Kirk-Othmer Encyclopedia of Chemical Technology.

WASTES, INDUSTRIAL

Recent legislation in the United States (ca 1997) has added several new parameters to the requirements for effluent permits. Parameters to be considered now, depending on the plant location, are biochemical oxygen demand (BOD), total suspended solids (TSS), chemical oxygen demand (COD), volatile organic compounds (VOC), priority pollutants, aquatic toxicity, heavy metals, nitrogen, and phosphorus. Because most industries have an existing wastewater treatment plant, in order to meet these new criteria upgrading, pretreatment, or tertiary treatment will be required. Innovative technologies and modifications to existing technologies are now (ca 1997) becoming available.

1. Waste Minimization

Before end-of-pipe wastewater treatment or modifications to existing wastewater treatment facilities to meet new effluent criteria are undertaken, 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 United States to reduce many kinds of industrial wastewaters.

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 wastes.

Many of these techniques involve source reduction, the preferred option in the U.S. Environmental Protection Agency's (EPA's) hierarchy of waste management techniques. Others deal with on- and off-site recycling. The best way to determine how these general approaches can be designed to fit a particular company's needs is to conduct a waste minimization assessment. In practice, waste minimization opportunities are limited only by the extent of the ingenuity of the generator. In the end, a company looking carefully at overall returns of waste minimization may well conclude that the most feasible strategy would be to use a combination of source reduction and recycling projects. Waste minimization approaches as developed by the EPA are shown in Table 1.

The six major ways of reducing pollution are as follows:

(1) Recirculation. In the paper board industry, white water from a paper machine can be put through a saveall to remove the pulp and fiber and then be recycled to various points in the paper-making process.
(2) Segregation. Clean streams are separated for direct discharge. Concentrated or toxic streams are separated for separate treatment.
(3) Disposal. In many cases, concentrated wastes can be removed in a semidry state. In the production of ketchup, the kettle bottoms after cooking and preparation of the product are usually flushed to the sewer.

Table 1. Waste Minimization Approaches and Techniques

Approach	Related techniques
inventory management and improved operations	inventory and trace all raw materials
	purchase fewer toxic and more nontoxic production materials
	implement employee training and management feedback
	improve material receiving, storage, and handling practices
modification of equipment	install equipment that produces minimal or no waste
	modify equipment to enhance recovery or recycling options
	redesign equipment or production lines to produce less waste
	improve operating efficiency of equipment
	maintain strict preventive maintenance program
production process changes	substitute nonhazardous for hazardous raw materials
	segregate wastes by type for recovery
	eliminate sources of leaks and spills
	separate hazardous from nonhazardous wastes
	redesign or reformulate end products to be less hazardous
	optimize reactions and raw material use
recycling and reuse	install closed-loop systems
	recycle on-site for reuse
	recycle off-site for reuse
	exchange wastes

The total discharge BOD and suspended solids can be markedly reduced by removal of this residue in a semidry state for disposal. In breweries, the secondary storage units have a sludge in the bottom of the vats that contains both BOD and suspended solids. Removal of this as a sludge rather than flushing to the sewer will reduce the organic and solids load to treatment.

(4) Reduction. It is common practice in many industries, such as breweries and dairies, to have hoses continuously running for clean-up purposes. The use of automatic cutoffs can substantially reduce the wastewater volume.

(5) The use of drip pans to catch products, in cases such as a dairy or ice-cream manufacturing plant, instead of flushing this material to the sewer, considerably reduces the organic load. A similar case exists in the plating industry where a drip pan placed between the plating bath and the rinse tanks will reduce the metal dragout.

(6) Substitution. The substitution of chemical additives of a lower pollutional effect in processing operations, eg, substitution of surfactants for soaps in the textile industry.

Water reuse is usually a question of the tradeoff between the costs of raw water and the costs associated with treatment for reuse and for discharge. If biological treatment is to be employed, several factors must be considered. These are an increase in concentration of organics, both degradable and nondegradable. This may have a negative effect in terms of final effluent toxicity. An increase in temperature or total dissolved solids may adversely affect the performance of the biological process.

2. Characterization of Wastewaters

A comprehensive analytical program for characterizing wastewaters should be based on relevance to unit treatment process operations, the pollutant or pollutants to be removed in each, and effluent quality constraints. The qualitative and quantitative characteristics of waste streams to be treated not only serve as a basis for sizing system processes within the facility, but also indicate streams having refractory constituents, potential toxicants, or biostats. Such streams are not amenable to effective biological treatment, as indicated by the characterization results, and require treatment using alternative processes.

It should be recognized that the total volume of wastewater as well as the chemical analyses indicating the organic and inorganic components are required, backed by statistical validity, before the conceptualizing of the overall treatment plant design can begin. The basic parameters in wastewater characterization are summarized in Table 2.

3. Industrial Wastewater Flow

The design flows for industrial complexes generally consist of the following: (*1*) base process flows resulting from normal production operations; (*2*) sanitary sewage; (*3*) contaminated storm runoff; (*4*) other sources, eg, extraordinary dumps, tank draining, and ballast discharge. The base flow and sanitary contribution can be measured in open channels or closed conduits using a variety of methods, such as automatic metering devices, weirs, or less sophisticated devices. Care should be taken to ensure flows are measured during workday and weekend operations, different work shifts, and over a sufficiently long period of time to reflect statistical reliability.

Since the mid-1980s, contaminated storm runoff has become an object of increasing concern within industrial complexes. Storm flow is intermittent and unpredictable in nature, and little data has been collected to typify its characteristics. The level of flow and degree of contamination not only varies within an installation; it has its own geometric characteristics, which influence patterns of surface runoff.

4. Definition of Wastewater Constituents

Parameters used to characterize wastewaters can be classified as organic and inorganic analyses. The organic content of wastewater is estimated in terms of oxygen demand using biochemical oxygen demand (BOD), chemical oxygen demand (COD), or total oxygen demand (TOD). Additionally, the organic fraction can be expressed in terms of carbon, using total organic carbon (TOC). It should be understood that these parameters do not necessarily measure the same constituents. Specifically, they reflect the following: (*1*) BOD: biodegradable organics in terms of oxygen demand; (*2*) COD: organics amenable to chemical oxidation as well as certain inorganics, such as sulfides, sulfites, ferrous iron, chlorides, and nitrites; (*3*) TOD: all organics and some inorganics in terms of oxygen demand: and (*4*) TOC: all organic carbon expressed as carbon.

It is important to identify volatile organic carbon (VOC) and the presence of specific priority pollutants, in addition to the total organic content. The organic characteristics of various industrial wastewaters are shown in Table 3.

The inorganic characterization schedule for wastewaters to be treated using biological systems should include those tests which provide information concerning (*1*) potential toxicity, such as heavy metal, ammonia, etc; (*2*) potential inhibitors, such as total dissolved solids (TDS) and chlorides; (*3*) contaminants requiring specific pretreatment such as pH, alkalinity, acidity, suspended solids, etc; and (*4*) nutrient availability.

Aquatic toxicity is becoming (ca 1997) a permit requirement on all discharges. Aquatic toxicity is generally reported as an LC_{50} (the percentage of wastewater which causes the death of 50% of the test organisms in a specified period ie, 48 or 96 h, or as a no observed effect level (NOEL), in which the NOEL is the highest effluent concentration at which no unacceptable effect will occur, even at continuous exposure.

Toxicity is also frequently expressed as toxicity units (TU), which is 100 divided by the toxicity measured:

$$\mathrm{TU} = \frac{100}{\mathrm{LC}_{50}\,\mathrm{or\ NOEL}}$$

Table 2. Basic Parameters in Wastewater Characterization[a]

Parameter	Examples
Basic parameters in wastewater characterization	
	source information for the individual points of origin
	waste constituents (specific compounds or general composition)
	discharge rate (average and peak)
	batch discharges
	frequency of emergency discharges or spills
chemical composition	organic and inorganic constituents
	gross organics
	chemical oxygen demand (COD)
	total organic carbon (TOC)
	biochemical oxygen demand (BOD)
	extractables
	toxics, hazardous compounds, priority pollutants
	gross inorganics—total dissolved solids
	specific inorganic ions (As, Ba, Cd, CN, Hg, Pb, Se, Ni, Sn, nitrates)
	pH, acidity, alkalinity
	nitrogen and phosphorus
	oil and grease
	oxidizing reducing agents, eg, sulfides
	surfactants
	chlorine demand
physical properties	temperature range and distribution
	particulates: colloidal, settleable, and flotable solids
	color
	odor
	foamability
	corrosiveness
	radioactivity
biological factors	biochemical oxygen demand
	toxicity (aquatic life, bacteria, animals, plants)
	pathogenic bacteria
flow characteristics	average daily flow rate
	duration and magnitude of peak flow rate
	maximum rate of change of flow rate
	storm-water flow rate (average and peak)
Causes of Variability in Waste Characterization	
	changes in production rate
	variations in plant product mix
	batch operations
	variations in efficiencies of production units
	changes in raw materials
	upsets in production processes
	maintenance (equipment shutdown and cleanout)
	miscellaneous leaks and spills
	contaminated drainage and runoff from rainstorms

[a] Ref. 1

inwhich the LC_{50} or the NOEL is expressed as the percent effluent in the receiving water. Therefore, an effluent having an LC_{50} of 10% contains 10 toxic units.

Effluent toxicity can also be defined as a chronic toxicity in which the growth or reproduction rate of the species is affected.

Table 3. Oxygen Demand and Organic Carbon of Industrial Wastewaters

Waste	BOD, mg/L	COD, mg/L	TOC, mg/L	BOD/TOC	COD/TOC
chemical[a]		4,260	640		6.65
chemical[a]		2,410	370		6.60
chemical[a]		2,690	420		6.40
chemical		576	122		4.72
chemical	24,000	41,300	9,500	2.53	4.35
chemical–refinery		580	160		3.62
petrochemical		3,340	900		3.32
chemical	850	1,900	580	1.47	3.28
chemical	700	1,400	450	1.55	3.12
chemical	8,000	17,500	5,800	1.38	3.02
chemical	60,700	78,000	26,000	2.34	3.00
chemical	62,000	143,000	48,140	1.28	2.96
chemical		165,000	58,000		2.84
chemical	9,700	15,000	5,500	1.76	2.72
nylon polymer		23,400	8,800		2.70
petrochemical					2.70
nylon polymer		112,600	44,000		2.50
olefin processing		321	133		2.40
butadiene processing		359	156		2.30
chemical		350,000	160,000		2.19
synthetic rubber		192	110		1.75

[a] High concentration of sulfides and thiosulfates.

5. Wastewater Treatment

In order to meet present (ca 1997) requirements, existing plants need to be retrofitted and new plants must incorporate advanced wastewater treatment technology. A substitution flow sheet showing available technology is shown in Figure 1. Options for meeting restrictive requirements are tertiary treatment following biological treatment, source treatment of toxic or refractory wastewaters, or modifications of the existing biological technology incorporating powdered activated carbon (PAC). These technologies are discussed herein in detail.

A summary of available technologies is given in Tables 4 and 5. Attainable effluent qualities are shown in Table 6.

6. Pre- or Primary Treatment

The principal objectives of pretreatment are to remove heavy metals prior to subsequent treatment, to neutralize the wastewater to a suitable pH for discharge or subsequent treatment; to remove high concentrations of suspended solids, to eliminate or reduce toxicity, and to eliminate or reduce volatiles.

The concentrations of various pollutants that make pretreatment desirable are summarized in Table 7.

