1
Wastewater Treatment

Wastewater treatment refers to the treatment of sewage and water used by residences, business, and industry to a sufficient level that it can be safely returned to the environment. It is important to treat wastewater to remove bacteria, pathogens, organic matter, and chemical pollutants that can harm human health, deplete natural oxygen levels in receiving waters, and pose risks to animals and wildlife.

1.1 Characteristics of Wastewaters

A number of chemical and physical characteristics are used to describe wastewater. The most common are:

- Biochemical Oxygen Demand (BOD). This is a measure of the amount of unstable organic matter in the water. It measures how much oxygen is required by the available microorganisms to break down the readily available organic matter into simpler forms, such as carbon dioxide, ammonia, and water.
- Total Nitrogen (TN) and Total Phosphorus (TP). These are the sum of all forms of nitrogen and phosphorus in the water, respectively.
- Fecal microbes (which include viruses, bacteria, and protozoans). These are found in wastewater and may cause disease.
- Suspended solids, biodegradable organics, nutrients, refractory organics, heavy metals, dissolved inorganic solids, and pathogens are important contaminants that may be found in the oil, gas, and chemical processing industry's wastewaters. Table 1.1 presents a list of important wastewater contaminants and reasons for their importance.

Suspended solids can be removed by physical treatment to some extent. Removal of biodegradable organics, suspended solids, and pathogens is achieved through the secondary treatment operation units.

Table 1.2 shows typical waste compounds classified as priority pollutants. The more stringent rules deal with the removal of nutrients and priority pollutants. When wastewater

Waste Management in the Chemical and Petroleum Industries, First Edition. Alireza Bahadori.

Table 1.1 Contaminant importance in wastewater treatment.

Contaminants	Reason for Importance
Physical suspended solids	Suspended solids are important for esthetical reasons and because they can lead to the development of sludge deposits and anaerobic conditions
Chemical biodegradable organics	Composed principally of proteins, carbohydrates, and fats, biodegradable organics are measured most commonly in terms of BOD (Biochemical Oxygen Demand) and COD (Chemical Oxygen Demand). If discharged untreated to the environment, the biological stabilization of these materials can lead to the depletion of natural oxygen resources and to the development of septic conditions.
Nutrients	Carbon, nitrogen, and phosphorus are essential nutrients for growth. When discharged to the aquatic environment, these nutrients can lead to the growth of undesirable aquatic life. When discharged in excessive amounts on land, they can also lead to the pollution of groundwater.
Refractory organics	These organics tend to resist conventional biological methods of wastewater treatment. Typical examples include surfactants, phenols, and agricultural pesticides
Heavy metals	Due to their toxic nature, certain heavy metals can negatively impact upon biological waste treatment processes and stream life.
Dissolved inorganic solids	Inorganic constituents, such as calcium, sodium, and sulfate, are added to the original domestic water supply as a result of water use and may have to be removed if the wastewater is to be reused.
Biological pathogens	Communicable diseases can be transmitted by the pathogenic organisms in wastewater.

is to be reused, rules normally include requirements for the removal of refractory organics, heavy metals, and in some case dissolved inorganic solids.

1.1.1 Suspended Solids

Typically, suspended solids carry a significant portion of organic material, thus significantly contributing to the organic load of the wastewater (solids can contribute up to 60% of the BOD of a wastewater). Hence, effective solids removal can significantly contribute to wastewater treatment. A widely-accepted means of testing a wastewater for suspended solids is to filter the wastewater through a 0.45 μm porosity filter. Anything left on the filter after drying at about 103 °C is considered a portion of the suspended solids. Table 1.3 provides another classification system for the solids found in wastewater.

1.1.2 Heavy Metals

Any cation having an atomic mass (weight) greater than 23 (atomic mass of sodium) is considered a heavy metal. Motivations for controlling heavy metal concentrations in gas streams are diverse. Some of them are dangerous to health or to the environment (e.g., mercury, cadmium, lead, chromium), some can cause corrosion (e.g., zinc, lead), some are

Table 1.2 *Typical waste compounds classified as priority pollutants.*

Name (Formula)	Concern
	Non-metals
Arsenic (As)	Carcinogen and mutagen. Long term: sometimes cause fatigue and loss of energy; dermatitis.
Selenium (Se)	Long term: red staining of fingers, teeth, and hair; general weakness; depression; irritation of nose and mouth.
	Metals
Barium (Ba)	Flammable at room temperature in powder form. Long term: increased blood pressure and nerve block.
Cadmium (Cd)	Flammable in powder form. Toxic by inhalation of dust or fume. A carcinogen. Soluble compounds of cadmium are highly toxic. Long term: concentrates in the liver, kidneys, pancreas, and thyroid; hypertension suspected effect.
Chromium (Cr)	Hexavalent chromium compounds are carcinogenic and corrosive on tissue. Long term: skin sensitization and kidney damage
Lead (Pb)	Toxic by ingestion or inhalation of dust or fumes. Long term: brain and kidney damage; birth defects.
Mercury (Hg)	Highly toxic by skin absorption and inhalation of fume or vapor. Long term: toxic to central nervous system; may cause birth defects.
Silver (Ag)	Toxic metal. Long term: permanent gray discoloration of skin, eyes, and mucus membranes.
	Organic compounds
Benzene (C_6H_6)	Carcinogen. Highly toxic. Flammable, dangerous fire risk.
Ethylbenzene ($C_6H_5C_2H_5$)	Toxic by ingestion, inhalation, and skin absorption; irritant to skin and eyes. Flammable, dangerous fire risk.
Toluene ($C_6H_5CH_3$)	Flammable, dangerous fire risk, Toxic by ingestion, inhalation, and skin absorption.
	Halogenated compounds
Chlorobenzene (C_6H_5Cl)	Moderate fire risk. Avoid inhalation and skin contact.
Chloroethene (CH_2CHCl)	An extremely toxic and hazardous material by all avenues of exposure. A carcinogen.
Dichloromethane (CH_2Cl_2)	Toxic. A carcinogen, narcotic.
Tetrachloroethene (CCl_2CCl_2)	Irritant to eyes and skin.
Pesticides, herbicides, insecticides (Pesticides, herbicides, and insecticides are listed by trade name. The compounds listed are also halogenated organic compounds.)	
Endrin ($C_{12}H_8OCl_6$)	Toxic by inhalation and skin absorption, carcinogen.
Lindane ($C_6H_6Cl_6$)	Toxic by inhalation, ingestion, skin absorption.
Methoxychlor [$Cl_3CCH(C_6H_4OCH_3)2$]	Toxic material.
Toxaphene ($C_{10}H_{10}Cl_8$)	Toxic by ingestion, inhalation, skin absorption.
Silvex [$Cl_3C_6H_2OCH(CH_3)COOH$]	Toxic material; use has been restricted.

