Kirk-Othmer Encyclopedia of Chemical Technology.

WATER, POLLUTION

Water is omnipresent on the earth. Constant circulation of water from the ocean to the atmosphere (evaporation) and from the atmosphere to land and the oceans (precipitation, runoff, etc) is generally known as the hydrologic cycle (see Fig. 1) (1, 2). Within the hydrologic cyclic, there are several minor and local subcycles where water is used and returned to the environment.

The volume of the freshwater amounts to only one-thirtieth of the 1.25×10^9 km^3 (300×10^6 mi^3) of the water in salty oceans. Approximately one-third of the freshwater exists permanently as snow and ice (3). A large portion of the remaining freshwater has infiltrated too far underground or is partially polluted with minerals and chemicals and therefore is not readily usable. The entire life system on the earth depends on the remaining freshwater sources; therefore, it is essential to protect the quality of the available waters.

The principal hydrologic parameters involved in the storage and transport of freshwater were studied as early as 1894 and are summarized in Table 1 (2).

Freshwater is withdrawn from various sources (rivers, lakes, groundwater, etc) and used many times before its discharge to the ocean. Water uses can generally be classified as follows: public water supply (domestic); industrial; commercial and institutional, eg, restaurants, schools; agricultural; and livestock.

These applications require withdrawal of water from a source and subsequent treatment and conveyance to the point of use. Water is also used without being withdrawn from a source, eg, for navigation, recreation, wild and aquatic life propagation, hydroelectric-power generation, and waste assimilation and transport. The principal types of withdrawal uses and their average rates are given in Table 2. Some of these withdrawal rates represent multiple uses of the same water along main rivers in metropolitan and industrialized areas.

Water-use data and withdrawal rates for public water-supply systems are well documented by municipalities. The U.S. Public Health Service (USPHS) (5), American Water Works Association (AWWA) (6–10), and Federal Housing Administration (FHA) (11) have compiled statistics at regular intervals for $>23,000$ municipalities in the United States.

The largest consumers of water in the United States are thermal power plants (eg, steam and nuclear power plants) and the iron and steel, pulp and paper, petroleum refining, and food-processing industries. They consume $>60\%$ of the total industrial water requirements (see also Power generation; Wastes,INDUSTRIAL).

1. Water Quality Management

Over the past decade, water pollution control has progressed from an art to a science. Increased emphasis has been placed on the removal of secondary pollutants, such as nutrients and refractory organics, and on water reuse for industrial and agricultural purposes. This in turn has generated both fundamental and applied research, which has improved both the design and operation of wastewater treatment facilities.

Solving water pollution problems today involves a multidisciplinary approach in which the required water quality is related to agricultural, municipal, recreational, and industrial requirements. In many cases, a

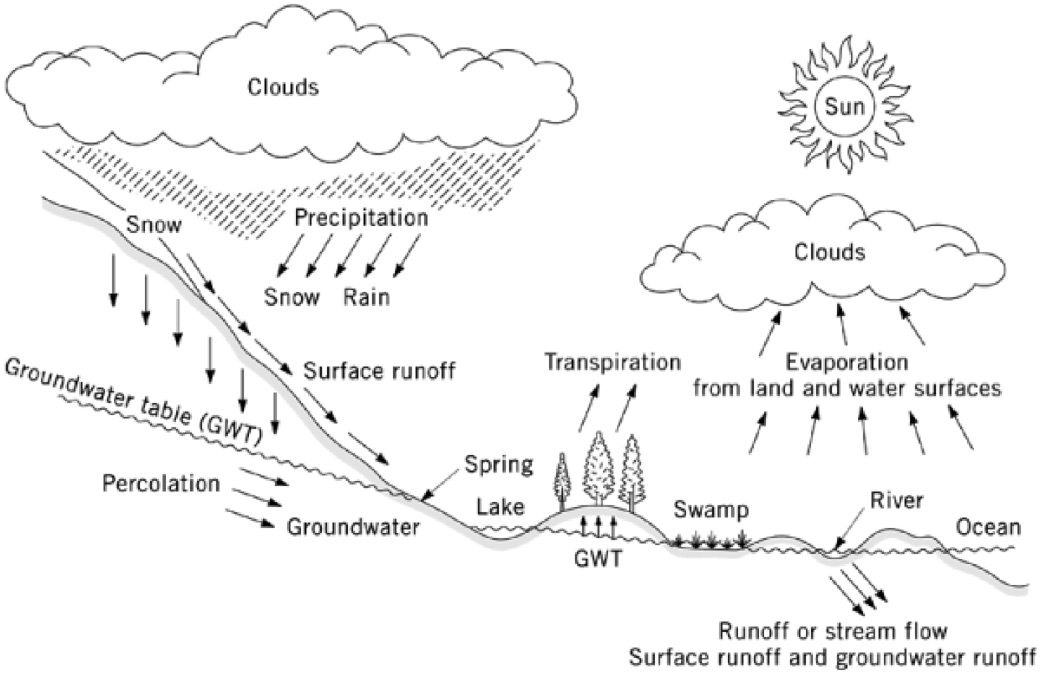

Fig. 1. Schematic diagram of the hydrologic cycle.

Table 1. Principal Hydrologic Parameters[a]

Storage	Transport
atmospheric water	evaporation from land surface; oceans, lakes, and other water bodies; and snow and ice
oceans and seas	precipitation
rivers	runoff
lakes and reservoirs	infiltration
swamps	
biological water	
soil moisture and groundwater	
frozen water (ice and snow)	

[a] Ref. 3.

cost–benefit ratio must be established between the benefit derived from a specified water quality and the cost of achieving that quality.

Wastewaters emanate from four primary sources: municipal sewage, industrial wastewaters, agricultural runoff, and stormwater and urban runoff.