6.1. Equalization

The objective of equalization is to reduce variability in flow or strength of industrial wastewaters so that they can be successfully treated using either biological or physical–chemical treatment processes. It is axiomatic that an increase in influent concentration will result in an increase in effluent concentration. A doubling of influent concentration will not necessarily result in a doubling of effluent concentration. If the wastewater is

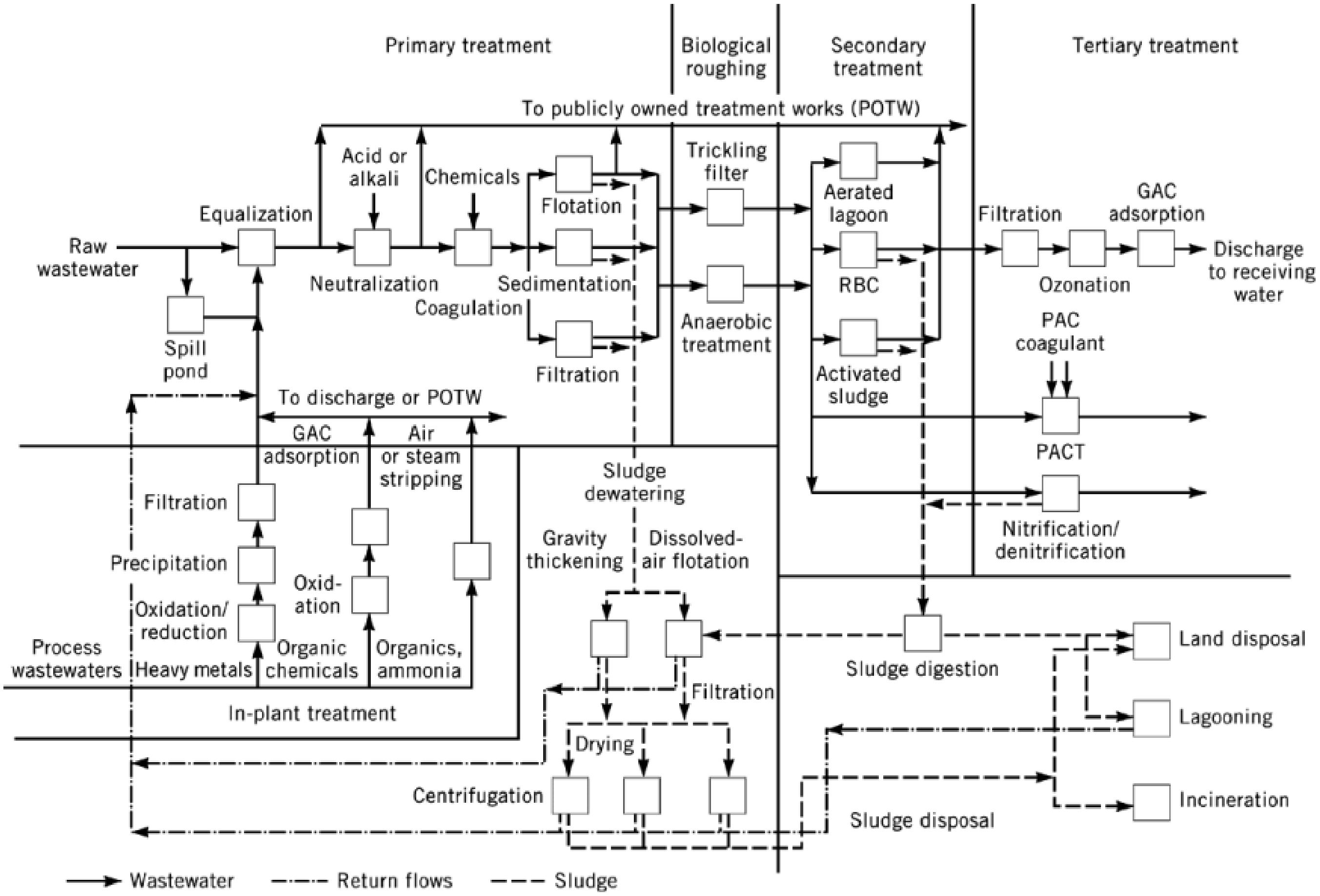

Fig. 1. Alternative wastewater treatment technologies, where GAC=granular activated carbon, PAC=powdered activated carbon, POTW=publicly owned treatment works, and RBC=rotating biological contactor; (⟶), wastewater; (–·–·⟶), return flows; (– – ⟶), sludge.

readily degradable, increased biological activity will reduce the effluent concentration. If inhibitory constituents exist, however, a doubling of the influent concentration may more than double the effluent concentration. It is therefore not possible to predict final effluent quality without a predication of influent quality. If the wastewater flow is fairly constant, as in a pulp and paper mill, a constant-volume basin can be employed in which wastewater strength is equalized.

If the wastewater flow and strength are highly variable, as in a batch process chemical plant, a variable-volume basin with a variable inflow and a constant outflow is employed to equalize both flow and strength.

If the wastewater is readily degradable, as in a brewery, aeration is provided in the equalization basin to avoid septicity and the generation of odors.

In order to handle accidental spills or overflows, a spill basin may be provided, into which the flow is diverted if the concentration of a particular constituent exceeds a predetermined value. If equalization precedes biological treatment, in addition to the organic loading, high fluctuations in temperature, salinity, and toxic organics must also be considered. After the spill is contained, the wastewater flow is diverted back

Table 4. Chemical Waste Treatment

Treatment method	Type of waste	Mode of operation	Degree of treatment	Remarks
ion exchange	plating, nuclear	continuous filtration with resin generation	demineralized water recovery; product recovery	may require neutralization and solids removal from spent regenerant
reduction and precipitation	plating, heavy metals	batch or continuous treatment	complete removal of chromium and heavy metals	one day's capacity for batch treatment; 3-h retention for continuous treatment; sludge disposal or de-watering required
coagulation	paperboard, refinery, rubber, paint, textile	batch or continuous treatment	complete removal of suspended and colloidal matter	flocculation and settling tank or sludge blanket unit; pH control required
adsorption	toxic or organics, refractory	granular columns of powdered carbon	complete removal of most organics	powdered carbon (PAC) used with activated sludge process
chemical oxidation	toxic and organics, refractory	batch or continuous ozone or catalyzed hydrogen peroxide	partial or complete oxidation	partial oxidation to render organics more bio-degradable

to the equalization basin. The contents of the spill basin are then pumped at a constant controlled rate to the equalization basin.

6.2. Neutralization

Wastewater discharge usually requires a pH between 6 and 9. Exceptions are a biological process in which microbial respiration degrades acidity (acetic acid is oxidized to CO_2 and H_2O), or one in which the CO_2 generated by microbial respiration neutralizes caustic alkalinity (OH^-) to bicarbonate HCO_3.

Neutralization usually follows equalization so that acidic and alkaline streams can be partially neutralized in the equalization basin. If the wastewater is always acidic, neutralization may occur at a stage prior to the stream reaching the equalization basin, so as to minimize corrosion in the equalization basin.

Acidic wastewaters can be neutralized with lime, magnesium hydroxide, caustic, or limestone. Lime or magnesium hydroxide is preferred over caustic because it is lower in cost and usually produces a more dewaterable sludge. A limestone bed is simple to operate and is applicable to moderately acidic wastewaters. The wastewater should have a near-constant acidity in order to maintain a constant effluent acidity. Highly acidic wastewaters require a two-stage process because of the logarithmic nature of pH. The first stage adjusts the pH to 3–3.5, and the second stage trims the pH to 6.5–7.5. A two-stage neutralization process is shown in Figure 2.

Alkaline wastewaters can be neutralized with H_2SO_4 or HCl, or by using flue gas (CO_2).

6.3. Removal of Oil and Grease

High concentrations of oil and grease can be removed in a gravity separator where the lighter oils and greases float to the surface, where they are skimmed off. The API gravity separator removes oil globules of 0.015 cm or greater and can achieve an effluent oil content of less than 50–100 mg/L. The corrugated plate separator with a narrow separation space can remove oil globules of 0.01 cm or greater. As a result, effluent oil concentrations as low as 10 mg/L are achievable. A corrugated plate oil separator is shown in Figure 3.

Low concentrations of oil can be removed by dissolved air flotation (DAF). In this process, an effluent recycle is pressurized in the presence of excess air, causing additional air to go into solution, in accordance with

Table 5. Biological Waste Treatment

Treatment method	Mode of operation	Degree of treatment	Land requirements	Equipment	Remarks
lagoons	intermittent or continuous discharge; faculative or anaerobic	intermediate	earth dug; 10–60 days' retention (may require lining)		odor control frequently required groundwater considerations
aerated lagoons	completely mixed or faculative continuous basins	high in summer; less in winter	lined earth basin, 2.44–4.88 m deep; 8.55–17.1 $m^3/(m^3{\cdot}d)$	pier-mounted or floating surface aerators or sub-surface diffusers	solids separation in lagoon; periodic de-watering and sludge removal groundwater considerations
activated sludge	completely mixed or plug flow; sludge recycle	$>90\%$ removal of organics	earth or concrete basin; 3.66–6.10 m deep; 0.561–2.62 $m^3/(m^3{\cdot}d)$	diffused or mechani-cal aerators; clari-fier for sludge separation and recycle	excess sludge dewatered and disposed of
trickling filter	continuous application; may employ effluent recycle	intermediate or high, depending on loading	5.52–34.4 $m^3/(10^3\ m^3{\cdot}d)$	plastic packing 6.10–12.19 m deep	pretreatment before POTW or activated sludge plant
RBC	multistage continuous	intermediate or high		plastic disks	solids separation required
anaerobic	complete mix with re-cycle; upflow or down-flow filter, fluidized bed; upflow sludge blanket	intermediate		gas collection required; pretreat-ment before POTW or activated sludge plant	
spray irri-gation	intermittent application of waste	complete; water percolation into groundwater and runoff to stream	$6.24 \times 10^{-7} - 4.68 \times 10^{-6}\ m^3/(s{\cdot}m^2)$	aluminum irrigation pipe and spray nozzles; movable for relocation	solids separation required; salt content in waste limited

Henry's Law. When this water is discharged to the inlet chamber of the flotation unit at close to atmospheric pressure, the dissolved air comes out of solution in the form of tiny air bubbles which attach themselves to and become enmeshed in suspended solids and oil globules. The primary design criteria is the air/solids ratio, which is defined as the mass of air released divided by the mass of solids fed. Sufficient air must be released to capture the solids in the influent wastewater. The performance of DAF for the treatment of several wastewaters is shown in Table 8. In cases where the oil globules are of a very small size, a coagulant, usually alum, and a polymer are added to flocculate the particles, thereby enhancing bubble attachment and flotation. A DAF system is shown in Figure 4.

Alternatively, induced air flotation (IAF) can be employed, in which air bubbles are generated through an inductor. The removal mechanism is the same as the DAF.

Emulsified oil contains a liquid film so that it will not separate by gravity without first breaking the emulsion. This is achieved by adding surfactants, emulsion breaking polymers or coagulants. After the emulsion is broken, the conventional technologies described above are applicable.

Table 6. Maximum Quality Attainable From Waste Treatment Processes

Process	BOD	COD	SS	N	P	TDS
sedimentation, % removal	10–30		59–90			
flotation[a], % removal	10–50		70–95			
activated sludge, mg/L	<25	[b]	<20	[c]	[c]	
aerated lagoons, mg/L	<50		<50			
anaerobic ponds, mg/L	>100		<100			
deep-well disposal	[d]					
carbon adsorption, mg/L	<2	<10	<1			
denitrification and nitrification, mg/L	<10			<5		
chemical precipitation, mg/L			<10		<1	
ion exchange, mg/L			<1	[e]	[e]	[e]

[a] Higher removals are attained when coagulating chemicals are used.

[b] $\mathrm{COD_{inf}} - [\mathrm{BOD_{ult}}(\text{removed}/0.9)]$.

[c] $\mathrm{N_{inf}} - 0.12$ (excess biological sludge), kg; $\mathrm{P_{inf}} - 0.026$ (excess biological sludge), kg.

[d] Total disposal of waste.

[e] Depends on resin used, molecular state, and efficiency desired.

Table 7. Concentration of Pollutants That Make Prebiological Treatment Desirable

Pollutant or system condition	Limiting concentration	Kind of pretreatment
suspended solids, mg/Ld	>125	sedimentation, flotation, lagooning
oil or grease	>35	skimming tank or separator
toxic ions, mg/L		precipitation or ion exchange
Pb	≤ 0.1	
Cu + Ni + CN	≤ 1	
$\mathrm{Cr^{6+}}$ + Zn	≤ 3	
$\mathrm{Cr^{3+}}$	≤ 10	
pH	6 to 9	neutralization
alkalinity	[a]	neutralization for excessive alkalinity
acidity	[b]	neutralization
organic load variation	$>2{:}1$	equalization
sulfides, mg/L	>100	precipitation or stripping with recovery
ammonia, mg/L as N	>500	dilution, ion exchange, pH adjustment and stripping
temperature, °C in reactor	>38	cooling

[a] Alkalinity of 0.5 kg as $\mathrm{CaCO_3}$ BOD removed.