Table 1.3 *General classification of wastewater solids.*

Particle Classification	Particle Size, mm
Dissolved	Less than 10^{-6}
Colloidal	10^{-6} to 10^{-3}
Suspended	Greater than 10^{-3}
Settleable	Greater than 10^{-1}
Supracolloidal	10^{-3} to 10^{-1}

harmful in other ways (e.g., arsenic may pollute catalysts). Unlike organic pollutants, heavy metals do not decay and thus pose a different kind of challenge for remediation.

Currently, plants or microorganisms are tentatively used to remove some heavy metals such as mercury. Plants that exhibit hyper accumulation can be used to remove heavy metals from soils by concentrating them in their bio-matter. Some treatment of mining tailings has occurred where the vegetation is then incinerated to recover the heavy metals.

1.1.3 Dissolved Inorganic Solids

Total dissolved inorganic solids (TDIS) are a calculated value to assess the actual inorganic salt content of a water or process water.

The following procedure can be used to determine the inorganic dissolved solids in wastewaters. A sample of wastewater is filtered through a 0.45 μm filter, filtrate is collected, the water is vaporized first (at 103 °C) and then the organic fraction (at 550 °C) from the filtrate. The amount of material left in the vessel after incineration at 550 °C is referred to as the fixed or inorganic dissolved solids level.

1.1.4 Toxic Organic Compounds

Wastewater systems are known to contain toxic metals, organic micro pollutants, and pathogens that may add constraints to their beneficial uses. Environmental risks related to toxic inorganics, dioxins, furans, and pathogens can be controlled by:

1. Selecting a wastewater system with a low content of regulated contaminants that respects the local legislation for land application.
2. Application of a decontamination process to remove toxic metals.
3. The necessary step of sterilization for monocultures that eliminates pathogens.

These toxic organic compounds eventually reach sewage treatment plants and can be concentrated in wastewater systems. Disposal of wastewater systems is one way that these pollutants can be introduced into the environment. The presence of these toxic organic compounds can add constraints to the ultimate disposal of these sludges and/or reduce the possibilities for their beneficial use.

Tables 1.4 and 1.5 provide some organic compounds that are considered toxic and/or carcinogenic.

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Table 1.4 *Toxic organic compounds; occupational exposure to carcinogenic substances.*

Compound	Site	Comment
Organic substances for which there is wide agreement on carcinogenicity		
4-Aminodiphenyl	Bladder	A contaminant in diphenylamine
Benzidine	Bladder	Ingredient of aniline dyes, plastics, and rubber
Beta-naphthylamine (2-NA)	Bladder	Dye and pesticide ingredient; synonym, 2-naphthylamine exposed workers have 30 to 60 times more cases of bladder cancer
Bis (chloromethyl) ether	Lung	Used in making exchange resins; exposed workers have 7 times more cases of lung cancer; synonym, BCME
Vinyl chloride	Liver	Angiosarcoma cases among PVC workers
Additional organic substances on USDA-OSHA cancer-causing substances list		
Alpha-naphthylamine (1-NA)	Bladder	Human case implicated; used in making dyes, herbicides, (1-NA) food colors, color film; an antioxidant
Ethyleneamine	Unknown	Carcinogenic in animals; used in paper and textile processing and manufacture of herbicides, resins, rocket and jet fuels
3,3-Dichlorobenzidine	Unknown	Carcinogenic in animal species; exposure accompanies benzidine and betanaphthylamine
Methyl chloromethyl methyl ether	Unknown	Carcinogenic in animals; synonym, CMME; BCME contaminants CMME; used in resin-making, textile, and drug production.
4,4-Methylene bis (2-chloroaniline)	Unknown	Synonym MOCA. Tumorigenic in rats and mice. Skin absorption may be the hazard. Curing agent for iso-cyanate polymers.

Table 1.5 *Industrial substances suspected of carcinogenic potential for humans.*

Industrial Substance	Industrial Substance
Antimony trioxide production	Epichlorhydrin
Benzene (skin)	Hexamethyl phosphoramide (skin)
Benzo(a) pyrene	Hydrazine
Beryllium	4,4-Methylene bis (2-chloroaniline) (skin)
Cadmium oxide production	4,4-Methylene dianiline
Chloroform	Monomethyl hydrazine
Chromates of lead and zinc	Nitrosamines
3,3-Dichlorobenzidine	Propane sulfone
1,1-Dimethyl hydrazine	Beta-propiolactone
Dimethyl sulfate	Vinyl cyclohexene dioxide
Dimethylcarbamyl chloride	

1.1.5 Surfactants

Surfactants, or surface-active agents, are large organic molecules that are slightly soluble in water and cause foaming in wastewater treatment plants and in the surface waters into which the waste effluent is discharged.

The surfactants present in detergent products remain chemically unchanged during the washing process and are discharged down the drain with the dirty wash water. In the vast majority of cases, the drain is connected to a sewer and ultimately to a wastewater treatment plant, where the surfactants present in the sewage can be removed by biological and physical-chemical processes.

During aeration of wastewater, these compounds are collected on the surface of the air bubbles and thus create a very stable foam. The determination of surfactants is accomplished by measuring the color change in a standard solution of methylene blue active substance (MBAS).

1.1.6 Priority Pollutants

Priority pollutants (both inorganic and organic) are selected on the basis of their known or suspected carcinogenicity, mutagenicity, teratogenicity, or high acute toxicity. Many of the organic priority pollutants are also classified as volatile organic compounds (VOCs).

Representative examples of the priority pollutants are shown in Table 1.2. Within a wastewater collection and treatment system, organic priority pollutants may be removed, transformed, generated, or simply transported through the system unchanged. Five primary mechanisms are involved: (1) volatilization (also gas stripping); (2) degradation; (3) adsorption to particles and sludge; (4) transport through the entire system; (5) generation as a result of chlorination or as byproducts of the degradation of precursor compounds.