Estimating municipal wastewater flows and loadings can be done in one of several ways, based on knowledge of past and future growth plans for the community, sociological patterns, and land use planning. Two possible ways are as follows: (*1*) *Population Prediction Techniques*. Several mathematical techniques are available for estimating population growth. Caution should be employed in the use of these procedures, particularly in areas subject to rapid industrial expansion, rapid suburban development, and changing land use patterns; (*2*) *Saturation Population from Zoning Practice*. Percentages of a saturation population can be estimated for fully developed areas based on zoning restrictions (single-dwelling residential, multiple-dwelling residential, commercial, etc).

Table 2. Average Daily Water Requirements for Categories of Withdrawal Use in the United States[a]

Use	Average daily requirement[b], 10^6 m^3/d (mgd)[c]
public[d]	102.2 (27,000)
rural	
domestic	9.84 (2,600)
livestock	7.19 (1,900)
agriculture	492.10 (130,000)
industrial	794.90 (210,000)

[a] Ref. 4.
[b] Estimated 206×10^6 people served.
[c] mgd = million (10^6) gallons per day.
[d] Residential and municipal (domestic).

Table 3. Pollution from Urban and Agricultural Runoff

Constituent	Urban runoff[a] (stormwater)	Agricultural runoff[b]
suspended solids, mg/L	5–1200	
chemical oxygen demand (COD), mg/L	20–610	
biological oxygen demand (BOD), mg/L	1–173	
total phosphorus, mg/L	0.02–7.3	0.10–0.65
nitrate nitrogen, mg/L		0.03–5.00
total nitrogen, mg/L	0.3–7.5	0.50–6.50
chlorides, mg/L	3–35	

[a] From Ref. 12.
[b] From Ref. 13.

Provisions should be included for infiltration in the case of separate sewers as well as storm flows in the case of combined sewers.

As municipal and industrial wastewaters receive treatment, increasing emphasis is being placed on the pollutional effects of urban and agricultural runoff. The range of concentration of pertinent characteristics in these wastewaters is given in Table 3. Present research on stormwater treatment considers large holding basins in which the stormwaters are treated in the municipal facility after the storm (an *in situ* treatment by screening, sedimentation, chlorination, etc). In the future, water quality management in highly urbanized areas will have to consider stormwater as a primary pollutant.

Agricultural runoff is a large contributor to etrophication in lakes and other natural bodies of water. Effective control measures have yet to be developed for this problem. Runoff of pesticides is also receiving increasing attention.

1.1. Water Quality Standards

Water quality standards are usually based on one of two primary criteria, stream standards or effluent standards. Stream standards are based on dilution requirements for the receiving water quality based on a threshold value of specific pollutants or a beneficial use of the water. Effluent standards are based on the concentration of pollutants that can be discharged or on the degree of treatment required.

Stream standards are usually based on a system of classifying the water quality based on the intended use of the water.

Although stream standards are the most realistic in light of the use of the assimilative capacity of the receiving water, they are difficult to administer and control in an expanding industrial and urban area. The equitable allocation of pollutional loads for many industrial and municipal complexes also poses political and economic difficulties. A stream standard based on minimum dissolved oxygen at low stream flow intuitively implies a minimum degree of treatment. One variation of stream standards is the specification of a maximum concentration of a pollutant (ie, the BOD) in the stream after mixing at a specified low flow condition.

Note that the maintenance of water quality and hence stream standards are not static, but subject to change with the municipal and industrial environment. For example, as the carbonaceous organic load is removed by treatment, the detrimental effect of nitrification in the receiving water increases. Eutrophication may also become a serious problem in some cases. These considerations require an upgrading of the required degree of treatment.

Effluent standards are based on the maximum concentration of a pollutant (mg/L) or the maximum load (lb/day) discharged to a receiving water. These standards can be related to a stream classification.

In 1972 the U.S. Legislature passed Public Law 92-500, which requires certain levels of treatment for industrial wastewater discharges. Effluent guideline criteria (expressed as kilograms pollutant per unit of production) have been developed for each industrial category to be met by specified time periods.

The BPT is defined as the level of treatment that has been proven to be successful for a specific industrial category and that is currently in full-scale operation. Sufficient data exist for this level of treatment so that it can be designed and operated to achieve a level of treatment consistently and with reliability. For example, in the pulp and paper industry, BPT has been defined as biological treatment using the aerated lagoon or the activated sludge process with appropriate pretreatment.

The BAT is defined as the level of treatment beyond BPCTCA that has been proven feasible in laboratory and pilot studies and that is, in some cases, in full-scale operation. BAT in the pulp and paper industry may include such processes as filtration, coagulation for color removal, and improved in-plant control to reduce the wasteload constituents.

In general, effluent guidelines are developed by considering an exemplary plant in a specific industrial category and multiplying the wastewater flow per unit production by the effluent quality attainable from the specified BPT process to obtain the effluent limitation in pounds or kilograms per unit of production. The effluent limitations consider both a maximum 30-day average and a 1-day maximum level. In general, the daily maximum is two to three times the 30-day average. For example, the average wastewater flow from an exemplary plant is 30,000 gal/ton of production and the average effluent BOD is 30 mg/L.

The effluent limitation can then be computed:

$$(30,000 \text{ gal/ton}) \times \left(8.34 \times 10^{-6}\right) \times (30 \text{ mg/L}) = 7.5 \text{ lb/ton}$$

It is recognized that the wastewater volume and characteristics from a specific industrial category will depend on such factors as plant age, size, raw materials used and in-plant processing sequences.

The U.S. Environmental Protection Agency (EPA) has also developed pretreatment guidelines for those industrial plants which discharge into municipal sewer systems. In general, compatible pollutants such as BOD, suspended solids, and coliform organisms can be discharged providing the municipal plant has the capability of treating these wastewaters to a satisfactory level. Noncompatible pollutants, such as grease and oil, heavy metals, etc, must be pretreated to specified levels. Rigid limitations have been developed for the discharge of toxic substances to the nation's waterways.

In several cases, such as shellfish areas and aquatic reserves, the usual water quality parameters do not apply because they are nonspecific as to detrimental effects on aquatic life. For example, COD is an overall measure of organic content, but it does not differentiate between toxic and nontoxic organics. In these cases, a species diversity index has been employed as related to either free-floating or benthic organisms. The index indicates the overall condition to the aquatic environment. It is related to the number of species in the sample. The higher the species diversity index, the more productive the aquatic system. The species diversity index K_{D} is computed by the equation $K_{\mathrm{D}} = (S - 1)/\log_{10} l$, where S is the number of species and l the total number of individual organisms counted.