[b] Free mineral acidity.

Table 8. Air Flotation Treatment of Oily Wastewaters

Wastewater	Coagulant, mg/L	Oil concentration, mg/L		
		Influent	Effluent	Removal, %
refinery	0	125	35	72
	100 alum	100	10	90
	130 alum	580	68	88
	0	170	52	70
oil tanker ballast water	100 alum + 1 mg/L polymer	133	15	89
paint manu-facture	150 alum + 1 mg/L polymer	1,900	0	100
aircraft mainte-nance	30 alum + 10 mg/L activated silica	250–700	20–50	90+
meat packing		3,830	270	93
		4,360	170	96

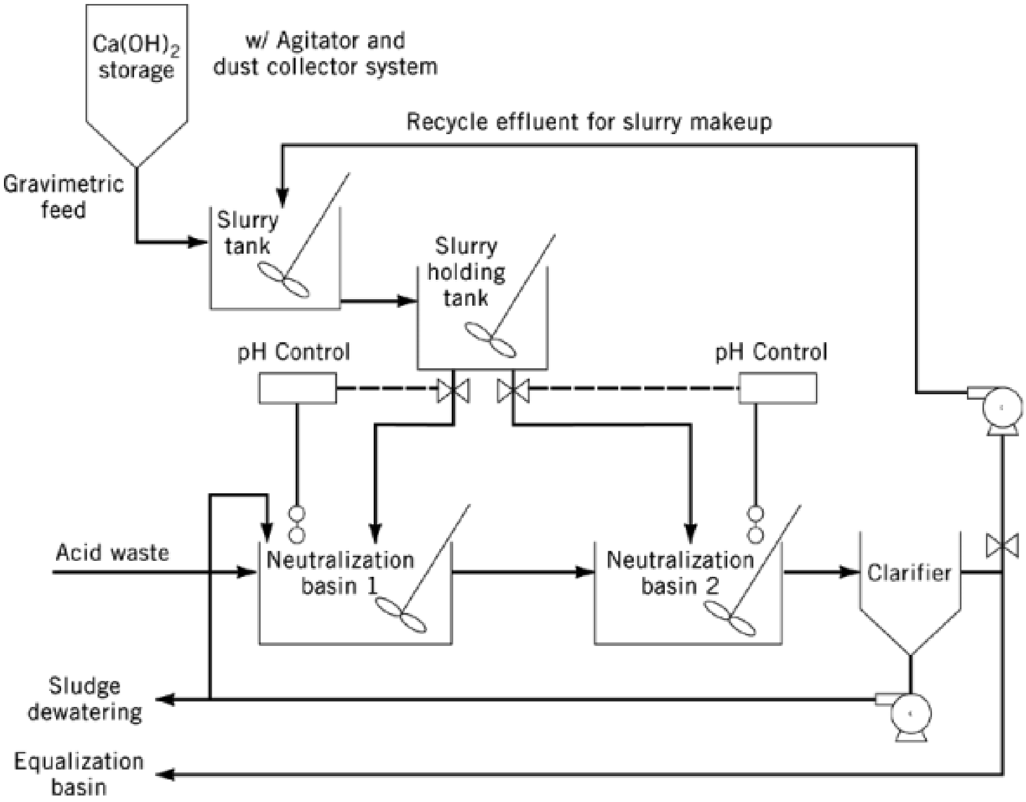

Fig. 2. Schematic diagram of a two-stage pH neutralization system.

6.4. Suspended Solids Removal

Depending on the concentration and characteristics of the suspended solids, they can be removed by filtration, flotation, or sedimentation. Coarse solids are removed by screening. Settleable suspended solids are removed in a clarifier, which may be circular or rectangular. The efficiency of solids removal is a function of the overflow rate ($m^3/m^2{\cdot}d$ ($gal/ft^2{\cdot}d$) as shown in Figure 5.

Inorganic and organic colloidal suspensions in wastewater can be removed by chemical coagulation. Coagulation has been defined as the addition of a positively charged ion such as Al^{3+}, Fe^{3+}, or cationic polyelectrolyte that results in particle destabilization and charge neutralization. Coagulation involves the formation of complex oxides that form flocculent suspensions which subsequently are separated from the liquid by sedimentation. Examples include colloidal dispersions of turbidity and color. The coagulants commonly employed are alum (Al_2SO_{43}), iron ($FeCl_3$), and sometimes lime ($CaOH_2$). Cationic or anionic polyelectrolytes are also used to enhance coagulation. A sludge blanket unit with sludge recirculation that will frequently result in lower coagulant requirements and enhanced clarification is shown in Figure 6.

The application of coagulation for removal of dispersed and colloidal solids of several industrial wastewaters is shown in Table 9.

Filtration is employed when the suspended solids concentration is less than 100 mg/L and high effluent clarity is required. Finely dispersed suspended solids require the addition of a coagulant prior to filtration. Filters most commonly used in wastewater treatment are a dual media (anthrafilt and sand) or a moving bed

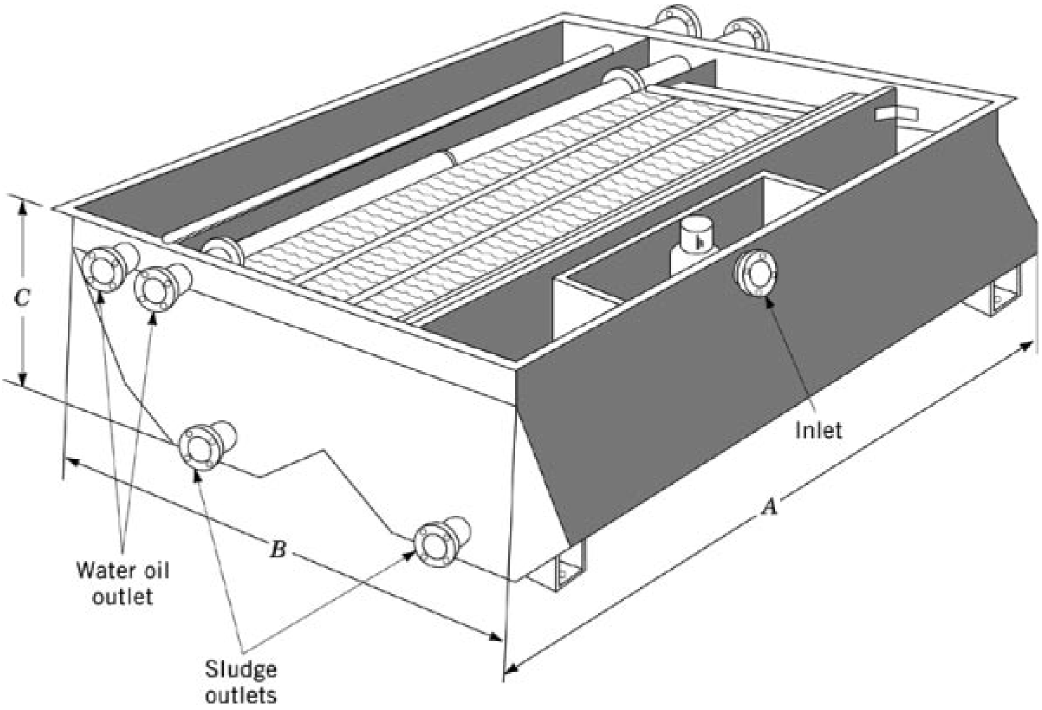

Fig. 3. Cutaway of a corregated plate oil separator.

Table 9. Coagulation of Industrial Wastewaters

Wastewater	Parameter	Influent, mg/L	Effluent, mg/L
board mill	BOD	127	68
	TSS	593	44
tissue mill	BOD	140	36
	TSS	720	15
ball bearing	TSS	544	40
	O/G	302	28
laundry	ABS	63	0.1
	BOD	243	90
latex	COD	4,340	178
	BOD	1,070	90
	total solids	2,550	446

or continuous-backwash sand filter. Performance data for the tertiary filtration of municipal and industrial wastewater are shown in Table 10.

6.5. Heavy Metals Removal

Heavy metals should be removed prior to biological treatment or use of other technologies which generate sludges to avoid comingling metal sludges with other, nonhazardous sludges.

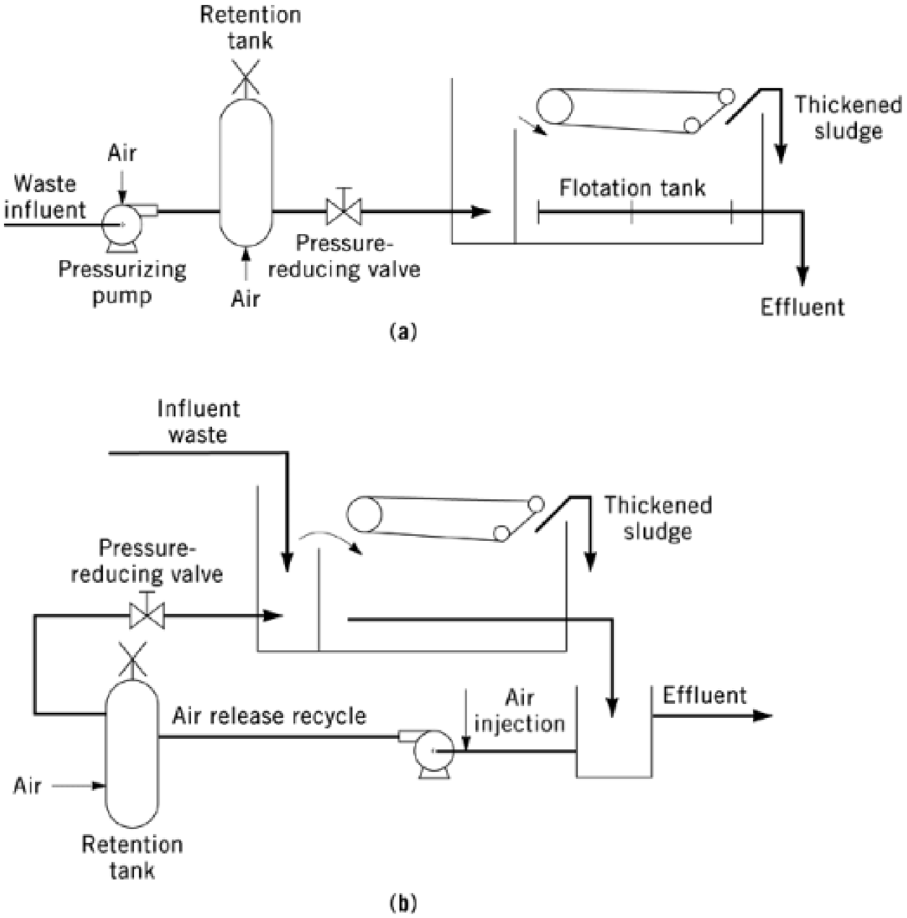

Fig. 4. Schematic of a pressurized dissolved air flotation system. (**a**) Influent pressurization; (**b**) recycle pressurization.

6.5.1. Technologies Available

The technologies available for metals removal are summarized in Table 11. In the case of precipitation of the metals as hydroxide, lime or caustic is added, usually to the pH of minimum solubility. This process has limitations in cases where multiple metals are present with a pH range of minimum solubility. Another technology is precipitation as the carbonate. Precipitation as the sulfide has the advantage of having a wide range of minimum solubility. A disadvantage is that a poorer thickening sludge is generated and sulfide presents a potential odor and health hazard. Solubility relationships are shown in Figure 7.

As a result, sulfide precipitation is frequently used as a polishing step following hydroxide precipitation.

Coprecipitation is a technology by which many metals such as arsenic will adsorb on alum or iron flocs and be effectively removed over a near-neutral pH range. The disadvantage of coprecipitation is the generation of large quantities of sludge.

New chelating ion-exchange resins are able to selectively remove many heavy metals in the presence of high concentrations of univalent and divalent cations such as sodium and calcium. The heavy metals are held as weakly acidic chelating complexes. The order of selectivity is $\mathrm{Cu} > \mathrm{Ni} > \mathrm{Zn} > \mathrm{Co} > \mathrm{Cd} > \mathrm{Fe}^{2+} > \mathrm{Mn} > \mathrm{Ca}$. This process is suitable for end-of-pipe polishing and for metal concentration and recovery.

