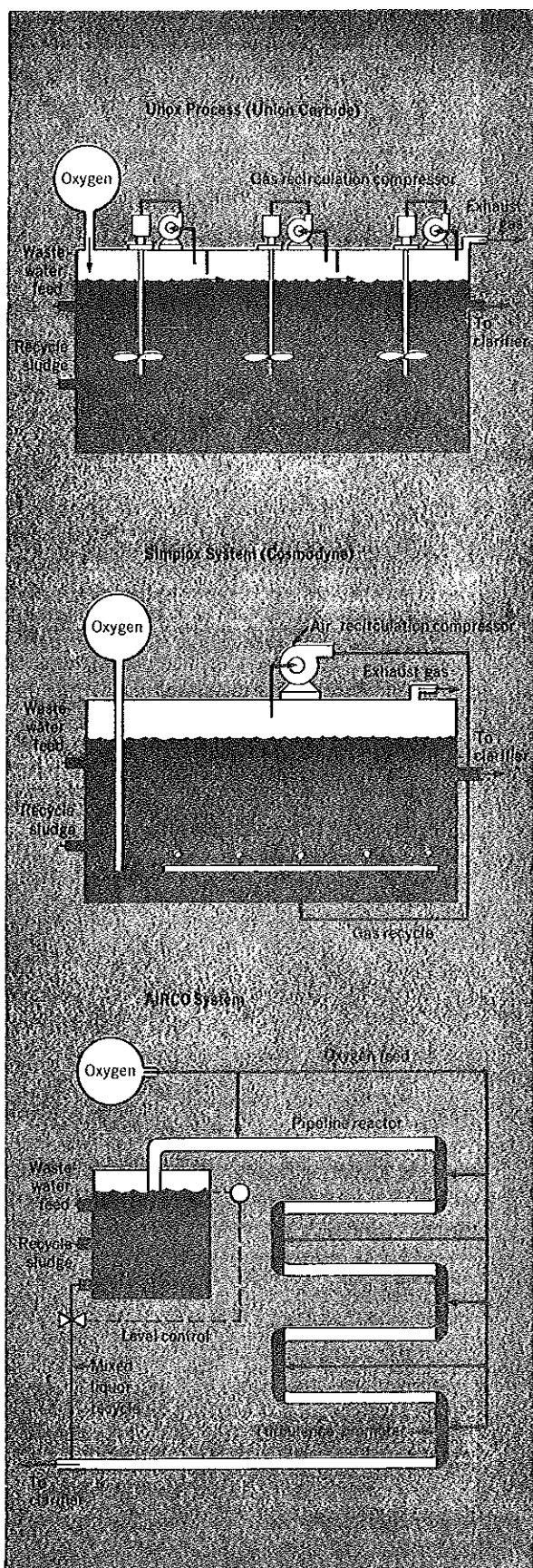
- $N$  Rate of mass Transfer
- $C$  Oxygen concentration in liquid phase
- $C^*$  Oxygen concentration in liquid phase that is in equilibrium with gas phase oxygen
- $k_L$  Mass transfer coefficient
- $a$  Interfacial area
- $t$  Time

Consequently, maximum oxygen transfer rates compatible with conventional aerobic treatment occur when DO is at the critical level. High purity oxygen raises the driving force ( $C^* - C$ ) for mass transfer by providing a higher oxygen concentration in the gas phase, which is related to  $C^*$ .

Advantages claimed for high purity oxygen systems are:

- Economic operation at high DO levels compared to conventional aeration.
- Operation under high rate, high mixed liquor suspended solids levels. Sludge settles easily and compacts well.
- Low net sludge production with low retention time and high space loading.
- Higher rates of microbial metabolism.

Union Carbide, Cosmodyne and Airco have developed systems for contacting oxygen with wastewater. These are diagramed in Fig. 5.



THREE PROCESSES for using high-purity oxygen in biological treatment plants—Fig. 5.

## Oxygen Role Still Uncertain

Recent evaluations of data comparing high purity and air oxygenation cast doubt on some of the early claims for superior performance of high purity systems. For example, Ball and Humenick<sup>18</sup> have discussed the use of high purity oxygen in municipal wastewater treatment and found that substrate removal per unit mass of volatile solids in oxygen systems was not significantly different from that in air systems operating at the same loading. The overall reaction rate was increased in oxygen systems by maintaining a higher concentration of mixed liquor suspended solids.