Regulations establishing effluent limitations guidelines, pretreatment standards and new source performance standards for the organic chemicals, plastics, and synthetic fibers (OCPSF) were promulgated in 1987. In these regulations, specific organic chemicals are defined by the EPA as priority pollutants (see Table 4).

Table 4. Organic Compounds Specified as Pollutants by the EPA

- acenaphthene
- acrolein
- acrylonitrile
- benzene
- benzidine
- carbon tetrachloride (tetrachloromethane)

- chlorinated benzenes (other than dichlorobenzene)

  - chlorobenzene
  - 1,2,4-trichlorobenzene
  - hexachlorobenzene
- chlorinated ethanes[a]
  - 1,2-dichloroethane
  - 1,1,1-trichloroethane
  - hexachloroethane
  - 1,1-dichloroethane
  - 1,1,2-trichloroethane
  - 1,1,2,2-tetrachloroethane
  - chloroethane (ethyl chloride)
- chloroalkyl ethers[b]
  - bis(chloromethyl)ether

  - bis(2-chloroethyl)ether
  - 2-chloroethyl vinyl ether (mixed)
- chlorinated naphthalene
  - 2-chloronaphthalene
- chlorinated phenols[c]
  - 2,4,6-trichlorophenol
  - *p*-chloro-*m*-cresol
  - chloroform (trichloromethane)

  - 2-chlorophenol
- dichlorobenzenes

  - 1,2-dichlorobenzene
  - 1,3-dichlorobenzene
  - 1,4-dichlorobenzene
- dichlorobenzidine
  - 3,3′-dichlorobenzidine
- dichloroethylenes[e]
  - 1,1-dichloroethylene
  - 1,2-*trans*-dichloroethylene
  - 2,4-dichlorophenol
- dichloropropane and dichloropropene
  - 1,2-dichloropropane
  - 1,2-dichloropropylene (1,2-dichloro- propene)

  - 2,4-dimethylphenol
- dinitrotoluene
  - 4-nitrophenol
  - 2,4-dinitrophenol
  - 4,6-dinitro-*o*-cresol
- nitrosamines
  - *N*-nitrosodimethylamine
  - *N*-nitrosodiphenylamine
  - *N*-nitroso-di-*n*-propylamine

  - pentachlorophenol
  - phenol
- phthalate esters
  - bis(e-ethylhexyl) phthalate
  - butyl benzyl phthalate
  - di-*n*-butyl phthalate
  - di-*n*-octyl phthalate
  - diethyl phthalate
  - dimethyl phthalate
- polynuclear aromatic hydrocarbons (PAHs)
  - benzo(*a*)anthracene (1,2-benzanthracene)
  - benzo(*a*)pyrene (3,4-benzopyrene)
  - 3,4-benzofluoranthene

  - benzo(*k*)fluoranthene (11,12-benzo- fluoranthene)

  - chrysene
  - acenaphthylene
  - anthracene
  - benzo(*ghi*)perylene (1,12-benzoperylene)
  - fluorene
  - phenanthrene

  - dibenzo(*a*,*h*)anthracene (1,2,5,6- dibenzanthracene)

  - indeno(1,2,3-cd)pyrene(2,3-*o*- phenylenepyrene)

  - pyrene
  - tetrachloroethylene
  - toluene
  - trichloroethylene
  - vinyl chloride (chloroethylene)
- pesticides and metabolites
  - aldrin
  - dieldrin
  - chlordane (technical mixture and metabolites)

- DDT and metabolites
  - 4-4′-DDT
  - 4,4′-DDE (*p*,*p*′-DDX)
  - 4,4′-DDD (*p*,*p*′-TDE)

Table 4. ***Continued***

  - 2,4-dinitrotoluene
  - 2,6-dinitrotoluene
  - 1,2-diphenylhydrazine
  - ethylbenzene
  - fluoranthene
- haloethers[c]
  - 4-chlorophenyl phenyl ether
  - 4-bromophenyl phenyl ether
  - bis(2-chloroisopropyl) ether
  - bis(2-chloroethoxy) methane
- halomethanes[c],[d]
  - methylene chloride (dichloromethane)
  - methyl chloride (chloromethane)
  - methyl bromide (bromomethane)
  - bromoform (tribromomethane)
  - dichlorobromomethane
  - trichlor ofluoromethane
  - dichlorodifluoromethane
  - chlorodibromomethane
  - hexachlorobutadiene
  - hexachlorocyclopentadiene
  - isophorone
  - naphthalene
  - nitrobenzene
- nitrophenols[f]
  - 2-nitrophenol
- endosulfan and metabolites
  - α-endosulfan-alpha
  - β-endosulfan-beta
  - endosulfan sulfate
- endrin and metabolites
  - endrin
  - endrin aldehyde
- heptachlor and metabolites
  - heptachlor
  - heptachlor epoxide
- hexachlorocyclohexane (all isomers)
  - α-BHC-alpha
  - β-BHC-beta
  - γ-BHC (lindane)-gamma
  - †-BHC-delta
- polychlorinated biphenyls (PCBs)
  - PCB-1242 (Arochlor 1242)
  - PCB-1254 (Arochlor 1254)
  - PCB-1221 (Arochlor 1221)
  - PCB-1232 (Arochlor 1232)
  - PCB-1248 (Arochlor 1248)
  - PCB-1260 (Arochlor 1260)
  - PCB-1016 (Arochlor 1016)
  - toxaphene
  - 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD)

[a] Including 1,2-dichloroethane, 1,1,1-trichloroethane, and hexachloroethane.

[b] Chloromethyl, chloroethyl, and mixed ethers.

[c] Other than those listed elsewhere.

[d] Including trichlorophenols and chlorinated aresols.

[e] 1,1-Dichloroethylene and 1,2-dichloroethylene.