1.1.7 Volatile Organic Compounds

Wastewaters are collected and treated in a variety of ways, some of which result in the emission of volatile organic compounds (VOCs) from the wastewater to the air. Water may come into direct contact with organic compounds during a variety of different chemical processing steps, thus generating wastewater streams that must be discharged for treatment or disposal. Direct contact wastewater includes:

- Water used to wash impurities from organic compound products or reactants.
- Water used to cool or quench organic compound vapour streams.
- Condensed steam from jet eductor systems pulling vacuum on vessels containing organic compounds.
- Water from raw material and product storage tanks.
- Water used as a carrier for catalysts and neutralizing agents (e.g., caustic solutions).
- Water formed as a byproduct during reaction steps.

Direct contact wastewater is also generated when water is used in equipment washes and spill clean-ups. This wastewater is normally more variable in flow-rate and concentration than the streams listed above and may be collected in a way that is different from process wastewater. Wastewater streams generated by unintentional contact with organic compounds through equipment leaks are defined as “indirect contact” wastewater. Indirect contact wastewater may become contaminated as a result of leaks from heat exchangers, condensers, and pumps.

Organic compounds that have a boiling point $\leq$ 100 °C and/or a vapor pressure $>$ 1 mm Hg (or 133.3 Pa) at 25 °C are generally considered to be volatile organic compounds (VOCs), e.g., vinyl chloride. The release of these compounds in sewers and treatment plants, especially at the head works, is of particular concern with respect to the health of collection system and treatment plant workers.

1.2 Treatment Stages

Generally, the terms "preliminary" and/or "primary" refer to physical unit operations; "secondary" refers to chemical and biological unit processes; and "advanced" or "tertiary" refer to combinations of all three.

The application and definition of the various stages of treatment and methods to perform specific functions are described in the following sections. Figure 1.1 shows a schematic of wastewater treatment stages.

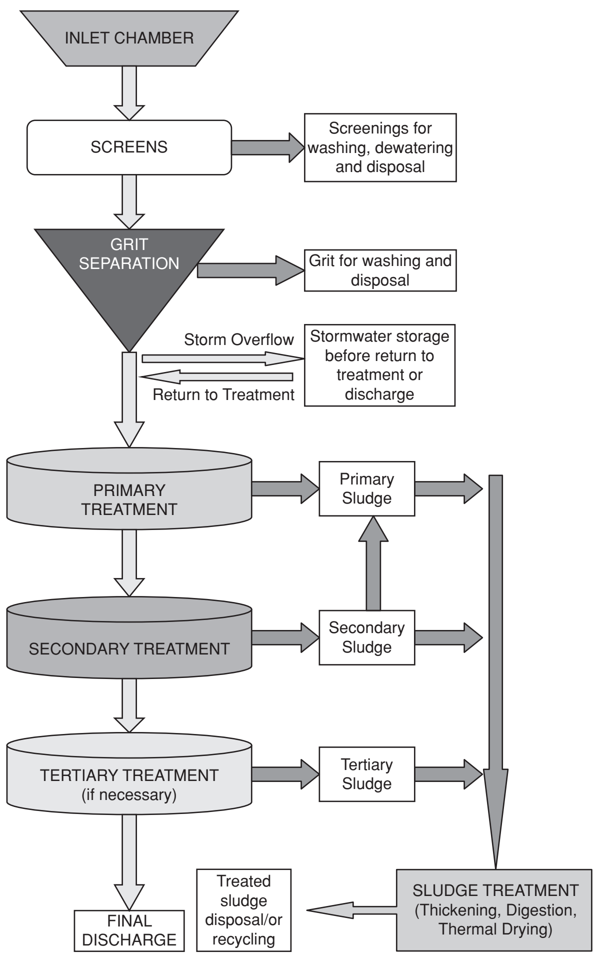

Figure 1.1 *A simplified schematic of wastewater treatment stages.*

Table 1.6 *Typical wastewater qualities.*

Parameter	Unit	Oily Wastewater	Stripped Sour Water	Combined High TDS Waters (Ion Exchange Waste, Boiler Blowdown, RO Reject)	Cooling Tower Blow-down
Temperature	°C	30–60	30–35	30–40	–
pH	–	7–8	7–8	7–8	8
TDS	mg/L	150–5000	50–150	500–2500	5000–6000
TSS	mg/L	300–800	10–20	50–100	16 000–19 000
Cl2 Residual	–	–	–	–	0.3–0.5
BOD	mg/L	300–500	100–300	5–150	–
COD	mg/L	300–1200	200–500	100–500	–
TOC	mg/L	–	–	<100	–
Hardness	mg/L as $CaCO_3$	–	–	–	1200–1400
Total Alkalinity	mg/L as $CaCO_3$	–	–	–	100–125
Ca^{2+}	mg/L	–	–	–	1000
Cl^-	mg/L	50–2000	–	–	1000–1500
NH_3	mg/L	20–50	40–80	–	<5
Cyanides	mg/L	1–3	–	–	–
Phenols	mg/L	5–20	20–80	–	–
H_2S	mg/L	5–10	10–40	–	–

1.2.1 Sources of Wastewater

Sources of wastewater in the oil, gas, and chemical processing industries include oily wastewater, sour water, stripped sour water, water treatment waste, and blow-down streams (cooling tower, boiler, and gasifier) and so on. Each of these sources produces wastewater with slightly different characteristics and treatment requirements.

Table 1.6 provides typical wastewater qualities for some of the wastewater streams in the oil, gas, and chemical processing industries.

1.2.2 Discharge Options and Quality Requirements

Produced water in the oil and gas industry has a complex composition, but its constituents can be broadly classified into organic and inorganic compounds including: dissolved and dispersed oils, grease, heavy metals, radionuclides, treating chemicals, formation solids, salts, dissolved gases, scale products, waxes, microorganisms, and dissolved oxygen.

The four discharge alternatives listed below are all technically feasible. Selection of the preferred alternative is a function of the selected process, recycling opportunities, economics, regulatory limitations, and social requirements. Process effects, which relate primarily to dissolved solid concentrations and financial implications, will be examined here.

- Physical and biological treatment followed by discharge to a river.
- Physical, biological, and chemical treatment followed by discharge to a river.
- Physical and biological treatment and recycling with deep well injection, thus no surface discharge.
- Physical and biological treatment, evaporation and crystallization, thus no discharge.

1.2.3 Preliminary Wastewater Treatment

Preliminary wastewater treatment is defined as the removal of wastewater constituents that may cause maintenance or operational problems within the treatment operations, processes, and ancillary systems.