Published data present results of oxygen vs. air in tests at Batavia, N.Y.<sup>19</sup> Though not theoretically rigorous, the data imply virtually no dependence of the unit reaction rate on reactor concentration, which is equal to effluent concentration for a continuously stirred reactor. A comparison of clarifier effluent BOD and suspended solids showed very little soluble BOD and, in fact, even raw municipal sewage contains relatively little soluble BOD (about 60 mg./l. at Batavia). The conclusion at this time is that high purity oxygen systems appear most useful in treating wastes with high concentrations of soluble organic compounds. In this situation, dissolved oxygen frequently becomes the rate-limiting factor.<sup>20</sup>

It is true that oxygen systems exhibit low net sludge production. Experience shows that net solids production is a function of detention time, which is longer in oxygen systems because of higher solids concentrations. Low solids production is certainly an advantage, but the separate issues of effluent quality and solids disposal should not be confused when considering the costs of alternative systems.

## Measuring Process Performance

There are no absolute measures of pollution; only relative ones. Thus the performance of a particular treatment process should be assessed in terms of what the process could do ideally. This is the basis of the "delta" concept,<sup>7</sup> in which the progression of an appropriate parameter in an idealized batch reactor is compared with results from an actual continuous process.

In a municipal sewage operation, the parameter for assessing performance may be any easily measured general property such as chemical oxygen demand, total organic carbon or total oxygen demand. With industrial wastes, the parameter is frequently one of the specific components that the process was designed to remove.

A batch reactor with initial conditions identical to the system under study is operated for a period of time equal to the theoretical hydraulic detention time of the continuous process. If a plot of COD (or other parameter chosen) shows the reaction is not complete at the end of the time period, then the continuous system obviously could not complete the reaction under existing conditions.

Another way to look at the same situation is the concept of "effluent refractory assessment." This is a test that simply involves holding a portion of mixed liquor from the biological system for an additional time, say 24 hours.

If the dissolved organic concentration after additional aeration remains substantially unchanged, the process is operating efficiently.

## Physical/Chemical Treatment

Physical/chemical wastewater treatment processes have experienced a new surge of interest recently. Individual unit processes will effectively remove particulates, colloidal solids, soluble inorganics such as nitrogen and phosphorous compounds, bacteria and viruses. Brief discussions follow covering the processes most frequently applied, and more detailed information has been published elsewhere.<sup>12</sup>

Particulate removal can be enhanced by adding chemical coagulants that increase settling velocities of suspended material. Inorganic coagulants such as alum and lime also remove phosphates by precipitation. Some recent research shows that lime addition at the proper pH destroys microorganisms and removes color and hardness.<sup>13,14</sup>

Gentle mixing after coagulation brings about further particle aggregation to enhance settling. Shallow depth basins are being designed more frequently for sedimentation. The concept offers a theoretically sound basis for operating clarifiers at surface rates 2 to 4 times higher than in deep, conventional basins.

Particulates may also be removed by filtration. In a single medium filter, most of the solids are removed at near the bed's surface. Thus, only a small part of the total voids in the bed are actually used to store particulates. As one result, head loss increases rapidly during the filtering cycle.

Effective filter depth can be increased by using dual media—one layer of coarse material on top of a layer of fine, dense particles. Settling velocities of the two media are such that the layers return to their initial locations after backwashing. The mixed media concept improves on this principle and has been used successfully in industrial applications.<sup>12</sup>

## Removing Nutrients

Lime coagulation is an effective way to combine phosphate removal with other waste treatment objectives. Aluminum sulfate will also reduce phosphate concentration by chemical precipitation. Compact modular units are available, which combine precipitation with shallow-depth settling and mixed-media filtration. An ion exchange process for phosphate removal has been demonstrated.<sup>15</sup> This has the advantage of not producing sludge, which presents a disposal problem.

The three primary methods for removing nitrogen are ammonia stripping, selective ion exchange and microbial denitrification. With microbial action, nitrogen compounds in wastewater are biologically oxidized to nitrates under aerobic conditions. Then the effluent is subjected to an anaerobic environment where microorganisms reduce nitrates and nitrites to nitrogen gas, which escapes from solution. The process is inexpensive and has the

advantage of not creating any liquid waste products.