[f] Including 2,4-dinitrophenol and dinitrocresol.

These chemicals are regulated as a concentration level in the effluent. In most cases, these levels are in the microgram-per-liter range.

Recent air pollution regulations limit the amount of volatile organic carbon (VOC) that can be discharged from wastewater treatment plants. Benzene is a particular case in which air emission controls are required if the concentration of benzene in the influent wastewater exceeds 10 mg/L.

2. Pollution Control

In past years, municipal wastewaters were treated to improve their appearance and bacteriological safety. Treatment included reduction in biochemical oxygen demand (BOD), suspended solids, pathogens, and inorganic dissolved solids. Before 1960, the activated-sludge process, developed in the U.K. in 1914, was used (17). It was based on the capabilities of microorganisms to assimilate organic compounds through oxidative and respiratory mechanisms. The organisms involved could be flocculated and settled in conventional sedimentation vessels (clarifiers).

The effluent was relatively clear and required only disinfection before discharge to receiving waters. Preliminary treatment removed grit, sand, and floating debris. It was followed by primary clarification for the removal of suspended solids, grease, and scum. The effluent from the primary clarifiers, containing colloidal

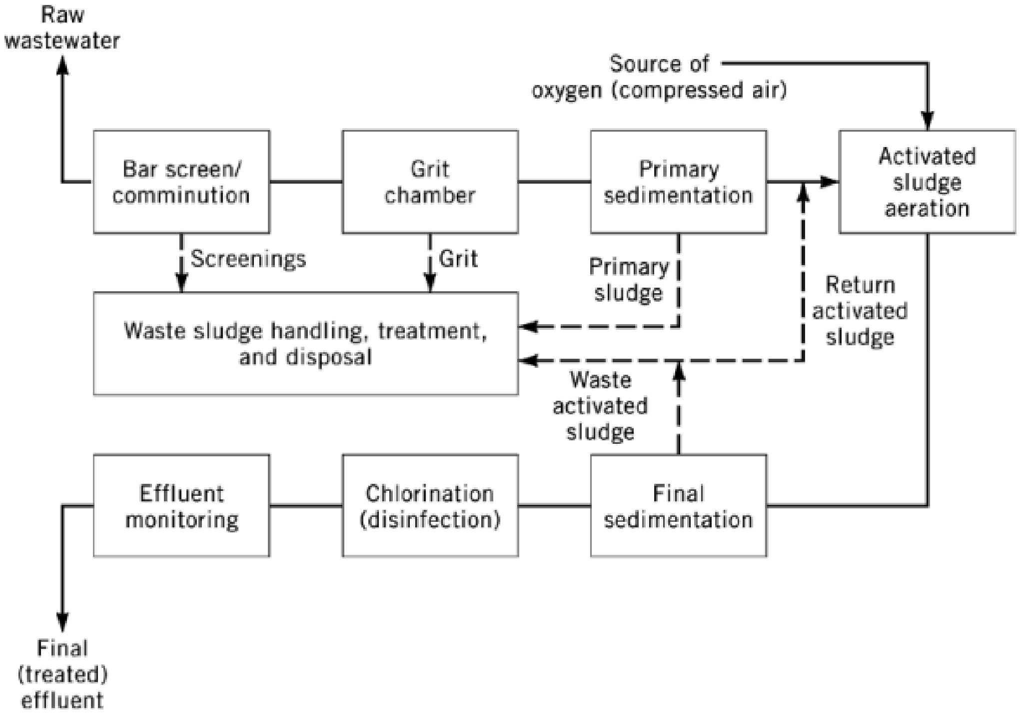

Fig. 2. Typical flow sheet for a domestic wastewater treatment plant utilizing the activated-sludge process.

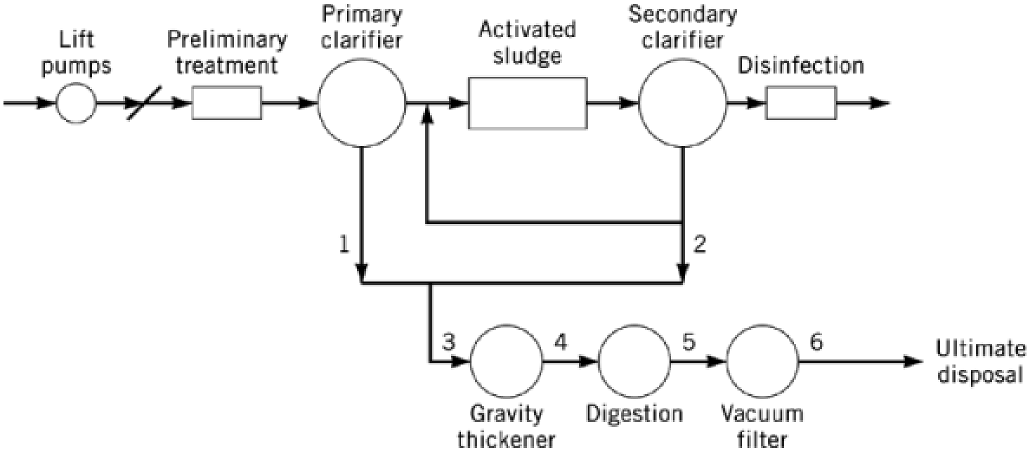

Fig. 3. Process components for the activated-sludge process, with aerobic digestion at plants <473.1 m^3/h and two-stage anaerobic digestion at plants >473.1 m^3/h (39,40). To convert m^3/h to mgd, divide by 157.7.

and dissolved organic matter, was subjected to activated-sludge treatment and disinfection (eg, chlorination) before discharge. A typical process flow sheet is given in Figure 2 (18); the process components are shown in Figure 3.

Table 5. Design Parameters for the Activated-Sludge Process[a]

Parameter, mg/L	Influent[b]	Effluent
BOD_5[c]	210	20
COD[d]	400	45
TSS[e]	230	20
total-P	11	7
NH_3-N	0	0
UOD[f]	406	107

[a] Refs. (19, 20).