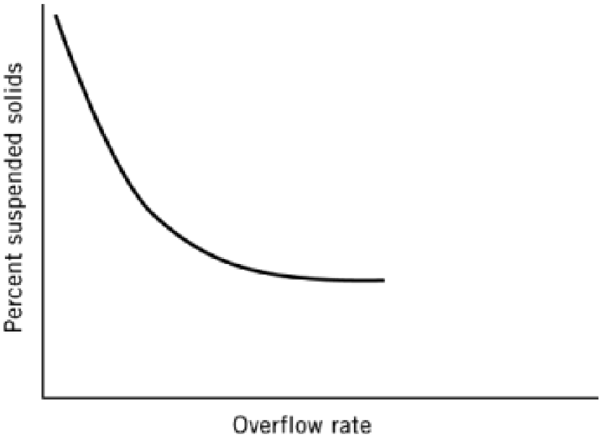

Fig. 5. Relationship between suspended solids removal design parameters and overflow rate.

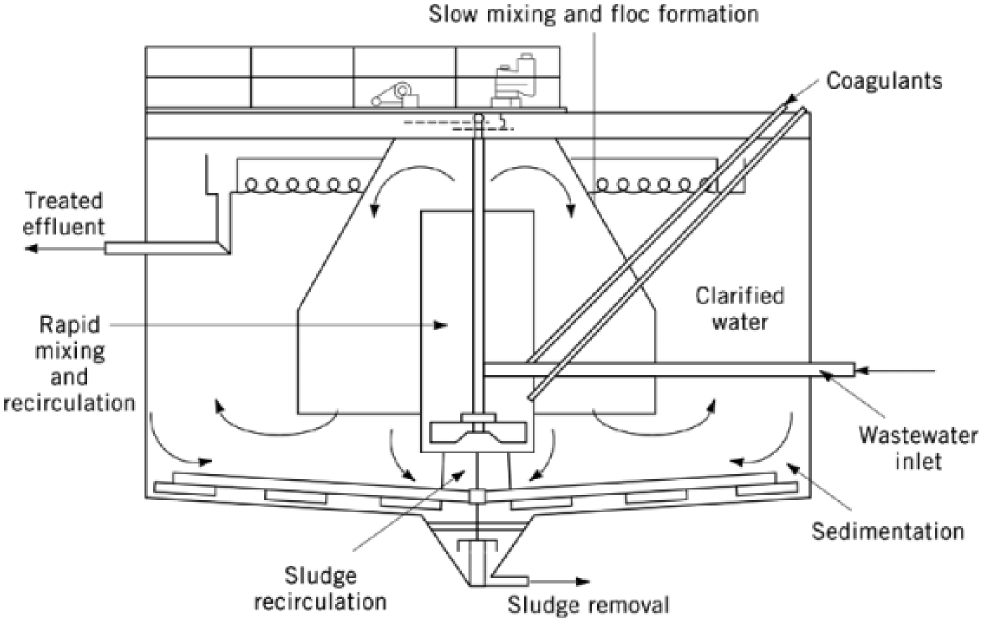

Fig. 6. A reactor clarifier designed for both coagulation and settling.

Many heavy metals are removed on activated carbon. A primary mechanism is sulfide precipitation on the carbon.

Reverse osmosis (RO) can be employed to remove and recover heavy metals, particularly nickel.

Achievable effluent concentrations of heavy metals is summarized in Table 12.

6.6. Removal of Volatile Organics

Volatile organics, eg, benzene and toluene, should usually be removed prior to biological treatment.

Table 10. Filtration Performance

				Removal, %		Effluent, mg/L	
Filter type	Wastewater	Filter depth, m	Hydraulic loading, L/(min·m^2)	SS	BOD	SS	BOD
gravity downflow	TF effluent	0.61–0.91	122	67	58		2.5
pressure upflow	AS effluent	1.52	90	50	62	7.0	6.4
dual media	AS effluent	0.76	204	74	88	4.6	2.5
gravity downflow	AS effluent	0.30	216	62	78	5	4
dynasand	metal finishing	1.01	163–244	90		2–5	
	AS effluent	1.01	122–407	75–90		5–10	
	oily wastewater	1.01	81–244	80–90[a]		5–10[a]	
hydroclear	poultry	0.30	81–204	88		19	
	oil refinery	0.30	81–204	68		11	
	unbleached kraft	0.30	81–204	74		17	

[a] Free oil.

Table 11. Heavy Metals Removal Technologies

Process type	Examples
conventional precipitation	hydroxide sulfide carbonate coprecipitation
enhanced precipitation	dimethyl thio carbamate diethyl thio carbamate trimercapto-*s*-triazine, trisodium salt
other methods	ion exchange adsorption
recovery opportunities	ion exchange membranes electrolytic techniques

The removal of volatile organics by air stripping is accomplished in packed or tray towers in which air is introduced to the bottom of the tower counterflow to the liquid passing down the tower. Stripping can also be accomplished using diffused or surface aeration. Removal of volatiles is a function of Henry's constant, the air/liquid ratio, and the transfer efficiency of packing. High concentrations of volatiles require treatment of the off-gas through vapor phase carbon or combustion or a biofilter.

Volatile removal is a function of the air/liquid ratio, and media height is shown in Figure 8. Typical stripping towers are shown in Figure 9.

In a steam stripper, steam is introduced into a packed tower, which causes volatiles to be removed in the vapor phase. An azeotropic mixture is formed, resulting in a separation of the volatiles from the water. An effluent recycle is usually employed to reduce volatiles in the liquid effluent.

Most volatile organics adsorb on activated carbon in the liquid state. Low concentrations of biodegradable volatiles can be removed by adsorption and biodegradation on activated carbon.

Many volatiles can be chemically oxidized using conventional or advanced chemical oxidants.

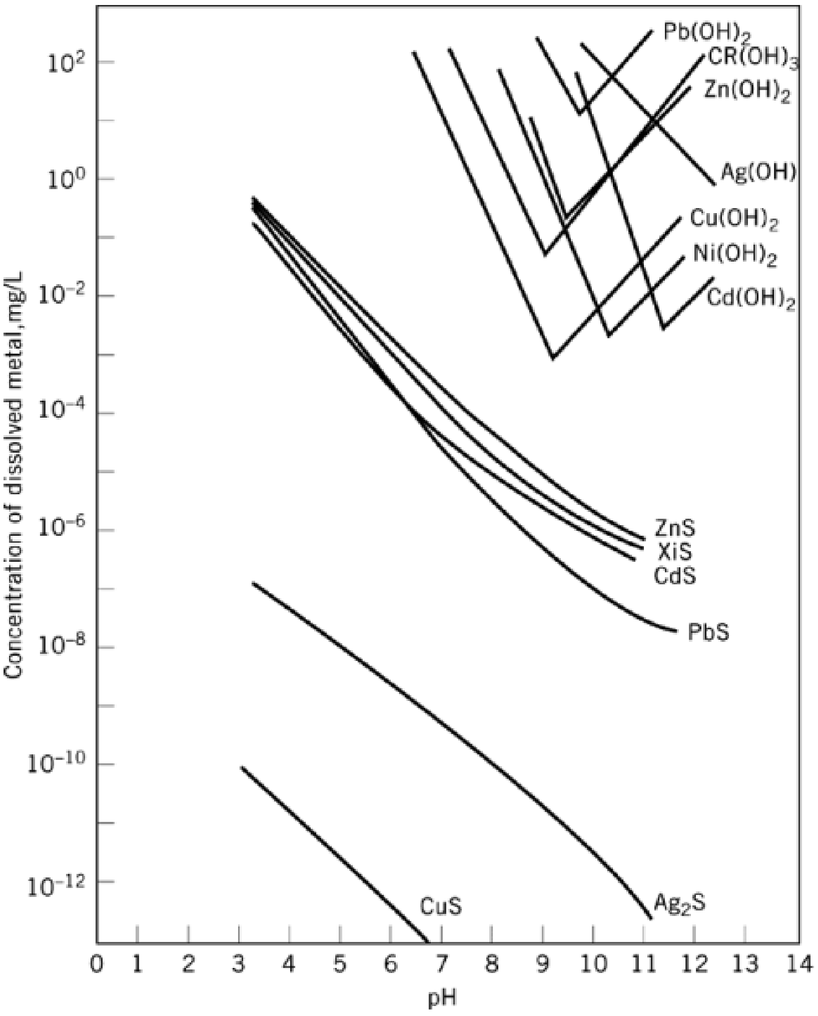

Fig. 7. Solubility of metal hydroxides and sulfides as a function of pH.

7. Biological Treatment

Aerobic treatment is generally applied to lower strength wastewaters, whereas anaerobic treatment is employed as a pretreatment for high strength wastewaters. The choice of process depends both on the concentration of organics and the volume of wastewater to be treated.

The objective of biological treatment is to remove biodegradable organics. In an aerobic biological treatment process, organic removal can occur through biodegradation, stripping, or sorption on the biological flocs.

7.1. Stripping

Degradable VOC, ie, benzene will both biodegrade and strip from the solution. The percentage stripped will depend on the power level in the aeration basin or the type of aeration equipment, ie, enhanced stripping with

Table 12. Effluent Levels Achievable in Heavy Metal Removals

Metal	Achievable effluent concentration, mg/L	Technology
arsenic	0.05	sulfide ppt with filtration
	0.06	carbon adsorption
	0.005	ferric hydroxide co-ppt
barium	0.5	sulfate ppt
cadmium	0.05	hydroxide ppt at pH 10–11
	0.05	co-ppt with ferric hydroxide
	0.008	sulfide precipitation
copper	0.02–0.07	hydroxide ppt
	0.01–0.02	sulfide ppt
mercury	0.01–0.02	sulfide ppt
	0.001–0.01	alum co-ppt
	0.0005–0.005	ferric hydroxide co-ppt
	0.001–0.005	ion exchange
nickel	0.12	hydroxide ppt at pH 10
selenium	0.05	sulfide ppt
zinc	0.1	hydroxide ppt at pH 11

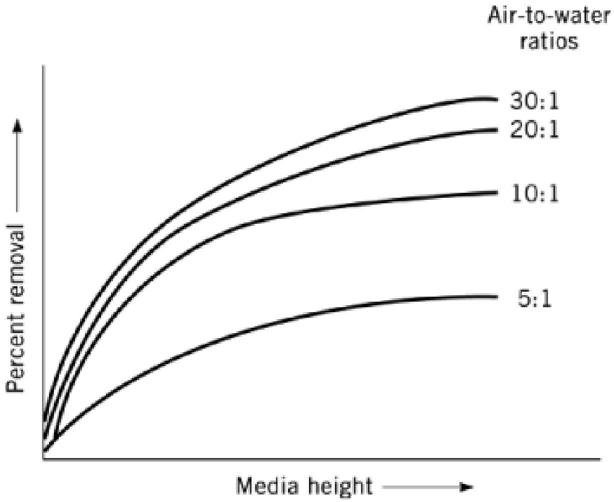

Fig. 8. Illustrative relationships of air stripping removal efficiencies to media height and air-to-water ratios.

surface aerators. The biodegradation rate will decrease with increased halogenation, and hence the percentage stripped will increase.

7.2. Sorption

Most organics are sorbed to a very small degree on the biofloc, ie, $<$ 2 percent. Exceptions are the nondegradable pesticide Lindane, other pesticides, and PCBs. Heavy metals will complex with the cell wall and precipitate within the floc. Metal accumulation will increase with increasing sludge age.

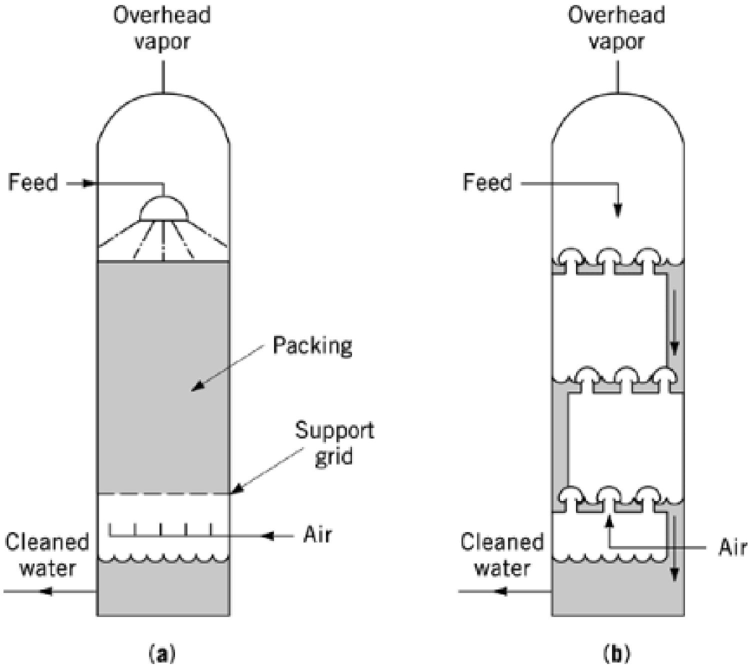

Fig. 9. Air stripping towers. (**a**) Packed tower; (**b**) tray tower.