Battelle has developed a selective ion exchange process for ammonia removal.<sup>16</sup> The process is based on a natural zeolite, clinoptilolite. It is regenerated by a lime slurry, which provides hydroxyl ions to react with ammonium ions, yielding an aqueous ammonia solution. Ammonia is removed by air stripping, which permits recycling of the lime. At this time, ion exchange appears to be a rather costly way to remove nitrogen.

Ammonia may also be removed from wastewater by conventional air stripping methods. This approach has climatic limitations, but is cheap and relatively easy to control.<sup>12</sup>

## Modular Units Vs Regional Plants

There is presently wide support among various groups for regional treatment plants to clean up industrial wastes. While it is true that there may be economies of scale and some process advantages, there are also a number of factors that mitigate against the regional approach for industrial waste treatment. The main ones are:

- If water is to be recycled, it may have to be transported substantial distances back to the point of demand.
- Reaction rate differences caused by the varying character of industrial wastes frequently have a detrimental effect on process performance.<sup>7</sup>
- Groundwater infiltration in long gravity sewers disproportionately increases the flow to a centralized plant.
- To maintain stream quality, a high volume point discharge must be of much better quality than the same volume discharged at numerous points.

As industrial emphasis on waste treatment as an essential part of manufacturing becomes more widespread, and as direct water reuse becomes more vital, techniques for on-the-spot treatment at the individual process unit become more important. Fig. 6 represents a "zero discharge" plant employing modular units for wastewater treatment. This approach favors water reuse within a process unit, and permits individual treatment of waste streams whose reaction characteristics merit or require separate handling.

Modular units offer the utmost in flexibility. They may be relocated, and each unit is a "full scale pilot plant" that can be installed, operated and assessed on a particular waste to determine the necessary number of units. Multiple units offer standby capacity or provision for plant expansions. Finally, when pollution control becomes part of normal overhead costs, treatment modules will be the simplest method for assigning control costs to each production unit. This will permit clear assessment of product profitability.

Another point worth noting is that batch reactors become more attractive as water reuse and effluent quality requirements tighten. The fill-and-draw systems used years ago offer a means of off-setting the hydraulic deficiency of continuous flow systems. Batch reactors also have benefits where certain processes operate for short, random intervals. A large industrial waste treatment facility was recently designed this way.<sup>9</sup>

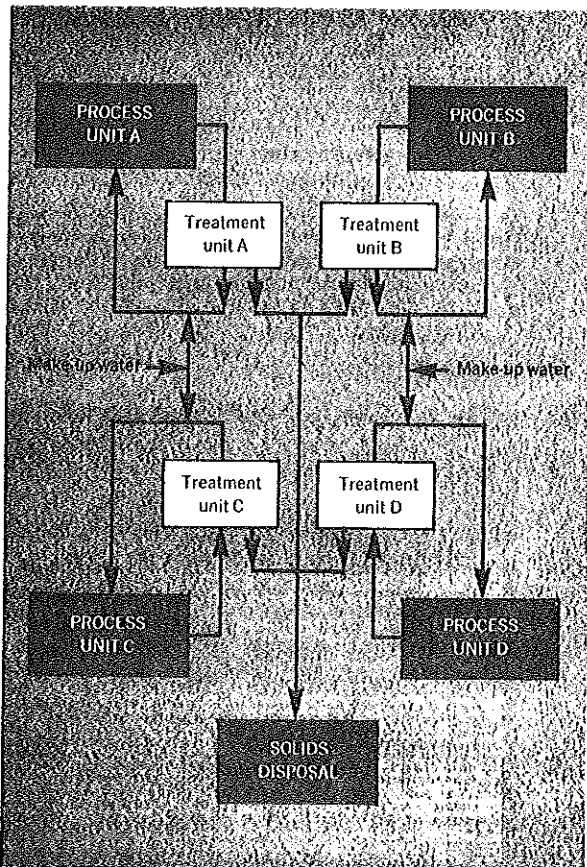
### Maximizing Pollution

The historical use of our natural waters to their full capacities for disposing of man-made pollution is no longer a valid or viable engineering policy. If one accepts partial treatment to avoid degrading stream quality below some arbitrary level, the policy becomes one of "maximizing pollution" although disguised under the concept of fully utilizing assimilative capacity.