[b] Aerobic digestion at plants <473.1 m^3/h (3 mgd) and two-stage anaerobic digestion at plants >473.1 m^3/h.

[c] 5-d Biochemical oxygen demand.

[d] Chemical oxygen demand.

[e] Total suspended solids.

[f] Ultimate oxygen demand.

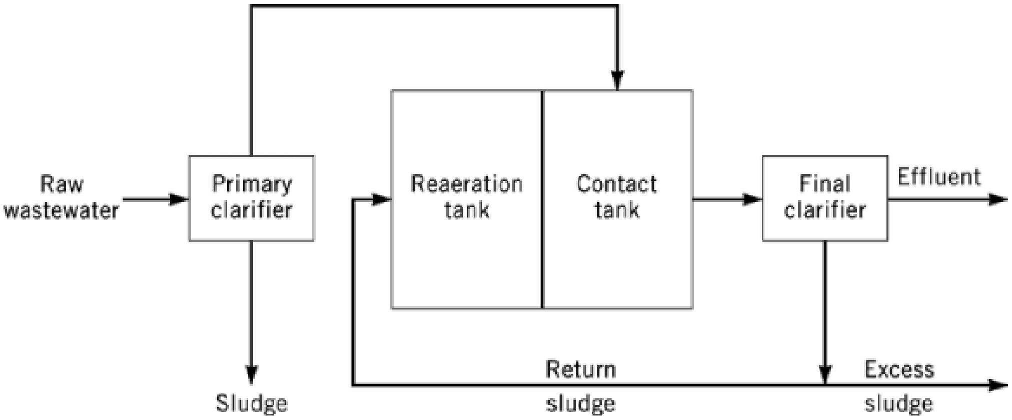

Fig. 4. Contact stabilization plant. Conventional activated-sludge process. The reaeration and contact tanks can be replaced by an aeration tank (21).

When industrial wastewaters are mixed with municipal wastes, as in many urban systems, toxic and inhibitory materials are removed in the pretreatment system where nutrient chemicals, eg, nitrogen and phosphorus, are added.

Biological processes (eg, activated sludge, trickling filters, etc) generate primary and biological sludges. These by-products require further treatment and processing before they are suitable for ultimate disposal. In general, the waste sludge is thickened, stabilized by anaerobic or aerobic digestion, and dewatered before land application or land disposal (19, 20). The design parameters for the selection and sizing of various process units are given in Table 5 and Figure 3.

Before 1960, research and development work was directed toward the improvement of aerobic biological treatment systems. Fixed media were utilized on which microorganisms could attach and grow, eg, stone or plastic trickling filters, rotating biological contactors, etc (see Fig. 4) (21, 22). Other designs of attached-growth biological systems include the use of synthetic and redwood media, as well as granular media (Figs. 5 and 6).

The post–World War II growth in industrial activity has significantly altered the composition of wastewaters in urban treatment facilities. Pollutants that are resistant to biological oxidation have become

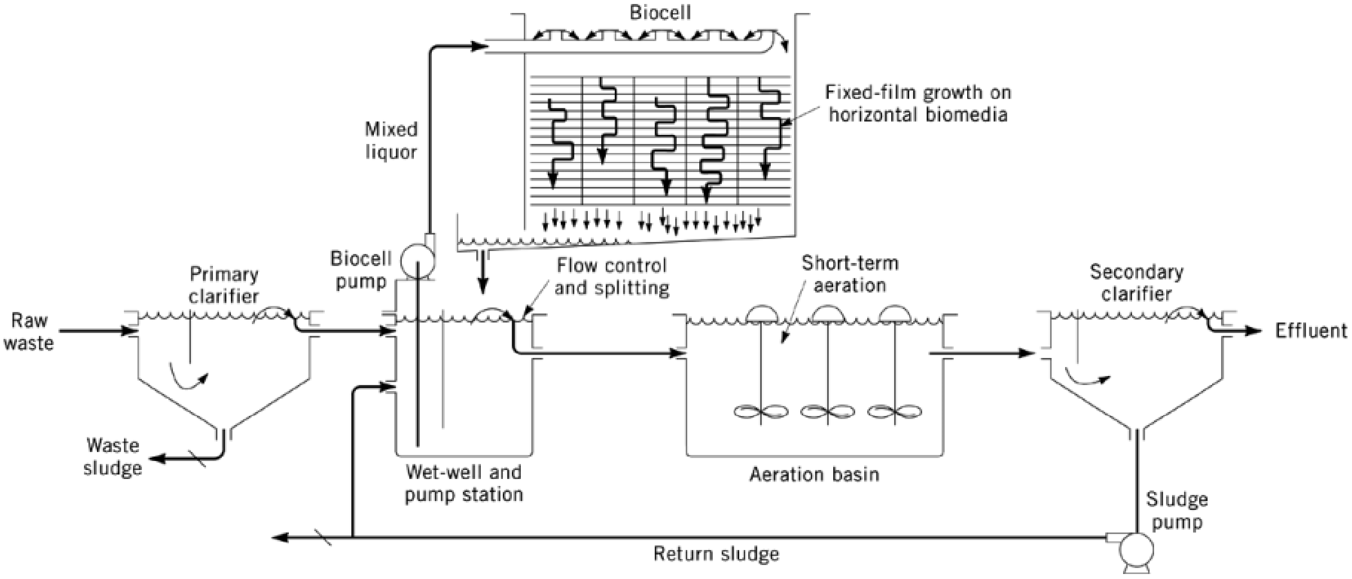

Fig. 5. ABF (activated bio filter) process flow diagram (redwood medium) (22, 23).