7.3. Biodegradation

The biodegradation properties of various organics are shown in Table 13. The mechanism of aerobic degradation is shown in Figure 10.

Approximately one-half of the organics removed are oxidized to CO_2 and H_2O, and one-half synthesized to biomass. Three to 10 percent of the organics removed result in soluble microbial products (SMP). The SMP is significant because it causes aquatic toxicity.

Nitrogen and phosphorus are required in the reaction at an approximate ratio of BOD:N:P of 100:5:1. Nitrogen and phosphorus are amply available in municipal wastewaters, but frequently are deficient in industrial wastewaters. It should be noted that only ammonia nitrogen or nitrate is available for biosynthesis.

The reactions in an aerobic biological process are as follows:

$$\text{organics} + O_2 + N + P \xrightarrow[K]{\text{Cells}} \text{new cells} + CO_2 + H_2O + \text{SMP}$$

in which K is a reaction rate coefficient which is a function of the degradability of the wastewater and SMP is the nondegradable soluble microbial products and

$$\text{cells} + O_2 \longrightarrow CO_2 + H_2O + N + P + \text{nondegradable cellular residue} + \text{SMP}$$

The generation of SMP is directly proportional to the degradable COD removed in the process. Some of the SMP is toxic to aquatic species.

In the activated sludge process, performance is related to the food-to-microorganism ratio (F/M), which is the kg BOD applied/d/kg volatile suspended solids (VSS).

Table 13. Relative Biodegradability of Certain Organic Compounds

Biodegradable organic compounds[a]	Compounds generally resistant to biological degradation
acrylic acid	ethers
aliphatic acids	ethylene chlorohydrin
aliphatic alcohols (normal, iso, secondary)	isoprene
	methyl vinyl ketone
aliphatic aldehydes	morpholine
aliphatic esters	oil
alkyl benzene sulfonates with exception of propylene-based	polymeric compounds
benzaldehyde	polypropylene benzene sulfonates
aromatic amines	selected hydrocarbons
dichlorphenols	aliphatics
ethanolamines	aromatics
glycols	alkyl–aryl groups
ketones	tertiary aliphatic alcohols
methacrylic acid	tertiary benzene sulfonates
methyl methacrylate	trichlorophenols
monochlorophenols	
nitriles	
phenols	
primary aliphatic amines	
styrene	
vinyl acetate	

[a] Some compounds can be degraded biologically only after extended periods of seed acclimation.

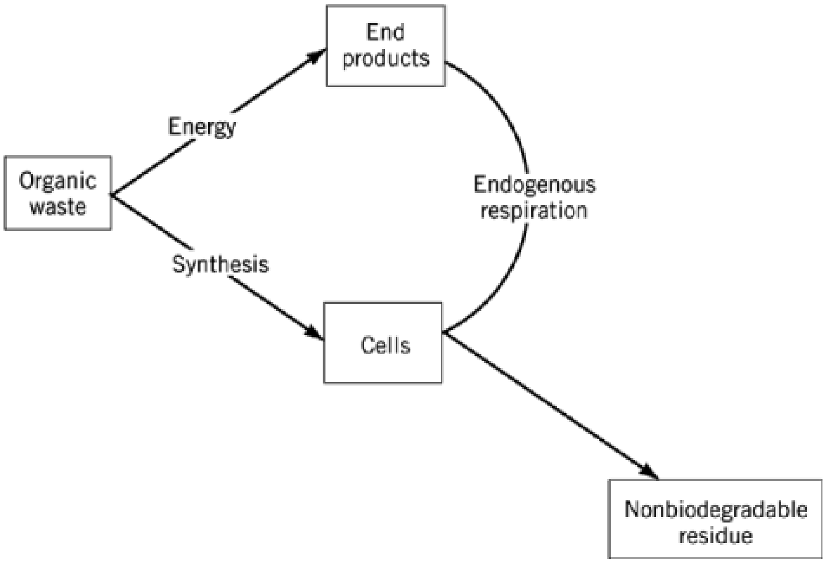

Fig. 10. The mechanism of aerobic biological oxidation.

For a soluble wastewater, the VSS is proportional to the biomass concentration. Process performance may also be related to the sludge age, which is the average length of time the organisms are in the process.

$$\text{sludge age} = \frac{\text{mass of organisms under aeration}}{\text{mass wasted/d}}$$

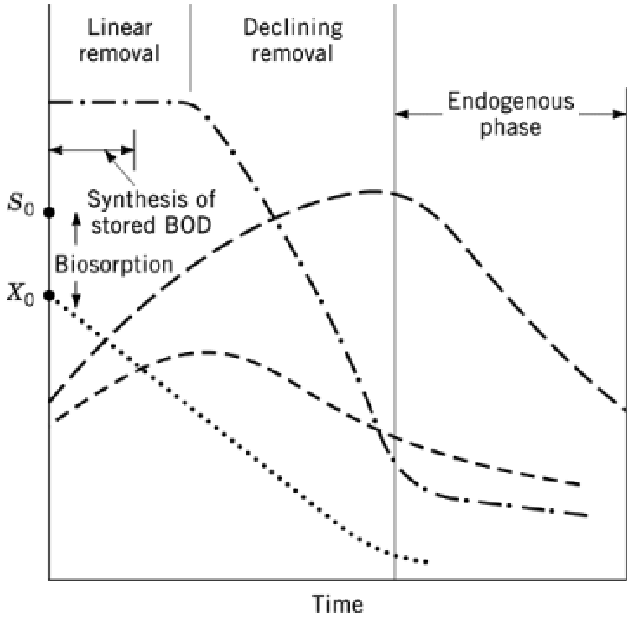

Fig. 11. Aerobic biological treatment, where S_0=initial organic concentration and X_0=initial biomass concentration; (———) total cell weight; (–·–·) specific oxygen uptake rate; (– – –) cell N and P; (....) organic substrate remaining.

Figure 11 depicts a batch oxidation. Note that readily degradable organics will be sorbed by the floc forming organisms immediately on contact. As organics are removed, oxygen is consumed and biomass is synthesized, as shown. Continued aeration after organic removal will result in oxidation of the biomass, generally referred to as endogenous respiration.

The performance, therefore, is related to the F/M or sludge age and the degradability, K. As the F/M decreases or the sludge age increases, greater removals are achieved. It should be noted that the sludge age is proportional to the reciprocal of the F/M. The reaction rate coefficient, K, as related to wastewaters characteristics.

As shown in Figure 10, all of the organics removed in the process are either oxidized to CO_2 and H_2O or synthesized to biomass generally expressed as volatile suspended solids. As previously noted, a small portion of the organics removed results in SMP products.

The fraction of the organics removed that result in synthesis varies, depending on nature and biodegradability of the organics in question. A rough estimate is to assume that one-half is oxidized and one-half synthesized.

For a soluble wastewater, the net sludge to be wasted from the process may be computed as synthesis minus oxidation, ie, endogenous respiration.

$$\text{net sludge wasted} = \text{sludge synthesized} - \text{oxidation}$$

As the sludge age is increased, more of the sludge is oxidized and the net sludge wasted is decreased. If the wastewater contains influent volatile suspended solids, such as that in a pulp and paper mill, the solids not oxidized in the process must be added to the net wasted.

The oxygen requirements are computed in a similar manner:

oxygen required = organic oxidation + endogenous oxidation.

Onaverage, it takes 1.4 kg oxygen to oxidize 1 kg cells as VSS. Therefore, for each kilogram of VSS substracted from the sludge yield, 1.4 kg oxygen must be added to the oxygen required.

Process performance is affected by temperature. The reaction rate decreases with temperature over a range of 4–31°C. As the temperature decreases, dispersed effluent suspended solids increase. In one chemical plant in West Virginia, the average effluent suspended solids was 42 mg/L during the summer and 105 mg/L during the winter. Temperatures above 37°C may result in a dispersed floc and poor settling sludge. It is therefore necessary to maintain aeration basin temperature below 37°C to achieve optimal effluent quality.

Biological sludges generally fall into one of three classifications. A flocculent sludge is one in which the major part of the biomass consists of flocculent organisms, with some filaments growing within the floc. The advantage this provides is that the filaments form a backbone which strengthens the floc. Filamentous bulking occurs when the filaments grow out from the floc in the bulk of the liquid. This condition hinders sludge settling. The pinpoint case occurs at very low loadings, causing floc dispersion, as shown in Figure 12.

Sludge quality is defined by the sludge volume index (SVI), ie, the volume occupied by one dry weight gram after settling for one-half hour, which therefore defines the bulkiness of the sludge. A bulking sludge is usually caused by an excess of filamentous-type organisms. Filamentous organisms thrive best with readily degradable organics as a food source. Wastewater containing complex organics is not subject to filamentous bulking because the filaments cannot degrade these organics. If all things are maintained equal, ie, adequate O_2, N and P, and BOD, the floc-forming organisms are predominant. In order to maintain conditions favorable to the floc formers, adequate oxygen, nutrients, and BOD must diffuse through the floc and reach all the organisms.

As the oxygen uptake or F/M increases, the dissolved oxygen must be increased to provide sufficient driving force to penetrate the floc. Minimum concentrations of nitrogen and phosphorus are necessary in the effluent.

Generalized flow configurations are shown in Figure 13. Refractory wastewaters can be treated in a complete mix basin because filamentous bulking is not an issue. For readily degradable wastewaters, high concentrations of BOD are necessary to penetrate the floc, requiring a plug flow configuration. Alternatively, a selector can be employed to absorb the readily degradable organics so they are not available as a food source for the filaments. The removal of specific priority pollutants follows the Monod kinetic relationship, which states that effluent quality is a function of sludge age. Thus the only way to reduce the effluent concentration of a specific organic is to increase the sludge age.

8. Nutrient Removal

In many locations, nitrogen and phosphorus must be removed in order to meet effluent limitations.

8.1. Nitrogen

Nitrogen is most commonly removed through the process of biological nitrification and denitrification, as shown in Figure 14. In this process, organic nitrogen is hydrolyzed to ammonia. Ammonia, in turn, is oxidized to nitrite through the action of a specific organism, *Nitrosommonas*. This reaction also generates two hydrogen ions for each nitrogen oxidized so that alkalinity must be available to neutralize the acidity.

The nitrite, in turn, is oxidized to nitrate through the action of a specific organism, *Nitrobacter*. Since the *Nitrobacter* has a much higher growth rate than the *Nitrosommonas*, the critical design parameter is that the

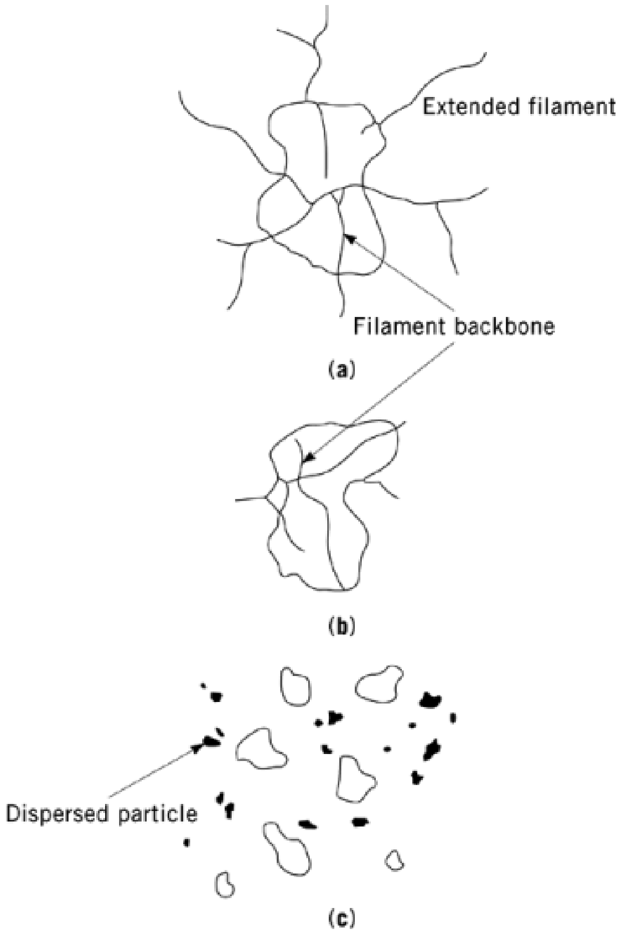

Fig. 12. Activated sludge types: (**a**) filamentous bulking; (**b**) nonbulking; (**c**) pinpoint.

sludge age in the process must exceed the growth rate of the *Nitrosommonas*, or they will be washed out of the system.