Screening and comminution for the removal of debris and rags, grit removal for the elimination of coarse suspended matter that may cause wear or clogging of equipment, and flotation for the removal of large quantities of oil and grease are examples of preliminary operations.

1.2.4 Primary Wastewater Treatment

In primary treatment a portion of the suspended solids and organic matter is removed from the wastewater. This removal is usually accomplished with physical operations such as screening and sedimentation.

The effluent from primary treatment will ordinarily contain considerable organic matter and will have a relatively high BOD. The principal function of primary treatment continues to be as a precursor to secondary treatment.

Following primary treatment, the treated water is suitable for use as cooling water and utility water but will require further treatment to be used as boiler feed water.

1.2.5 Conventional Secondary Wastewater Treatment

Secondary treatment is directed principally toward the removal of biodegradable organics and suspended solids. Disinfection is frequently included in the definition of conventional secondary treatment.

Conventional secondary treatment is defined as the combination of processes customarily used for the removal of these constituents, and includes biological treatment by activated sludge, fixed film reactors, or lagoon systems and sedimentation.

1.2.6 Nutrient Removal or Control

Nutrient removal or control is generally required for:

1. Discharges to confined bodies of water where eutrophication might be caused or accelerated.
2. Discharges to flowing streams where nitrification could tax oxygen resources or where rooted aquatic plants could flourish.
3. Recharge of groundwaters that might be used indirectly for public water supplies.

The nutrients of principal concern are nitrogen and phosphors, and they may be removed by biological, chemical, or a combination of these processes. In many cases, the nutrient removal processes are coupled with secondary treatment; for example, biological denitrification may follow an activated-sludge process that produces a nitrified effluent.

1.2.7 Advanced Wastewater Treatment/Wastewater Reclamation

Advanced wastewater treatment or tertiary treatment is normally defined as the level of treatment required beyond conventional secondary treatment to remove constituents of concern, including nutrients, toxic compounds, and increased amounts of organic material and suspended solids.

In addition to the nutrient removal processes, unit operations or processes frequently employed in advanced wastewater treatment are chemical coagulation, flocculation, and sedimentation followed by filtration and activated carbon. Less used processes include ion exchange and reverse osmosis for specific ion removal or for reduction of dissolved solids.

Advanced wastewater treatment is also used in a variety of reuse applications where quality water is required, such as for industrial cooling water and groundwater recharge.

1.2.8 Toxic Waste Treatment/Specific Contaminant Removal

The removal of toxic substances and specific contaminants is a complex subject and concentrations of toxic pollutants are usually controlled by pre-treatment prior to discharge to the final treatment system. Many toxic substances, such as heavy metals, are reduced by some form of chemical-physical treatment such as chemical coagulation, flocculation, sedimentation, and filtration.

Some degree of removal is also accomplished by conventional secondary treatment. Wastewaters containing volatile organic constituents may be treated by air stripping or by carbon adsorption. Small concentrations of specific contaminants may be removed by ion exchange. Table 1.7 presents a list of typical pollutants that have an inhibitory effect on the activated-sludge process.

1.2.9 Sludge Processing

When a liquid sludge is produced, further treatment may be required to make it suitable for final disposal. Typically, sludges are thickened (dewatered) to reduce the volumes transported off-site for disposal.

Processes for reducing water content include lagooning in drying beds to produce a cake that can be applied to land or incinerated; pressing, where sludge is mechanically filtered, often through cloth screens, to produce a firm cake; and centrifugation where the sludge is thickened by centrifugally separating the solid and liquid. Sludges can be disposed of by liquid injection to land or by disposal in landfill. For the most part, the methods and systems reported in Table 1.8 are used to process the sludge removed from the liquid portion of the wastewater.

Table 1.7 *Threshold concentrations of pollutants inhibitory to the activated-sludge process.*

	Concentration, mg/L	
Pollutant	Carbonaceous Removal	Nitrification
Aluminum	15–26	–
Ammonia	480	–
Arsenic	0.10	–
Borate (Boron)	0.05–100	–
Cadmium	10–100	–
Calcium	2500	–
Chromium (hexavalent)	1–10	0.25
Chromium (trivalent)	50	–
Copper	1	0.005–0.50
Cyanide	0.1–5	0.34
Iron	1000	–
Manganese	10	–
Magnesium	–	50
Mercury	0.1–5	–
Nickel	1–2.5	0.25
Silver	5	–
Sulfate	–	500
Zinc	0.8–1	
Phenols:	200	4–10
Phenol	–	10–16
Cresol	–	150
2-4 Dinitrophenol		

1.3 Treatment Processes

Industrial wastewater treatment processes cover the mechanisms and processes used to treat waters that have been contaminated in some way by anthropogenic industrial or commercial activities, prior to its release into the environment or its reuse.

The oil, gas, and chemical industries produce some contaminants in wastewater that should be removed by physical, chemical and/or biological means. Figure 1.2 shows a schematic of wastewater treatment in chemical industries.

Unit operations and processes that are commonly used in wastewater treatment are listed in Table 1.9. The following instructions should be taken into consideration for the selection of treatment technologies:

- Technologies should be categorized into those that work, those that have the potential to work, and those that have no place in the particular application.
- Technologies should be evaluated based on their effectiveness (ability to reliably attain treatment goals), implementability (availability of materials and services), and costs (capital and operation and maintenance).
- Viable technologies should be identified for each of the individual wastewater streams. Streams that use the same technologies should be combined to create composite waste

Table 1.8 *Sludge processing and disposal methods.*

Processing or Disposal Function	Unit Operation, Unit Process, or Treatment Method
Preliminary operation	Sludge pumping Sludge grinding Sludge blending and storage Sludge degritting
Thickening	Gravity thickening Flotation thickening Centrifugation Gravity belt thickening Rotary drum thickening
Conditioning	Chemical conditioning Heat treatment
Disinfection	Pasteurization Long-term storage
Dewatering	Vacuum filter Centrifuge Belt press filter Filter press Sludge drying beds Lagoons
Heat drying	Dryer variations Multiple-effect evaporator
Thermal reduction	Multiple-hearth incineration Fluidized bed incineration Co-incineration with solid wastes Wet air oxidation Vertical deep well reactor
Ultimate disposal	Land application Distribution and marketing Landfill Lagooning Chemical fixation

treatment trains. These should be compared to current manufacturing and waste treatment practices to identify possible candidates for waste segregation and independent treatment.