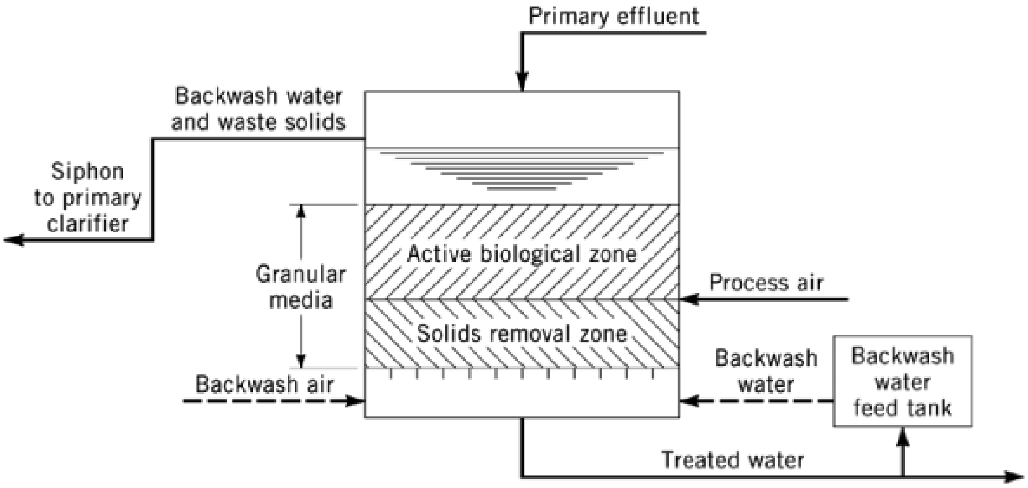

Fig. 6. Biological aerated filter.(Courtesy of Envirotech, Inc.)

predominant (eg, synthetic detergents, petrochemicals, synthetic rubber, etc), requiring the development of new nonbiological processes and approaches to water-pollution control. Today, the industrial-wastewater engineer must be familiar with the manufacturing process and the chemistry of the raw materials, products, and by-products.

2.1. Primary Investigation

The basic systems engineering approach is the most suitable method for developing a solution to industrial wastewater management. The preliminary investigation includes a plant survey and the characterization of the wastewater source.

A wastewater survey provides the facts and data necessary to complete a wastewater management plan which comprises the following steps: segregation of clean water for potential recovery and reuse; isolation and segregation of noncompatible waste streams for separate pretreatment (eg, ion-exchange-regeneration wastes, inorganic and organic waste streams, waste streams that contain potentially toxic compounds, etc); isolation and segregation of concentrated waste streams and streams containing solvents for possible recovery or separate treatment and disposal (ie, thermal decomposition with heat recovery); and identification and characterization of batch discharges and spills in order to incorporate protective systems (eg, equalization) for the treatment facility.

Point number	Sludge, kg/m^3	Concentration, %
1	129.4	4
2	98.3	0.8
3	227.7	2.6
4	227.7	8
5	113.8	5
6	113.8	20

2.2. In-Plant Waste Control

Pollution can be reduced or eliminated by process modification, chemical and raw materials substitution, or recovery of by-products. In addition, process modification generally increases product yield by incorporating control devices.

2.3. Waste Minimization

Before end-of-pipe wastewater treatment or modifications to existing wastewater treatment facilities to meet new effluent criteria, a program of waste minimization should be initiated.

Reduction and recycling of waste are inevitably site and plant specific, but a number of generic approaches and techniques have been used successfully across the country to reduce many kinds of industrial wastes.

Generally, waste minimization techniques can be grouped into four major categories: inventory management and improved operations, modification of equipment, production process changes, and recycling and reuse. Such techniques can have applications across a range of industries and manufacturing processes and can apply to hazardous as well as nonhazardous waste.

Many of these techniques involve source reduction—the preferred option on the EPA's hierarchy of waste management (24). Others deal with on- and off-site recycling. The best way to determine how these general approaches can fit a particular company's needs is to conduct a waste minimization assessment, as discussed above. In practice, waste minimization opportunities are limited only by the ingenuity of the generator. In the end, a company looking carefully at bottom-line returns may conclude that the most feasible strategy would be a combination of source reduction and recycling projects.

Waste minimization approaches as developed by the U.S. EPA are as follows:

2.3.1. Inventory Management and Improved Operations

(*1*) Inventory and trace all raw materials. (*2*) Purchase fewer toxic and more nontoxic production materials. (*3*) Implement employee training and management feedback. (*4*) Improve material receiving, storage, and handling practices.

2.3.2. Modification of Equipment

(*1*) Install equipment that produces minimal or no waste. (*2*) Modify equipment to enhance recovery or recycling options. (*3*) Redesign equipment or production lines to produce less waste. (*4*) Improve operating efficiency of equipment. (*5*) Maintain strict preventive maintenance program.

2.3.3. Production Process Changes

(*1*) Substitute nonhazardous for hazardous raw materials. (*2*) Segregate wastes by type for recovery. (*3*) Eliminate sources of leaks and spills. (*4*) Separate hazardous from nonhazardous wastes. (*5*) Redesign or reformulate end products to be less hazardous. (*6*) Optimize reactions and raw material use.

2.3.4. Recycling and Reuse

(*1*) Install closed-loop systems. (*2*) Recycle on site for reuse. (*3*) Recycle off site for reuse. (*4*) Exchange wastes.

In order to implement the program, an audit needs to be made, as described in the following:

2.3.5. Phase I: Preassessment

(*1*) Audit focus and preparation. (*2*) Identify unit operations and processes. (*3*) Prepare process flow diagrams.

2.3.6. Phase II: Mass Balance

(*1*) Determine raw material inputs. (*2*) Record water usage. (*3*) Assess present practice and procedures. (*4*) Quantify process outputs. (*5*) Account for emissions: to atmosphere, to wastewater, and to off-site disposal. (*6*) Assemble input and output information. (*7*) Derive a preliminary mass balance. (*8*) Evaluate and refine the mass balance.

2.3.7. Phase III: Synthesis

(*1*) Identify options: identify opportunities, target problem areas, and confirm options. (*2*) Evaluate options: technical, environmental, and economic. (*3*) Prepare action plan: waste reduction plan, production efficiency plan, and training.

For further information see Wastes,INDUSTRIAL and Ref. 16.

2.4. Toxic Organic Materials

The term toxic organics includes synthetic organic compounds such as pesticides, herbicides, PCBs, and chlorinated hydrocarbons, usually produced by the manufacturers and formulators of these products.