As in all biological reactions, nitrification is a function of temperature. For municipal wastewaters, a minimum sludge age of 3.5 d is required at 20°C while the minimum sludge age must be increased to 12 d at 10°C in order to achieve nitrification.

The nitrifying organisms are relatively sensitive to many toxic organics, so that the treatment of industrial wastewaters requires special attention to the presence of toxics.

In one chemical plant, the required sludge age was found to be 22 d at 22°C, whereas for a nontoxic municipal wastewater, the required sludge age is 3 d.

Denitrification is a process in which facultative organisms will reduce nitrate to nitrogen gas in the absence of molecular oxygen. This consequently results in the removal of BOD_5. The denitrification process also generates one hydroxyl ion so that alkalinity requirements are reduced to half when both nitrification and denitrification are practiced.

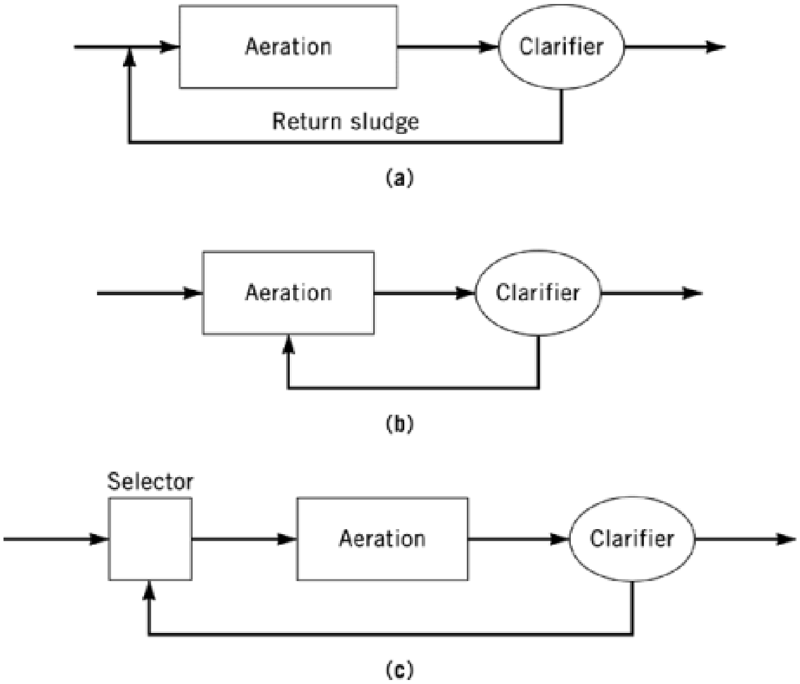

Fig. 13. Types of activated sludge processes: (**a**) plug flow; (**b**) complete mix; (**c**) selector-activated sludge.

The process of nitrification–denitrification can be practiced in one of two ways. In the oxidation ditch, nitrification occurs in the vicinity of the aerators. When the dissolved oxygen is depleted as the sludge–wastewater mixture passes from the aerator, denitrification occurs.

In the two-stage process, nitrification occurs under aerobic conditions in the second stage. The nitrified mixed liquor from the second stage is internally recycled to the anoxic first stage, where denitrification occurs.

High concentrations of ammonia can be removed by air or steam stripping. Ammonia can only be stripped in the nonionic form, NH_3. Since the amount of ammonia in the NH_3 form is a function of pH, a high (> 10.5) pH is necessary for effective stripping. Ammonia can be oxidized by breakpoint chlorination to nitrogen gas. One disadvantage of this technology is the possible generation of chlorinated organic compounds other than ammonia and the production of chlorides, 10 parts of chloride for each ammonia oxidized. An ion-exchange resin specific for ammonia, clinotilite, will remove ammonia.

8.2. Phosphorus Removal

Phosphorus can be removed from wastewater either chemically or biologically.

8.2.1. Chemical Removal

Phosphorus can be precipitated with lime to form $Ca_3(PO_4)_2$. The actual composition of the precipitate is a complex compound called apitate. Achieving minimum phosphorus concentrations requires a pH in excess of 10.5. Alum or iron will precipitate phosphorus as $AlPO_4$ or $FePO_4$. This procedure is generally employed in conjunction with the activated sludge process, in which the coagulant is added at the end of the aeration basin or between the aeration basin and the final clarifier.

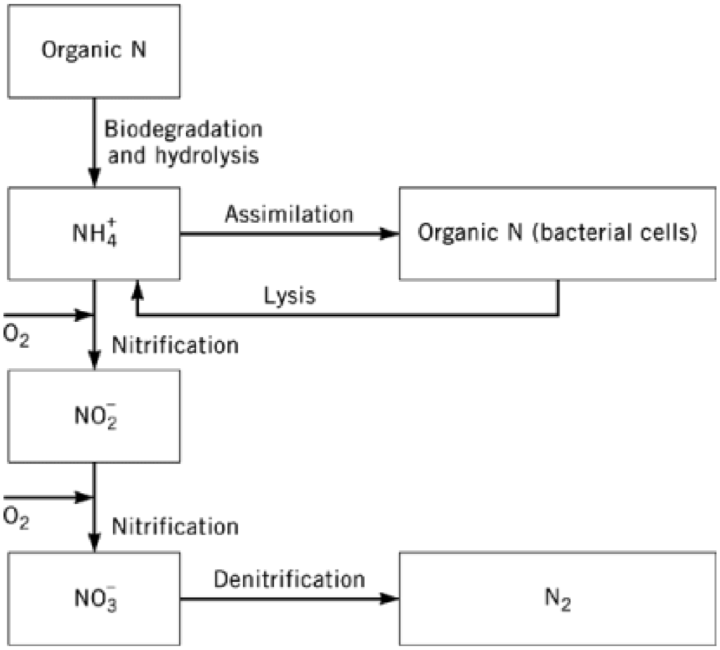

Fig. 14. Nitrogen transformation.

8.2.2. Biological Removal

Certain organisms normally present in activated sludge have the ability to store phosphorus. The process configuration for bio-P removal involves an anaerobic step in which phosphorus is released and acetate taken up by the bio-P organisms. This is followed by an aerobic step in which phosphorus is rapidly taken up by the bio-P. Under proper operating conditions, soluble effluent phosphorus levels of 0.1 mg/L are achievable from municipal wastewater.

9. Alternative Biological Treatment Technologies

9.1. Lagoons

Where large land areas are available, lagooning provides a simple and economical treatment for nontoxic or nonhazardous wastewaters. There are several lagoon alternatives.

The impounding and absorption lagoon has no overflow or there may be an intermittent discharge during periods of high stream flow. These lagoons are particularly suitable to short seasonal operations in arid regions.

Anaerobic ponds are loaded such that anaerobic conditions prevail throughout the liquid volume. One of the major problems with anaerobic ponds is the generation of odors. The odor problem can frequently be eliminated by the addition of sodium nitrate at a dosage equal to 20% of the applied oxygen demand. An alternative is the use of a stratified facultative lagoon, in which aerators are suspended 3 meters below the liquid surface in order to maintain aerobic surface conditions, with anaerobic digestion occurring at the lower depths.

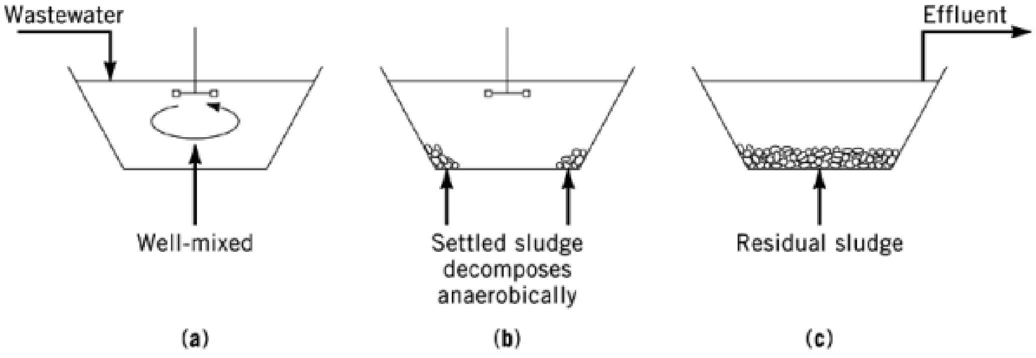

Fig. 15. Aerated lagoon types: (**a**) aerobic; (**b**) facultative; (**c**) settling.

Aerobic lagoons depend on algae to produce oxygen by photosynthesis. This oxygen, in turn, is used by the bacteria to oxidize the organics in the wastewater. Since algae are aerobic organisms, the organic loading to the lagoons must be sufficiently low to maintain dissolved oxygen.

9.2. Aerated Lagoons

An aerated lagoon system is a two- or three-basin system designed to remove degradable organics (BOD). The first basin is fully mixed, thereby maintaining all solids in suspension. This maximizes the organic removal rate. A second basin operates at a lower power level, thereby permitting solids to deposit on the bottom. The solids undergo anaerobic degradation and stabilization. A third basin is frequently employed for further removal of suspended solids and enhanced clarification. In order to avoid groundwater pollution, these basins must usually be lined. The process is shown in Figure 15.

Aerated lagoons are employed for the treatment of nontoxic or nonhazardous wastewaters such as food processing and pulp and paper. Retention time varies from 3 to 12 d, so a large land area is usually required.

9.3. Activated Sludge

There are several generic activated sludge processes presently available. Complete Mix (CMAS) is applicable to refractory-type wastewaters in which filamentous bulking is not a problem. This process has the advantage of dampening fluctuations of influent wastewater quality.

Plug flow is applicable for readily degradable wastewaters subject to filamentous bulking. Upstream controls are required to avoid shock loadings.

The selector process is applicable for readily degradable wastewaters; it also requires upstream controls. In a selector, degradable organics are removed by the floc formers by biosorption and therefore are not available as a food source for the filaments.

The sequencing batch reactor (SBR) or intermittent process is a combination of complete mix and plug flow, and usually controls filamentous bulking. The nature of the process eliminates the need for an external clarifier.

The oxidation ditch process is usually considered when nitrogen removal is required.

Other processes include deep tank aeration such as the Biohoch, the use of high purity oxygen, and the Deep Shaft process.

Performance of the activated sludge process may be summarized as follows: effluent quality is related to the sludge age, with higher sludge ages required for the more refractory wastewaters; degradable priority pollutants can be reduced to μg/L levels under optimal operating conditions as related to sludge age; effluent

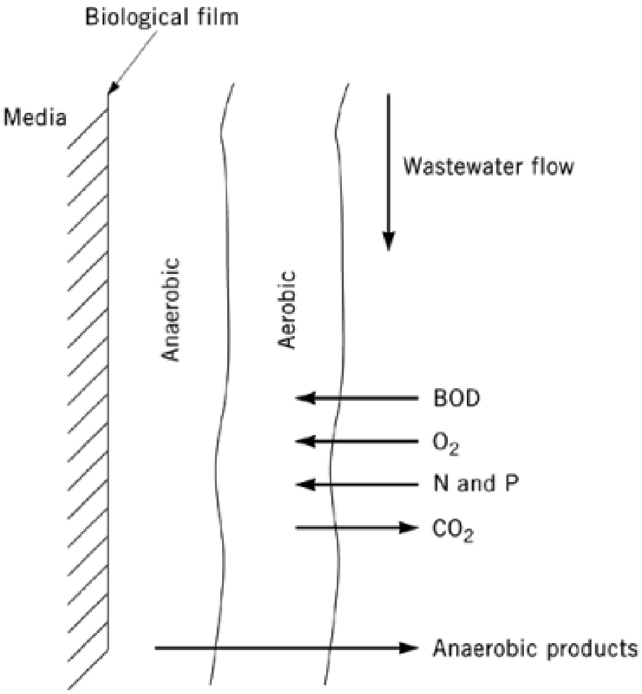

Fig. 16. Removal mechanisms in a fixed-film reactor.

soluble BOD levels $<10\ \mathrm{mg/L}$ are achievable in most cases, and nitrification and denitrification can be achieved through process modifications.