- The level of wastewater treatment and method of effluent discharge should be established to protect the receiving body of water or the water table and its usages.

The level of treatment of the facility to be designed should be determined by the ability of the receiving waters to accept residual wastes and the allocation set up by effluent standards. The degree of treatment can be determined by comparing the influent wastewater characteristics to the required effluent wastewater characteristics.

In the case of wastewater reuse applications, the quality of water used as make-up will govern the wastewater treatment needed and the degree of reliability required for the

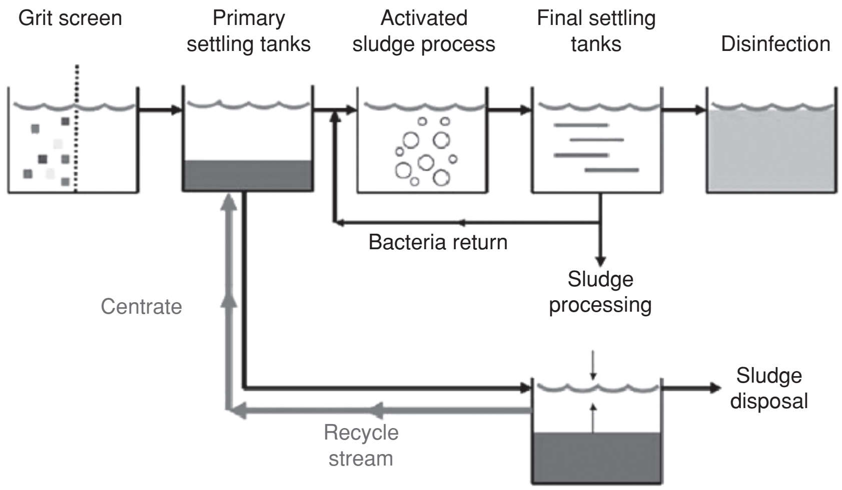

Figure 1.2 *A schematic of wastewater treatment (Reproduced with permission from [10] © Elsevier, 2011).*

treatment processes and operations. The reliability of the proposed treatment processes and operations must be evaluated to provide a continuous supply of water with consistent water quality.

All toxic and highly chemically active materials should be treated at source and not discharged in any active state into the sewers loading to the waste treatment plant. This may include removal of soluble and insoluble forms of metals such as lead, zinc, copper, or their derivatives, and other similarly dangerous classified metals and their byproducts.

It should be required that highly active metals, inclusive of finely divided magnesium and aluminium alloys, are not discharged in the sewers but are treated and removed by special methods and equipment at source.

It should be required that all highly toxic inorganic chemicals, inclusive of cyanides, fluorides, and related objectionable anions, must be treated and removed from the water at or near the source to the degree specified in the code regulations. This includes the chromates and other special complex anion derivatives.

Another group excluded from discharge of waste in the sewer should be acting oxidizing agents, particularly peroxides of organic and inorganic structures. This group should also include other powerful oxidizing agents, inclusive of chlorates, perchlorates, nitric acid, and other similar products.

The discharge of volatile organic materials into the waste should also be restricted and these materials should be isolated and treated at source. This restriction is a must, because disastrous explosions can occur in sewer systems where the volatilization of the organic matter creates an explosive mixture or some other conditions set off chemical reactions.

In general, all toxic materials, particularly of the organic family that are known to be dangerous to plant, animal, or human life, should be treated at source.

All solutions containing radioactive products must also be kept isolated and treated at source.

Table 1.9 *Unit operations, unit processes, and systems for wastewater treatment.*

Contaminant	Unit Operation, Unit Process, or Treatment System
Suspended solids	• Sedimentation • Screening and comminution • Filtration • Flotation • Chemical-polymer addition • Coagulation/sedimentation
Biodegradable organics	• Activated sludge variations • Fixed film: trickling-filters • Fixed film: rotating biological contractors • Lagoon and oxidation pond variations • Intermittent sand filtration • Land treatment systems • Physical-chemical systems
Pathogens	• Chlorination • Hypochlorination • Ozonation • Land treatment systems
Nutrients: a) Nitrogen	• Suspended-growth nitrification and denitrification variations. • Fixed-film nitrification and denitrification variations • Ammonia stripping • Ion exchange • Breakpoint chlorination • Land treatment systems
b) Phosphorus	• Metal-salt addition • Lime coagulation/sedimentation • Biological-chemical phosphorus removal • Land treatment systems
c) Nitrogen and phosphorus	• Biological nutrient removal • Carbon adsorption
Refractory organics	• Tertiary ozonation • Land treatment systems
Heavy metals	• Chemical precipitation • Ion exchange • Land treatment systems
Dissolved inorganic solids	• Ion exchange • Reverse osmosis • Electrodialysis

1.3.1 Selection of Treatment Processes

1. The removal of all wastewater contaminants will be achieved only through the various treatment operation units. Selection of the most probable appropriate treatment sequences will provide more desirable treated wastewater.
2. The two general categories of approach to develop the treated wastewater are physical/chemical treatment and biological treatment. The essential difference between the

Table 1.10 *Selective list of unit processes used for particular waste constituents.*

Unit Process	Removal Mechanism	Waste Constituent
Sedimentation/ flotation	Gravity	Solid phase organics/inorganics
Coagulation/ sedimentation	Particle aggregation/gravity	Solid phase organics/inorganics
	Chemical bonding	Colloidal phase organics/inorganics
		Colloidal phase inorganics
Biological treatment	Particle aggregation/ biological	Solid phase organics/inorganics
		Colloidal phase organics/inorganics
	Metabolism/gravity	Soluble phase biodegradable organics
Filtration	Entrapment	Solid phase organics/inorganics
	Particle aggregation/ adsorption	Colloidal phase organics/inorganics
Carbon adsorption	Adsorption	Soluble phase adsorbable organics/inorganics
	Entrapment	Solid phase organics/inorganics
	Particle aggregation/ adsorption	Colloidal phase organics/inorganics

capabilities of a physical/chemical process and a biological process is the ability of each to remove certain types of organic materials.

The physical/chemical process is subject to apparent inefficiencies caused by a certain amount of non-adsorbable organics in the wastewater. The biological process is subject to apparent inefficiencies as a result of non-biodegradable organics in the wastewater. A selective listing of unit processes and the waste constituents for which they are generally applied and/or are effective is shown in Table 1.10.