There will always be unintentional pollution or uncontrollable pollution such as storm water runoff, agricultural drainage, spills, illicit dumps, etc. Thus it seems better not to allow intentional discharge of pollutants based on assimilative capacity of a stream.

The goal of wastewater treatment is good effluent quality, obviously. With this in mind, the terms "advanced" and "tertiary" treatment are misnomers because there should be no semantic constraints on the processes necessary to attain quality effluent. Primary (sedimentation) and secondary (aeration) treatment are not *requirements* for quality effluent, as evidenced by recent advances in physical/chemical processes.

When the chemical engineer can consider wastewater treatment alternatives on the basis of effluent quality, rather than being constrained by traditional approaches, a big step will have been taken toward solving our water pollution problems. ■



**MODULAR UNITS** for wastewater treatment are one approach to zero discharge—Fig. 6.

### Meet the Authors



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### References

1. Busch, A. W., Grady, L., Shivajirao, T. and Swilley, E. L., B.O.D. Progression in Soluble Substrates, IV. A Short Term Total Oxygen Demand Test, *Journal W.P.C.F.*, 34, 4 354 (1962).
2. Grady, L. and Busch, A. W., B.O.D. Progression in Soluble Substrates, VI, Cell Recovery Techniques in the T.O.D. Test, 18th Industrial Waste Conference, Purdue, *Proceedings*, (1963).
3. Grady, L. and Busch, A. W., Further Developments in the Total Biological Oxygen Demand Test, 14th Oklahoma Industrial Waste Conference, Oklahoma State University, *Proceedings*, (1963).
4. Hiser, L. L. and Busch, A. W., An 8-Hour Biological Oxygen Demand Test Using Mass Culture Aeration, *Journal W.P.C.F.*, 36, 4, 505, (1964).
5. Busch, A. W., Biochemical Oxidation of Process Waste Water, *Chem. Eng.*, March 1 and 29, 1965.
6. Hiser, L. L., A New Approach to Controlling Biological Processes, *Env. Sci. Tech.*, 4, 8, 648, (1970).
7. Busch, A. W., "Aerobic Biological Treatment of Waste Water," Oligodynamic Press, Box 35774, Houston, 77035, 1971.
8. Busch, A. W., and Characklis, W. G., Effluent Refractory Assessment Concept, Presented at AIChE National Meeting, Cincinnati, May, 1971. (Publication in *Water 1971* forthcoming).
9. Irvine, R. L. and Davis, W. B., Waste Treatment Design for CPC International at Corpus Christi, Texas, *Proceedings*, 26th Industrial Waste Conference, Purdue University, 1971.
10. Brodkey, R. S., Fluid Motion and Mixing. "Mixing: Theory and Practice," Academic Press, New York, (1966).
11. Matson, J. V., personal communication.
12. Culp, R. L. and Culp, G. L., "Advanced Wastewater Treatment," Van Nostrand Reinhold Co., New York, (1971).
13. Stander, G. J. and Van Vuuren, L. R. J., The Reclamation of Potable Water from Wastewater, *Journal W.P.C.F.*, 41, 3, pp. 355-367 (1969).
14. Crissey, W. E., unpublished data.
15. Yee, W. C., Selective Removal of Mixed Phosphates by Activated Alumina, *Journal American Water Works Assoc.*, 58, 2, pp. 239-247, (1966).
16. Battelle Northwest, Ammonia Removal from Agricultural Runoff and Secondary Effluents by Selected Ion Exchange, Robert A. Taft Water Res. Center, Report No. TWRC-5 (Mar., 1969).
17. Eckenfelder, W. W. and O'Connor, D. J., "Biological Waste Treatment," Pergamon Press, New York, 1961.
18. Ball, J. E. and Humenick, M. J., High-Purity Oxygen in Biological Treatment of Municipal Wastewater, *Journal W.P.C.F.*, 44, 1, pp. 65-76, (1972).
19. "Investigation of the Use of High Purity Oxygen Aeration in the Conventional Activated Sludge Process," FWQA, Report No. 17050-DNW 05/70, Washington, D.C. (1970).
20. Matson, J. V., Characklis, W. G., and Busch, A. W., Oxygen Supply Limitations in Full-Scale Biological Treatment Systems, 27th Industrial Waste Conference, Purdue University, Lafayette, Indiana, May, 1972.