10. Fixed-Film Processes

10.1. Trickling Filter

A trickling filter is a packed bed, usually plastic on which a biofilm grows. As a wastewater passes over the film, organics and oxygen diffuse into the film, where they undergo biodegradation, as shown in Figure 16. The variables affecting performance are the organic loading rate, the hydraulic loading rate, temperature, and the degradability of the wastewater. For the treatment of industrial wastewaters, a trickling filter is considered a pretreatment process usually designed to remove about 50% of the BOD. This is largely the result of economic considerations. Trickling filter performance data are shown in Figure 17.

11. Rotating Biological Contactor (RBC)

An RBC is a fixed-film process in which a biofilm is developed on a rotating plastic cylinder which passes through the wastewater. As the cylinder passes through, the wastewater organics diffuse into the film. As the cylinder passes through the air, oxygen diffuses into the biofilm, causing degradation of the organics. Increased treatment is achieved by increasing the number of stages.

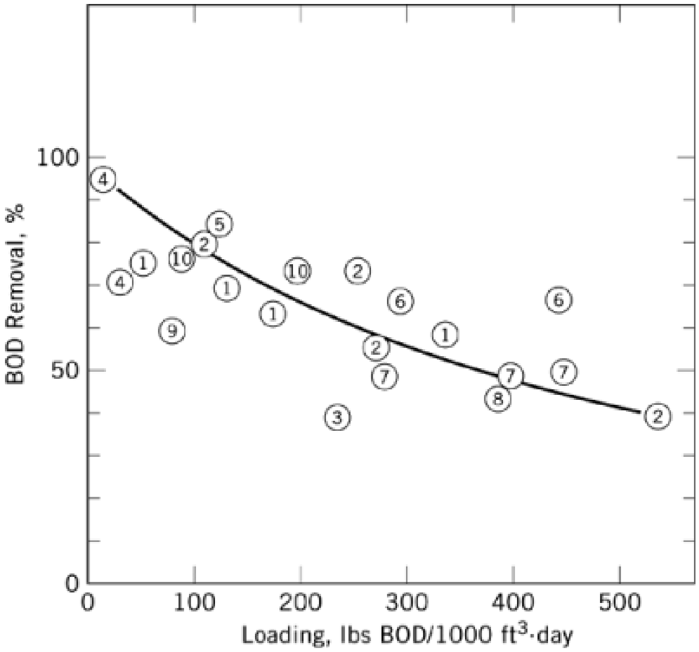

Fig. 17. Pretreatment of organic wastewater on trickling filters. Industry types for which coordinates have been plotted are 1, kraft pulp and paper; 2, mixed industry; 3, wet corn milling; 4, dairy; 5, tannery; 6, meat packing; 7, food; 8, pharmaceutical; 9, refinery; and 10, textile.

12. Anaerobic Treatment

Anaerobic treatment is usually employed for high strength wastewaters. In anaerobic treatment, complex organics are broken down through a sequence of reactions to end products of methane gas, CH_4, and carbon dioxide, CO_2:

$$\text{organics} \longrightarrow \text{volatile fatty acids} \longrightarrow CH_4 + CO_2$$

Because anaerobic treatment will not reach usual permit discharge levels, it is employed as a pretreatment process prior to discharge to a POTW or to a subsequent aerobic process. Therefore it is most applicable to high strength wastewaters. Whereas aerobic treatment requires energy to transfer oxygen, anaerobic processes produce energy in the form of methane gas. Successful anaerobic process operation depends on maintaining a population of methane organisms. It is therefore critical that the sludge age of the anaerobic sludge exceed the growth rate of the methane organisms. At 35°C the common design criterion is a solids retention time (SRT) of 10 d or more. Anaerobic sludge can be maintained dormant for long periods of time, thereby making the process attractive for seasonal industrial operations such as in the food processing industry. A disadvantage to the anaerobic process is that initial startup may take as long as 45–60 d. Should the process be killed by a toxic shock a long period will be required for a re-startup. Particular care must be taken, therefore, to avoid upset. From an economic perspective, anaerobic pretreatment should be considered when the BOD exceeds 1000 mg/L.

13. Types of Anaerobic Processes

There are five principal process variants which are propriety in nature. These are as follows:

(1) Anaerobic Filter. The anaerobic filter is similar to a trickling filter in that a biofilm is generated on media. The bed is fully submerged and can be operated either upflow or downflow. For very high strength wastewaters, a recycle can be employed.
(2) Anaerobic Contact. This process can be considered as an anaerobic activated sludge because sludge is recycled from a clarifier or separator to the reactor. Since the material leaving the reactor is a gas–liquid–solid mixture, a vacuum degasifier is required to separate the gas and avoid floating sludge in the clarifier.
(3) Fluidized Bed. This reactor consists of a sand bed on which the biomass is grown. Since the sand particles are small, a very large biomass can be developed in a small volume of reactor. In order to fluidize the bed, a high recycle is required.
(4) Upflow Anaerobic Sludge Blanket (UASB). Under proper conditions anaerobic sludge will develop as high density granules. These will form a sludge blanket in the reactor. The wastewater is passed upward through the blanket. Because of its density, a high concentration of biomass can be developed in the blanket.
(5) ADI Process. The ADI is a low rate anaerobic process which is operated in a reactor resembling a covered football field. Because of the low rate, it is less susceptible to upset compared to the high rate processes. Its disadvantage is the large land area requirement.

With the exception of the ADI process, anaerobic processes usually operate at a temperature of 35°C. In order to maintain this temperature, the methane gas generated in the process is used to heat the reactor. Anaerobic processes are shown in Figure 18. Anaerobic treatment performance data are shown in Table 14.

14. Advanced Wastewater Treatment

New regulations for toxics and priority pollutants frequently cannot be met by conventional technology. Other physical–chemical technologies must therefore be applied.

14.1. Chemical Oxidation

Chemical oxidation can be applied in industrial wastewater pretreatment for reduction of toxicity, to oxidize metal complexes to enhance heavy metals removal from wastewaters, or as a posttreatment for toxicity reduction or priority pollutant removal.

Complex organics and toxics are chemically oxidized to end products of CO_2 and H_2O or to intermediate products which are nontoxic and biodegradable.

The common oxidants are ozone, hydrogen peroxide, H_2O, catalyzed usually with ferrous iron, Fe^{2+}, and in some cases chlorine dioxide and uv light. Advanced oxidation systems include H_2O_2 + uv; ozone + uv; and H_2O_2, ozone, and uv. Depending on the application, the oxidation can be complete to end products as in a contaminated groundwater or partial to degradable intermediate products as in a process wastewater.

Wet air oxidation is based on a liquid-phase oxidation between the organic material in the wastewater and oxygen supplied by compressed air. The reaction takes place flamelessly in an enclosed vessel which is pressurized and at a high temperature, typically 13.79×10^3 Pa and 575°C. The system temperature, initiated by a start-up boiler, is maintained through auto thermal combustion of organics once the reaction starts.

Table 14. Performance of Anaerobic Processes

Wastewater	Process[a]	Loading, kg/($m^3 \cdot d$)	HRT, h	Temperature, °C	Removal, %
meat packing	anaerobic contact	3.2 (BOD)	12	30	95
meat packing		2.5 (BOD)	13.3	35	95
Keiring		0.085 (BOD)	62.4	30	59
slaughter house		3.5 (BOD)	12.7	35	95.7
citrus		3.4 (BOD)	32	34	87
synthetic	upflow filter	1.0 (COD)		25	90
pharmaceutical		3.5 (COD)	48	35	98
pharmaceutical		0.56 (COD)	36	35	80
guar gum		7.4 (COD)	24	37	60
rendering		2.0 (COD)	36	35	70
landfill leachate		7.0 (COD)		25	80
paper-mill foul condensate		10–15 (COD)	24	35	77
synthetic	expanded bed	0.8–4.0 (COD)	0.33–6	10–3	80
paper-mill foul condensate		35–48 (COD)	8.4	35	88
skim milk	UASB	71 (COD)	5.3	30	90
sauerkraut		8–9 (COD)			90
potato		24–45 (COD)	4	35	93
sugar		22.5 (COD)	6	30	94
champagne		15 (COD)	6.8	30	91
sugar beet		10 (COD)	4	35	80
brewery		95 (COD)			83
potato		10 (COD)			90
paper-mill foul condensate		4–5 (COD)	70	35	87
potato	ADI-BFV	0.2 (COD)	360	25	90
corn starch		0.45 (COD)	168	35	85
dairy		0.32 (COD)	240	30	85
confectionery		0.51 (COD)	336	37	85

[a] UASB = upflow anaerobic sludge blanket.

14.2. Carbon Adsorption

Carbon can be employed either as granular carbon in columns (GAC) or as powdered carbon added to an activated sludge plant (PACT). Carbon removes most organics except low molecular weight soluble organics such as sugars and alcohols. In general, those organics which adsorb the poorest biodegrade the best, whereas those which biodegrade poorly adsorb well on carbon.

Design data are available for the specific organics on the EPA's priority pollutant list. For mixed wastewaters, a laboratory study is necessary to determine adsorption characteristics. Wastewater is contacted with a range of concentrations of powdered carbon and adsorption occurs, as graphed in the form of a Freundlich Isotherm, shown in Figure 19.

Because several commercial carbons are available, a comparative isotherm study should be made for a wastewater to determine which carbon is the best.

Granular carbon is regenerated. Regeneration can be accomplished by acid, caustic, solvent, steam, or thermal. For specific organics, it is usually feasible to employ one of the first four and operate *in situ*. For a typical multicomponent wastewater, however, thermal regeneration must be used. This can be accomplished using a multiple-hearth furnace or a fluidized-bed furnace. Attrition and oxidation losses range from 5 to 10

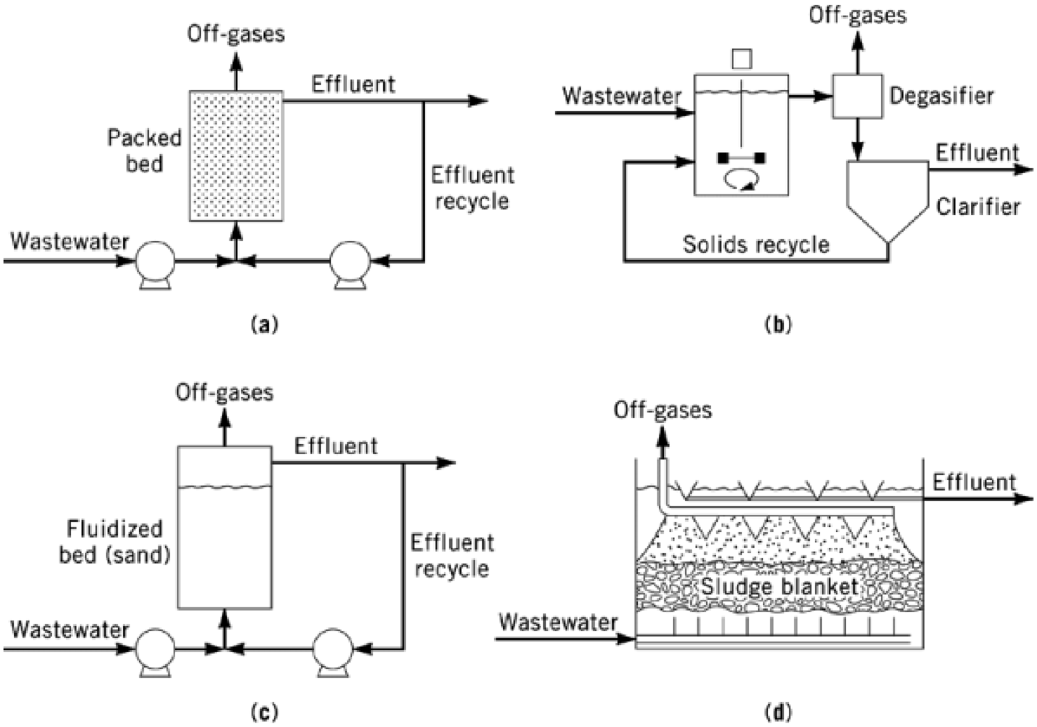

Fig. 18. Anaerobic wastewater treatment processes: (**a**) anaerobic filter reactor; (**b**) anaerobic contact reactor; (**c**) fluidized-bed reactor; (**d**) upflow anaerobic sludge blanket (UASB).

wt %. In addition, there is frequently a capacity loss, particularly for low molecular weight organics. Organic removal by activated carbon for several wastewaters is shown in Table 15.