Because these compounds persist over a long period of time in a natural environment, the most effective treatment technology at present is incineration. The recommended temperatures for incineration of chlorinated hydrocarbons and pesticides range from 982 to 1482°C. A sustained high temperature prevents the emission of degradation products. The incinerator stack gases generally contain HCl vapors that require the installation of scrubbers. In general, a vortex burner provides satisfactory performance. The mixture is preheated, the liquid vaporized, and the gases heated to ignition temperature (28, 29) (see Incinerators).

The vortex burner maintains stable combustion temperature when the organic concentration in the waste is sufficiently high and has a heating value of ca 10.5–12.6 MJ/kg (4500–5400 Btu/lb). Auxiliary fuel may be required when the chloride concentration in the waste exceeds 70% (30).

In wet-air oxidation, the aqueous mixture is heated under pressure in the presence of air, which oxidizes the organic material. The efficiency of the oxidation process is a function of reaction time and temperature. The oxidation products are generally less complex and can be treated by conventional biological methods (31). The reactor usually operates between 177 and 321°C with pressures of 2.52–20.8 MPa (350–3000 psig).

If the concentration of organic material is too low, the following technique discussed below may be used.

2.5. Membrane Separation

Reverse osmosis (qv) or ultrafiltration (qv) can be used to concentrate toxic organic substances, depending on the type of compounds and the stability of the membrane against chemical attack (see also Membrane technology). In general, high molecular weight compounds have higher rejection rates than those obtained with lower molecular weight compounds. Typical rejection rates are given in Table 6.

Table 6. Membrane Rejection Rates

Compound	Percent
lindane	84
DDT[a]	99.5
DDD[b]	99.9
2,4-D[c]	99.9
chlorinated hydrocarbons	98.95–100
organophosphorus pesticides	98.05–98.88
miscellaneous pesticides	72–100

[a] Dichlorodiphenyltrichloroethane.

[b] 1,1-Dichloro-2,2-bis(*p*-chlorophenyl)ethane.

[c] 2,4-Dichlorophenoxy acetic acid.

2.6. Chemical Treatment

Some organic compounds are attacked by chemical reagents such as potassium permanganate, sodium hydroxide, calcium hypochlorite, and ozone (29, 30).

Potassium permanganate oxidizes heptachlor with ca 80–90% efficiency (30). Sodium hydroxide degrades malathion, lindane, and DDT (30, 32). Ozone oxidizes dissolved organic compounds, including toxic substances, because of an oxidation potential higher than that of permanganate, hydrogen peroxide, or hypochlorite. The ozonation system must be designed to carry the reaction to completion in order to prevent the generation of toxic intermediates. Ultraviolet radiation in conjunction with ozone is a highly effective degradation technique for malathion, DDT, pentachlorophenol, dichlorobutane, dichlorobenzene, PCBs, and chloroform (33, 34).

Ozone alone oxidizes phenolic compounds to carbon dioxide and water. However, at concentrations of 1.5–2.5 parts ozone per part of phenol, the phenolic compounds can be converted to less toxic and biodegradable intermediates in a cost-effective manner (35).

2.7. Adsorption

Organic compounds are adsorbed on activated carbon and synthetic resins (eg, XAD-2 and XAD-4, Rohm and Haas Co.). This technique depends on the properties of the compound being removed and the regenerative capability of the adsorbent. The EPA has developed carbon-adsorption isotherms for various toxic organic compounds, and the results are shown in Table 7 (36). The following compounds are not adsorbed on activated carbon: acetone cyanohydrin, butylamine, choline chloride, cyclohexylamine, diethylene glycol, ethylenediamine, hexamethylenediamine, morpholine, and triethanolamine.

Table 7. Adsorption Capacities of Activated Carbon

Compound	Adsorption capacity, mg/g	Compound	Adsorption capacity, mg/g
bis(2-ethylhexyl) phthalate	11,300	guanine	120
butyl benzyl phthalate	1,520	styrene	120
heptachlor	1,220	1,3-dichlorobenzene	118
heptachlor epoxide	1,038	acenaphthylene	115
endosulfan sulfate	686	4-chlorophenyl phenyl ether	111
endrin	666	diethyl phthalate	110
fluoranthene	664	2-nitrophenol	99
aldrin	651	dimethyl phthalate	97
PCB-1232	630	hexachloroethane	97
β-endosulfan	615	chlorobenzene	91
dieldrin	606	*p*-xylene	85
hexachlorobenzene	450	2,4-dimethylphenol	78
anthracene	376	4-nitrophenol	76
4-nitrobiphenyl	370	acetophenone	74
fluorene	330		74
		1,2,3,4-tetrahydronaph-thalene	
DDT	322		
2-acetylaminofluorene	318	adenine	71
α-BHC	303	dibenzo[*a,h*]anthracene	69
anethole	300	nitrobenzene	68
3,3-dichlorobenzidine	300	3,4-benzofluoranthene	57
2-chloronaphthalene	280	1,2-dibromo-3-chloropropane	53
phenylmercuric acetate	270	ethylbenzene	53
hexachlorobutadiene	258	2-chlorophenol	51
γ-BHC (lindane)	256	tetrachloroethylene	51
p-nonylphenol	250	*o*-anisidine	50
4-dimethylaminoazobenzene	249	5-bromouracil	44
chlordane	245	benzo[*a*]pyrene	34
PCB-1221	242	2,4-dinitrophenol	33
	232	isophorone	32
1,1-dichloro-2,2-bis(*p*-chloro- phenyl)ethane (DDE)		trichloroethylene	28
acridine yellow	230	thymine	27
benzidine dihydrochloride	220	toluene	26
β-benzenehexachloride	220	5-chlorouracil	25
n-butyl phthalate	220	*N*-nitrosodi-*n*-propylamine	24
N-nitrosodiphenylamine	220	bis(2-chloroisopropyl) ether	24
phenanthrene	215	phenol	21
dimethylphenylcarbinol	210	bromoform	20
4-aminobiphenyl	200	carbon tetrachloride	11
2-naphthol	200	bis(2-chloroethoxy)methane	11
α-endosulfan	194	uracil	11
acenaphthene	190	benzo[*ghi*]perylene	11
	190	1,1,2,2-tetrachloroethane	11
4,4′-methylenebis(2-chloro-aniline)			
		1,2-dichloropropene	8.2
benzo[*k*]fluoranthene	181	dichlorobromomethane	7.9
acridine orange	180	cyclohexanone	6.2
1-naphthol	180	1,2-dichloropropane	5.9