Assembly of the most applicable process train is based on a full knowledge of the wastewater's condition and constituents.

In general, chemical/physical treatment is a suitable alternative:

- for a waste having a high particulate organic concentration, provided the soluble organic concentration, following chemical coagulation, sedimentation, and filtration, is less than 50 mg/L BOD5;
- for wastewater treatment systems where no influent flows will be received for substantial periods of time, for example batch treatment or systems experiencing significant flow variations;
- if land space is limited or toxic substances present in the raw wastewater.

Care should be exercised in the application of chemical-physical treatment systems to medium to high strength wastes (BOD_5 greater than 200 mg/L). For this situation, on-site pilot studies are desirable to determine the effluent quality that can be obtained and to ascertain if the biological activity anticipated in the carbon column will be more of a detriment (odor, plugging) than an asset (higher organic removal).

3. Land application of wastewater is viewed as an alternative to other secondary treatment schemes or as a final add-on step for liquid disposal and convenient water use. Alternative land disposal methods include various modes of surface and subsurface percolation and deep well injection.

Table 1.11 *Treatment processes used for the removal of toxic compounds.*

Process	Removal Application
Activated-carbon adsorption	Natural and synthetic organic compounds including VOCs; pesticides; PCBs; heavy metals
Activated-sludge powdered activated carbon	Heavy metals; ammonia; selected refractory priority pollutants
Air stripping	Volatile organic compounds (VOCs) and ammonia
Chemical coagulation, sedimentation, and filtration	Heavy metals and polychloro-biphenyls (PCBs)
Chemical oxidation	Ammonia; refractory and toxic halogenated aliphatic and aromatic compounds
Conventional biological treatment (activated-sludge, trickling-filter)	Phenols; PCBs; selected hydrogenated hydrocarbons

Combination land disposal and wastewater reclamation methods include infiltration-percolation, overland flow, irrigation, and groundwater recharge.

4. Many treatment methods can be used for toxic compounds. Because of the complex nature of toxicity, the treatment method must consider the specific characteristics of the wastewater and the nature of the toxic compounds.

   Treatment processes used to remove some of these specific compounds or groups of compounds are summarized in Table 1.11.

Various combinations of unit operations and processes and their interaction for the treatment of refinery wastewater are identified in Table 1.12. A summary of treatment methods for petrochemical wastes are also presented in Tables 1.13, 1.14, and 1.15. The selection of a process train or alternative process trains should be made on the basis of the ability of the individual unit processes to remove specific waste constituents.

1.3.1.1 Important Factors in Process Selection

The most important factors that must be considered when evaluating and selecting unit operations and processes are identified below:

1. **Process applicability**
   The applicability of a process should be evaluated on the basis of past experience, published data, data from full scale plants and from pilot plant studies. If new or unusual conditions are encountered, pilot plant studies are essential.
2. **Applicable flow range and flow variation**
   The process should be matched to the expected range of flow-rates. For example, stabilization ponds are not suitable for extremely large flow-rates. Most unit operations and processes have to be designed to operate over a wide range of flow-rates.

   Most processes work best at a relatively constant flow-rate. If the flow variation is too great, flow equalization is necessary. Table 1.16 identifies critical design and sizing factors for secondary treatment plant facilities and describes the potential performance impacts of flow-rate and constituent mass-loading variations.

Table 1.12 *Refinery treatment sequence options.*

Pre-treatment	Primary Treatment	Secondary Treatment	Tertiary Treatment	
Removal of phenolics, S-, NH_3, RSH, F-, acid sludge, oil, etc., water reuse; waste equalization	Removal of free oil suspended solids	Removal of emulsified oil, suspended and colloidal solids	Removal of dissolved organics (variable) produced biological sludge	
		Processes		
Unit separators Steam stripping Fuel gas stripping Air oxidation Neutralization Surge ponds	API separators CPI, PPI separators (Note: CPI = corrugated plate interceptor: PPI = parallel plate interceptor.)	Chemical coagulation and air flotation Chemical coagulation and filtration pH control Reduction of intermediate oxygen demand Equalization of wastes	Trickling-filter Activated oxidation pond Aerated lagoon Rotating biological contactors	Chemical coagulation and air flotation Chemical coagulation and filtration Carbon adsorption Carbon adsorption
Inhibitory contaminant surge control	↓Sludges	↓Sludges	↓Sludges	↓Sludges

Design provisions for flow-rate variations, in addition to flow equalization, may include flow splitting and unit process bypassing under certain peak flow-rate conditions. Minimum treatment requirements, if permitted by regulatory authorities, may include primary treatment and disinfection of the entire flow and secondary treatment of a portion of the flow. The advantages of a unit process flow-splitting and bypassing strategy are that:

- the biomass of the secondary treatment process can be preserved during peak storm conditions and not lost due to washout;
- the quality of the treatment plant effluent can be restored quickly after the storm event; and
- the entire treatment facilities need not be oversized to handle unusual events.

A disadvantage of flow-splitting and bypassing is that the effluent quality may violate the discharge permit for short periods of time.

However, any treatment sequence designed for flow-splitting and unit bypassing should be investigated in advance to ensure it meets with environmental regulation requirements.

Table 1.13 *Summary of physical treatment methods for petrochemical wastes classified by plant product.*

	Physical Treatment						
Plant Product	Sedimentation	Filtration	Separators (API)	Stripping	Absorption and Extraction	Evaporation	Submerged Comousion
General chemicals	√			√	√		
Nylon							√
Nylon chemical intermediates	√	√		√		√	
Organic chemicals			√			√	
Photochemicals		√					
Resins					√		
Rocket fuels			√				
Synthetic rubber			√				

Table 1.14 *Summary of chemical and biological treatments methods for petrochemical wastes classified by plant product.*

	Chemical Treatment		Biological Treatment		
Plant Product	pH Adjustment	Chemical Oxidation	Biological Filters	Activated Sludge	Lagoons
General chemicals	√	√			√
Nylon			√		
Nylon chemical intermediates		√	√		√
Organic chemicals	√				
Oxygenated hydrocarbons				√	
Photochemicals			√		
Powders			√		
Resins			√		√
Rocket fuels	√		√		
Rubber, textiles, and plastics				√	

3. **Influent wastewater characteristics**
   The characteristics of an influent wastewater affect the types of processes to be used (e.g., chemical or biological) and the requirements for their proper operation.
4. **Inhibiting and unaffected constituents**
   Identification should be made of:
   - The constituents that are present.
   - The constituents that may be inhibitory to the treatment processes.
   - The constituents that are not affected during treatment.