Powdered activated carbon (PAC) is added at a stage prior to, or directly to, the activated sludge aeration basin, as shown in Figure 20. The sludge is therefore a mixture of biomass and carbon. The degradable organics are biodegraded, and the nondegradable organics are adsorbed on the carbon. PAC may also be applied to enhance nitrification.

PAC sludge can be regenerated by wet air oxidation (WAO) or by a multiple-hearth furnace. Capacity losses might be high in WAO, particularly with low molecular weight organics. Weight loss in a furnace may exceed 20%.

15. Sludge Handling and Disposal

15.1. Types of Sludges

Municipal primary sludge consists of organic and inorganic particulates. The sludge must be stabilized before land disposal. Biological sludge consists of organisms and other particulates not degraded in the biological process. Chemical sludges consist of chemical precipitates, heavy metals, and other contaminants such as color precipitated from industrial wastewaters.

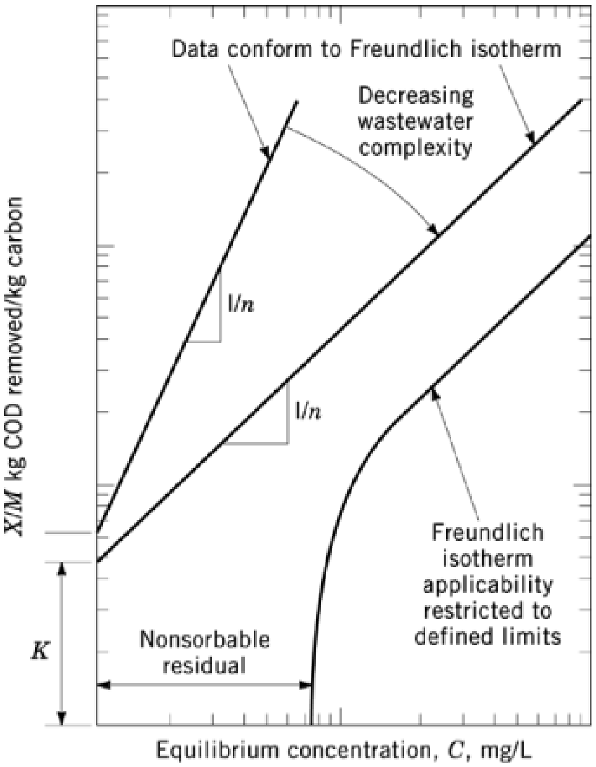

Fig. 19. Adsorption isotherm correlation, showing Freundlich isotherm application.

15.2. Sludge Stabilization

Organic sludges need to be stabilized before ultimate disposal except in the case of incineration. This is usually achieved by either aerobic or anaerobic digestion. In aerobic digestion, the degradable volatile solids are liquefied and oxidized to CO_2 and H_2O. In anaerobic digestion the solids are liquefied and fermented to CH_4 and CO_2.

15.3. Sludge Thickening

The mechanisms of sludge dewatering are shown in Figure 21. Thickening of sludge usually precedes dewatering. Depending on the nature of the sludge, several techniques are available for thickening.

(1) Gravity thickening is applicable to primary municipal sludges and most chemical sludges.
(2) Another technique is one in which the sludge is passed in a thin sheet over a porous drainage belt. This technique is particularly applicable to waste-activated sludge.
(3) In dissolved air flotation, air bubbles float the sludge, which is then removed by a scraper. It is generally applicable to large volumes of waste-activated sludge.
(4) In a centrifuge technique, various centrifuge types are used for sludge thickening.

Table 15. Granular Activated Carbon (GAC) Adsorption Effectively Removes Organics From a Variety of Industrial Wastewaters

Type of Industry	Wastewater TOC[a] or phenol, mg/L, or color index		Average removal, %	Carbon usage nkg/10^3 L
food	TOC	25–5,300	90	0.1–41
tobacco	TOC	1,030	97	6.9
textiles	TOC	9–4,670	93	0.12–29
	color	0.1–5.4	97	0.012–10
apparel	TOC	390–875	75	1.4–5.2
paper	TOC	100–3,500	90	0.4–19
	color	1.4	94	0.44
printing	TOC	34–170	98	0.52–0.55
chemicals	TOC	36–4,400	92	0.13–17
	phenol	0.1–5,325	99	0.20–22
	color	0.7–275	98	0.14–159
petroleum refining	TOC	36–4,000	92	0.13–17
	phenol	7–270	99	0.72–2.9
rubber and plastics	TOC	120–8,375	95	0.62–20
leather	TOC	115–9,000	95	0.36–38
stone, clay, glass	TOC	12–8,300	87	0.34–36
primary metals	TOC	11–23,000	90	0.06–222
fabricated metals	TOC	73,000	25	73

[a] TOC = Total organic carbon.

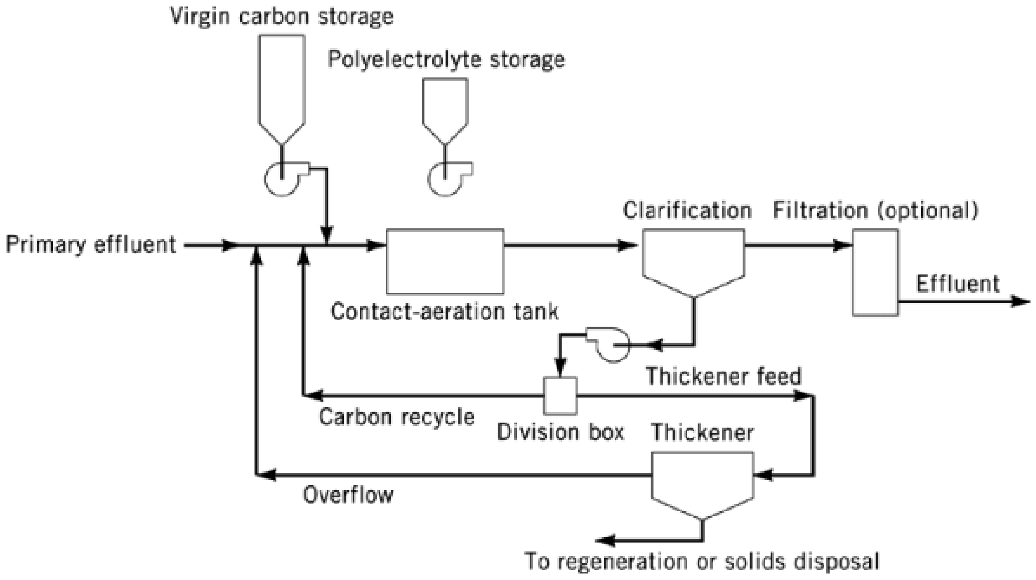

Fig. 20. Process flow diagram for PACT wastewater treatment system.

15.4. Sludge Dewatering

In a centrifuge technique for sludge dewatering, the solid bowl centrifuge concentrates the solids under centrifugal force. Both centrate and cake solids are continuously discharged from the machine. Polymer addition is required for most wastewater sludges.

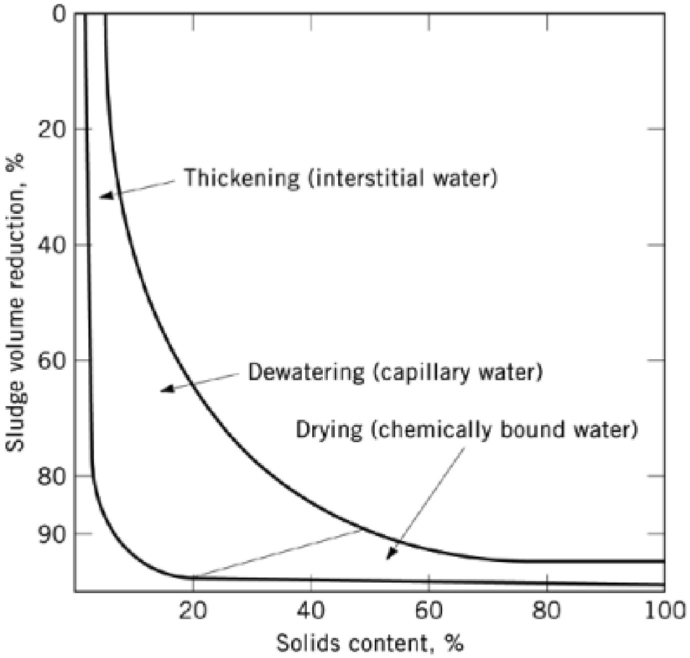

Fig. 21. Sludge thickening and dewatering relationships.

A vacuum filter is a cloth-covered drum which operates under an applied vacuum. As the drum passes through the sludge vat, solids are deposited on the filter. As the drum passes through the air, drying of the cake occurs. The cake is continuously discharged to a conveyor belt.

A belt filter press consists of a gravity drainage belt, followed by a series of roller presses which squeeze out water.

A pressure filter is a plate-and-frame press which operates on an intermittent time cycle. Drier cakes are generally attainable from a filter press.

Sludge drying beds are usually used for smaller sludge volumes, which drain and dry rapidly. Their application is usually restricted to the more arid climates.

Thickening and dewatering of various sludges is shown in Table 16.

15.5. Sludge Disposal

Land disposal of wet sludges can be accomplished in a number of ways: Lagooning or the application of liquid sludge to land by truck or spray system, or by pipeline to a remote agricultural or lagoon site.

In lagoons sludge is stored and in the case of organic sludges anaerobically disgested. Odor control is achieved either by chemical addition to the overlaying water (Cl_2 or H_2O_2) to oxidize sulfides, or by installing aerators in the liquid layer to maintain aerobic conditions.

Biological sludges can be incorporated into the soil. An important consideration is the heavy metal content of the sludge, which will dictate the total number of years sludge can be applied. The available nitrogen content of the sludge will determine the maximum yearly application.

Dewatered sludges can be employed as a landfill.

Table 16. Performance of Sludge Thickening and Dewatering Equipment

Equipment, and type of sludge[a]	Loading	Resultant solids content, wt %
gravity thickener		
municipal WAS, kg/m^2·d	20–122	1–3
inorganic sludge, kg/m^2·d	122–366	10–20
flotation thickener		
municipal WAS, kg/m^2·h	15–29	4–7
centrifuge, per unit		
paper-mill WAS, L/min	227–379	11
citrus-processing WAS, L/min	95	9–10
vacuum filter		
municipal WAS, kg/m^2·h	10–39	10–15
belt filter press, per unit of belt width or area		
chemical WAS, kg/m·h	149–343	13–17
paper-mill WAS, m^3/m-h	3–6	12–19
paper-mill primary sludge, m^3/m-h	12–30	18–37
meat processing WAS, m^3/m^2-h	3.6	17
tannery WAS, m^3/m^2-h	2.1	23
pressure filter		
chemical WAS		20–30
chemical WAS	4-h cycle	28
citrus-processing WAS	2-h cycle	27
tannery WAS, m^3/m^2-h	0.09	48

[a] WAS = waste-activated sludge.

Incineration can be accomplished in multiple-hearth furnaces, in which the sludge passes vertically through a series of hearths. In a fluidized-bed sludge, particles are fed into a bed of sand fluidized by upwardly moving air.

16. Storm-Water Control

In most industrial plants, it is now necessary to contain and control pollutional discharges from storm water. Pollutional discharges can be minimized by providing adequate diking around process areas, storage tanks, and liquid transfer points, with drainage into the process sewer. Contaminated storm water is usually collected on the basis of a frequency for the area in question, eg, a 10-year storm, in a holding basin. The collected water is then passed through the wastewater treatment plant at a controlled rate.

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