Table 7. ***Continued***

Compound	Adsorption capacity, mg/g	Compound	Adsorption capacity, mg/g
4,6-dinitro-*o*-cresol	169	1,1,2-trichloroethane	5.8
1-naphthylamine	160	trichlorofluoromethane	5.6
2,4-dichlorophenol	157	5-fluorouracil	5.5
1,2,4-trichlorobenzene	157	1,1-dichloroethylene	4.9
2,4,6-trichlorophenol	155	dibromochloromethane	4.8
2-naphthylamine	150	2-chloroethyl vinyl ether	3.9
pentachlorophenol	150	1,2-dichloroethane	3.6
2,4-dinitrotoluene	146	1,2-*trans*-dichloroethylene	3.1
2,6-dinitrotoluene	145	chloroform	2.6
4-bromophenyl phenyl ether	144	1,1,1-trichloroethane	2.5
p-nitroaniline	140	1,1-dichloroethane	1.8
1,1-diphenylhydrazine	135	acrylonitrile	1.4
naphthalene	132	methylene chloride	1.3
1-chloro-2-nitrobenzene	130	acrolein	1.2
1,2-dichlorobenzene	129	cytosine	1.1
p-chloro-*m*-cresol	124	benzene	1.0
1,4-dichlorobenzene	121	EDTA	0.86
benzothiazole	120	benzoic acid	0.76
diphenylamine	120	chloroethane	0.59
		N,*N*-dimethylnitrosamine	6.8×10^{-5}

Synthetic polymeric adsorbents have a high porosity, large surface area, and an inert hydrophobic surface. These resins can be regenerated chemically, which produces a concentrated waste stream requiring further treatment or disposal. The adsorption capacity of the polymeric adsorbent XAD-4 for a group of chlorinated hydrocarbons is given in Table 8. The EPA may recommend a combination of air stripping and carbon adsorption wherein air stripping removes most of the volatile organics and adsorption removes the rest (37).

Table 8. Adsorption Capacity of Amberlite XAD-4 Polymeric Resin[a]

Compounds	Maximum solubility in water, g/L	Influent concentration, mg/L	Adsorption capacity, kg/m^3
phenol	82	250	12.5
2-chlorophenol	26	350	38.5
2,4-dichlorophenol	4.5	430	81.6
2,4,6-trichlorophenol	0.9	510	192.3

[a] Ref. 36.

2.8. Heavy Metals

Heavy metals of particular concern in the treatment of wastewaters include copper, chromium, zinc, cadmium, mercury, lead, and nickel. They are usually present in the form of organic complexes, especially in wastewaters generated from textiles finishing and dye chemicals manufacture.

Inorganic heavy metals are usually removed from aqueous waste streams by chemical precipitation in various forms (carbonates, hydroxides, sulfide) at different pH values. The solubility curves for various metal hydroxides, when they are present alone, are shown in Figure 7. The presence of other metals and complexing agents (ammonia, citric acid, EDTA, etc) strongly affects these solubility curves and requires careful evaluation to determine the residual concentration values after treatment (see Table 9) (38, 39).

Other methods, including activated carbon, ion exchange, and reverse osmosis, can be used to concentrate waste streams and remove the heavy metals. Activated carbon is effective in reducing hexavalent chromium,

Table 9. Typical Residual Concentrations after Chemical Precipitation[a]

Metal	Agent	Residual concentration, mg/L
cadmium	soda ash	0.3
chromium (hexavalent)	sodium bisulfite and lime	0.05
chromium (total)	caustic, lime	0.5
copper	caustic, lime	0.5
nickel	soda ash	0.5
zinc	caustic, lime	0.5

[a] Ref. 38.

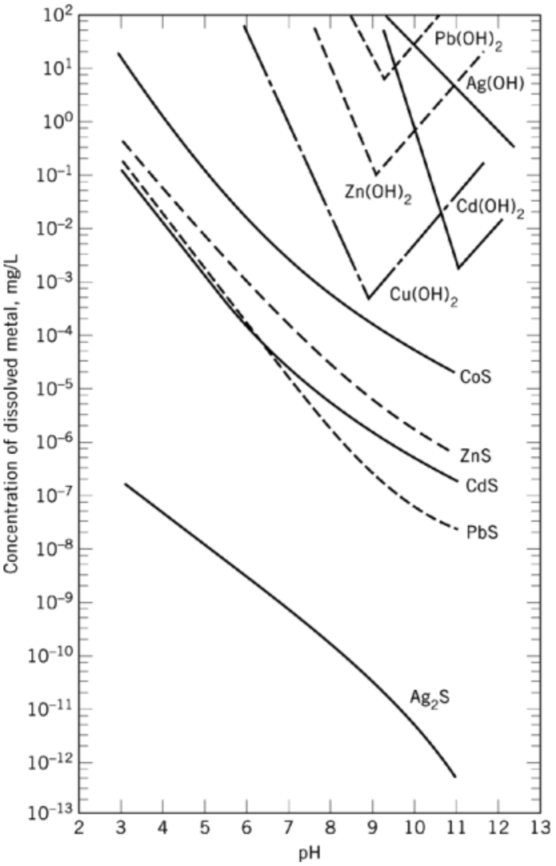

Fig. 7. Theoretical solubilities of metal hydroxides and sulfides as a function of pH (37).

mercury, and many metals complexed by organic liquids. Similarly, various ion-exchange resins have been found to be effective in reducing metal ions from solution. The spent resins and activated carbon may require chemical regeneration, however, which may produce a concentrated waste stream that again requires treatment.

See Wastes,INDUSTRIAL for more information on wastewater treatment.

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