Table 1.15 *Summary of ultimate disposal methods for petrochemical wastes classified by plant product.*

	Ultimate Disposal						
Plant Product	Controlled Dilution to Streams and Bays	At Sea	On Land Surfaces	Dumping or Burial	Deep Wells	Incineration	Salvage
Nylon			√		√	√	√
Nylon chemical intermediates	√					√	
Synthetic rubber	√					√	

Table 1.16 *Effect of flow-rates and constituent mass loadings on the selection and sizing of secondary treatment plant facilities.*

Unit Operation or Process	Critical Design Factor(s)	Sizing Criteria	Effects of Design Criteria on Plant Performance
Wastewater pumping and piping	Maximum hour flow-rate	Flow-rate	Wet well may flood, collection system may surcharge, or treatment units may overflow if peak rate is exceeded.
Screening	Maximum hour flow-rate	Flow-rate	Head losses through bar rack and screens increase at high flow-rates.
	Minimum hour flow-rate	Channel approach velocity	Solids may deposit in the approach channel at low flow-rates.
Grit removal	Maximum hour flow-rate	Overflow rate	At high flow-rates, grit removal efficiency decreases in Flowthrough-type grit chambers causing grit problems in other processes.
Primary sedimentation	Maximum hour flow-rate	Overflow rate	Solids removal efficiency decreases at high overflow rates; increases loading on secondary treatment system.
	Minimum hour flow-rate	Detention time	At low flow-rates, long detention times may cause the wastewater to become septic.
Activated sludge	Maximum hour flow-rate	Hydraulic residence time	Solid washout at high flow-rates; may need effluent recycling at low flow-rates.
	Maximum daily organic load	Food/microorganism ratio	High oxygen demand may exceed aeration capacity and cause poor treatment performance.
Tickling-filters	Maximum hour flow-rate	Hydraulic loading	Solids washout at high flow-rates may cause loss of process efficiency.
	Minimum hour flow-rate	Hydraulic and organic loading	Increased recycling at low flow-rates may be required to sustain process.
	Maximum daily organic load	Mass loading/ media Volume	Inadequate oxygen during peak load may result in loss of process efficiency and cause odors.
Secondary sedimentation	Maximum hour flow-rate	Overflow rate or detention time	Reduced solids removal efficiency at high overflow rates or short detention times.
	Minimum hour flow-rate	Detention time	Possible rising sludge at long detention times.
	Maximum daily organic load	Solids loading rate	Solids loading to sedimentation tanks may be limiting.
Chlorine-contact tank	Maximum hour flow-rate	Detention time	Reduced bacteria extermination at reduced detention time.

5. **Climatic constraints**
   Temperature affects the rate of reaction of most chemical and biological processes. Temperature also affects the physical operation of facilities. Warm temperatures may accelerate odor generation and also limit atmospheric dispersal.
6. **Reaction kinetics and reactor selection**
   Reactor sizing should be based on the governing reaction kinetics. Data for kinetic expressions are usually derived from experience, published literature, and the results of pilot plant studies.
7. **Performance**
   Performance is usually in terms of effluent quality, which must be consistent with the effluent discharge requirements.
8. **Treatment residuals**
   The types and amounts of solid, liquid, and gaseous residual produced should be known or estimated.
9. **Sludge processing**
   If there are any constraints that would make sludge processing and disposal infeasible or expensive, these should be identified. The extent of recycle loads from sludge processing that affect the liquid unit operations or processes should also be clarified.
10. **Environmental constraints and regulations**
    Environmental factors, such as prevailing winds, wind direction, and proximity to residential areas, may restrict or affect the use of certain processes, especially where odors may be produced.
    Noise and traffic may affect selection of a plant site. The receiving waters may have special limitations, requiring the removal of specific constituents. The characteristics of the treated water imposed by the final destination and/or environmental regulations will dictate special unit operations and processes for treatment of wastewater.
11. **Chemical requirements**
    The resources and the amounts that must be committed for a long period of time for successful operation of the unit operation or process need to be clarified. The effects that the addition of chemicals might have on the characteristics of the treatment residuals and the cost of treatment should also be determined.
12. **Energy requirements**
    The energy requirements, as well as probable future energy costs, must be known if cost-effective treatment systems are to be designed.
13. **Operating and maintenance requirements**
    Any special operating or maintenance requirements needed, along with the necessary spare parts and their availability and cost, should be determined.
14. **Reliability**
    The question of what the long-term reliability of the unit operation or process under consideration is must be answered. Is the operation or process easily upset? Can it withstand periodic shock loadings? If so, how do such occurrences affect the quality of the effluent? Because of variations in effluent quality performance, a treatment plant should be designed to produce an average effluent concentration below the permit requirements.
15. **Compatibility**
    The unit operation or process should be able to be used successfully within the existing facilities. Plant expansion should be able to be accomplished easily.

16. **Land availability**
    Sufficient space should be allocated to accommodate either the facilities currently under consideration or possible future expansion.
17. **Equipment availability**
    Most of the equipment used in wastewater treatment is custom manufactured, except for items such as small pumps, motors, and valves. Some items of equipment may require special manufacturing techniques or are proprietary and only available from limited sources. Therefore, the equipment components that make up the process or system should be considered carefully to determine their potential effects upon the design, construction, and operation and maintenance of the facilities.
18. **Personnel requirements**
    The selection of a treatment process should consider not only the number of operating and maintenance personnel needed but also the skills required.

    The extent and complexity of the control systems and the staffing levels required must be evaluated carefully.

1.4 Chemical Oxygen Demand (COD) in Wastewater Systems

This section first discusses the background of the COD method, then the method to calculate the theoretical oxygen demand. Chemical oxygen demand (COD) is the equivalent amount of oxygen consumed under specified conditions in the chemical oxidation of the organic and oxidizable inorganic matter contained in wastewater, corrected for the influence of chlorides. In American practice, unless otherwise specified, the chemical oxidizing agent is hot acid dichromate.

Microorganisms in natural water bodies consume oxygen when they degrade organic matter to biomass. Biochemical oxygen demand (BOD) is a parameter that describes the oxygen consumption when microorganisms "eat" organic mass. The more organic load enters the water body, the more oxygen the microorganisms will use for conversion. Large amounts of pollutants may cause oxygen loss in a water body and lead to harmful effects in nature so it is useful to know the oxygen consumption of wastewater before discharge.

BOD requires days for results and COD is used because it is a lot faster. So called standard methods for COD determination are open and closed reflux systems, where a strong oxidant is added to the water solution and is boiled in open or closed reflux for a few hours and then the amount of used oxidant is measured by titration methods. COD determination with standard methods usually takes a few hours, but colorimetric determination of COD requires less than an hour. COD measures the organic content of a solution.

Due to its rapidity, COD is used to measure the total amount of pollutants in water media. It is often used in water and wastewater quality determination.

The difference between COD and BOD is that, in COD, the amount of oxidant used for oxidation of organic components is measured, while BOD expresses the oxygen consumed by microorganisms when the sample is kept for five days at 20 °C. The dissolved oxygen is measured at the beginning and end of the test and the oxygen consumption is the difference between the amount of dissolved oxygen at the beginning and end. There is a correlation factor between BOD and COD so, when COD is known, the biochemical oxygen consumption in nature can also be determined.

1.4.1 Determination of the COD

Usually a strong oxidant, like potassium dichromate, is used in this measurement. The standard method for determination of the COD is titration with open or closed reflux, where the sample is heated either in a closed or an open vessel in the laboratory. The sample is boiled for two hours in the presence of the oxidant.

The amount of dichromate consumed can be determined when the difference in oxidant concentration at the beginning and end is determined. Potassium dichromate is considered to be the best oxidant because it has a strong oxidizing capability, it is applicable to many kinds of organic and inorganic matter, and it is easy to manipulate.

Oxidation of inorganic components interferes with COD determination because they also consume dichromate. In the oxidation process, the dichromate ion (Cr^{6+}) is oxidized to chromate (Cr^{3+}).

The study of Baker *et al.* (1999) declared that the COD for the chemicals, present in group one and group two well-correlated data groups, directly equalled the ThOD.

For chemicals in group three and group four (potentially well-correlated data) the COD could be estimated from the ThOD; and no correlation for chemicals presented in group five and group six could be determined.

1.4.2 Calculation of Theoretical Oxygen Demand

The Theoretical Oxygen Demand (ThOD) can be obtained for different chemicals from different studies. Because theoretical oxygen demand is not usually determined for all chemicals found in the wastewaters, the ThOD could be determined for every chemical with the method presented in the study of the Baker *et al.* (1999).

According to Baker *et al.* (1999) the amount of oxygen consumed by single component *i* can be determined with equations 1.1 and 1.2. Letters *n, m, k, j, i, h,* and *e* can be determined with equation 1.1. Equation 1.1 assumes that all compounds are oxidized completely to end products. Letters tell us how many molecules there are of element *i* in component *i*.

$$\begin{aligned} C_nH_mO_eX_kN_jS_iP_h + bO_2 \rightarrow nCO_2 + \left(\tfrac{m-k-3j-2i-3h}{2}\right) H_2O + kH_x \\ + jNH_3 + iH_2SO_4 + hH_3PO_4 \end{aligned} \tag{1.1}$$

$$b = n + \frac{m-k-3j-2i-3h}{4} - \frac{e}{2} + 2i + 2h \tag{1.2}$$

To determine the $ThOD_i$, the oxygen demand per one gram component *i* has to be determined. Oxygen demand per one gram component *i* is represented by $ThOD_{O,i}$ and determined with equation 1.3, where b_i is the amount of oxygen consumed in moles per one mole component *i*, M_i is the molar mass of a single component *i*, M_{O2} is the molar mass of an oxygen molecule, and c_i is the concentration of component "i" in water.

$$ThOD_{O,i} = b_i \tfrac{M_{O2}}{M_i} \tag{1.3}$$

$$ThOD_i = ThOD_{o,i} \times c_i \tag{1.4}$$

$$\sum ThOD = \sum_i^n ThOD_i = \sum_i^n \left(ThOD_{o,i} \times c_i\right) \tag{1.5}$$

Table 1.17 provides calculated oxygen demand per one mole component i, molar mass, and theoretical oxygen demand for various components.

Table 1.17 *Oxygen demand per one mole component i, molar mass, and theoretical oxygen demand.*

Component	Composition	Oxygen Demand Per One Mole Component i b	Molecular Weight Mi(g/mol)	Theoretical Oxygen Demand $ThOD_i$ (gO_2/gi)
Methanol	CH_4O	1.5	32.03	1.5
Phenol	C_6H_6O	7	94.1	2.38
Acetone	C_3H_6O	4	58.07	2.2
2-Aminoethanol	C_2H_7NO	2.5	61.08	1.31
Benzene	C_6H_6	7.5	78.11	3.07
Cumene	C_9H_{12}	12	120.2	3.19
Propanols	C_3H_8O	5	44.1	3.63
Toluene	C_7H_8	9	92.14	3.12
Total Nitrogen	NH_3	0	17.03	0
Xylenes	C_8H_{10}	10.5	106.17	3.16

For example, Phenol's chemical formula is C_6H_6O. If the concentration of phenol is 360 mg/L in a wastewater sample, the theoretical oxygen demand determination for this phenol concentration is shown in the calculations below.

According to equation 1.1: $n = 6, m = 6, e = 1, k = 0, j = 0, i = 0, h = 0$

When *n, m, k, j, i, h,* and *e* are used in equation 1.2, the amount of oxygen molecules needed to oxidize phenol into end products can be determined.

$$b_{C_6H_6} = 6 + \frac{6 - 0 - 3 - 2 - 3}{4} - \frac{1}{2} + 2 + 2 = 7\, mol\ O_2/(mol\ C_6H_6) \quad (1.6)$$

$$ThOD_{O,i} = 7\frac{mol\ O_2}{mol\ C_6H_6}\left(\frac{31.98}{94.1\frac{g_{C_6H_6}}{mol_{\ C_6H_6}}}\right) = 2.38\frac{g\ O_2}{g\ C_6H_6} \quad (1.7)$$

The total theoretical oxygen demand is determined by summing the single theoretical oxygen demands together.

$$ThOD_{C_6H_6} = ThOD_{o,C_6H_6} \times C_{C_6H_6} = 2.38\frac{mg\ O_2}{mg\ C_6H_6} \times 360\frac{mg\ C_6H_6}{Liter\ H_2O} = 856.8\frac{mg\ O_2}{Liter\ H_2O} \quad (1.8)$$