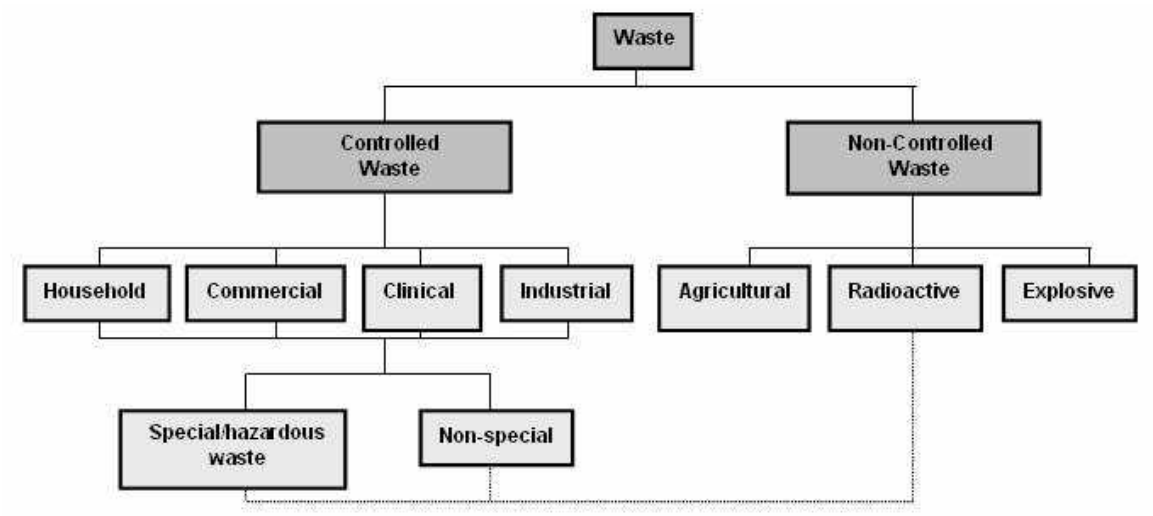
What is waste?

Waste as "an object the holder discards, intends to discard or is required to discard. Waste(s) is a pejorative term for unwanted materials. The term can be described as subjective and inaccurate because waste to one person is not waste to another.

"Wastes are materials that are not prime products (that is products produced for the market) for which the initial user has no further use in terms of his/her own purposes of production, transformation or consumption, and of which he/she wants to dispose. Wastes may be generated during the extraction of raw materials, the processing of raw materials into intermediate and final products, the consumption of final products, and other human activities. Residuals recycled or reused at the place of generation are excluded.

Waste is classified by its source and by its properties.



Classification of solid waste:

Main classification	Type	Short description	Examples
Hazardous waste	Solid or semi-solid	Substances that are either ignitable, corrosive, reactive, infectious or explosive	Some obsolete pesticides such as DDT, dieldrin, etc.
Non-hazardous waste	Putrescible	Easily decomposable/biodegradable solid waste	Food wastes
	Non-putrescible	Non-biodegradable solid waste, it includes combustible and non-combustible waste	Plastic bags, bottled water containers, tin cans, etc.

Waste management

Waste management is the collection, transport, processing or disposal, managing and monitoring of waste materials. The term usually relates to materials produced by human activity, and the process is generally undertaken to reduce their effect on health, the environment or aesthetics. Waste management is a distinct practice from resource recovery which focuses on delaying the rate of consumption of natural resources. All wastes materials, whether they are solid, liquid, gaseous or radioactive fall within the remit of waste management.

What is pollution?

Pollution is the introduction of contaminants into an environment that cause harm to human health, other living organisms, and the environment. Pollution can be in the form of chemical substances, or energy such as noise, heat, or light. Pollutants can be naturally occurring substances or energies, but are considered contaminants when in excess of natural levels.

Pollution is the state of being unnatural of anything!

Environmental pollution is defined as the undesirable change in physical, chemical and biological characteristics of our air, land and water. As a result of over-population, rapid industrializations, and other human activities like agriculture and deforestation etc., earth became loaded with diverse pollutants that were released as by-products.

Pollutants are generally grouped under two classes:

(a) Biodegradable pollutants - Biodegradable pollutants are broken down by the activity of micro-organisms and enter into the biogeochemical cycles. Examples of such pollutants are domestic waste products, urine and faucal matter, sewage, agricultural residue, paper, wood and cloth etc.

(b) Non- Biodegradable pollutants - Non-biodegradable pollutants are stronger chemical bondage, do not break down into simpler and harmless products. These include various insecticides and other pesticides, mercury, lead, arsenic, aluminum, plastics, radioactive waste etc.

Classification of environmental pollution

Pollution can be broadly classified according to the components of environment that are polluted. Major of these are: Air pollution, Water pollution, Soil pollution (land degradation), light pollution, radioactive pollution, thermal pollution and Noise pollution.

Water pollution

Water is one of the prime necessities of life. With increasing number of people depend on this resource; water has become a scarce commodity. Pollution makes even the limited available water unfit for use. Water is said to be polluted when there is any physical, biological or chemical change in water quality that adversely affects living organisms or makes water unsuitable for use. Sources of water pollution are mainly factories, power plants, coal mines and oil wells situated either close to water source or away from sources. They discharge pollutants directly or indirectly into the water sources like river, lakes, water streams etc.

Effects of water pollution

The impact of water pollution on aquatic life and land life can be devastating. Effects of water pollution can include:

- Spread of disease: Drinking polluted water can cause cholera or typhoid infections, along with diarrhea.
- Affects body organs: The consumption of highly contaminated water can cause injury to the heart and kidneys.
- Harms the food chain: Toxins within water can harm aquatic organisms, thus breaking a link in the food chain.
- Causes algae in water: Urea, animal manure and vegetable peelings are food for algae. Algae grow according to how much waste is in a water source. Bacteria feed off the algae, decreasing the amount of oxygen in the water. The decreased oxygen causes harm to other organisms living in the water.
- Flooding: The erosion of soil into waterways causes flooding, especially with heavy rainfall.
- Harms animals: Birds that get into oil-contaminated water die from exposure to cold water and air due to feather damage. Other animals are affected when they eat dead fish in contaminated streams.

The effects of water pollution are not always immediate. They are not always seen at the point of contamination. They are sometimes never known by the person responsible for the pollution. However, water pollution has a huge impact on our lives. With knowledge, consideration and preparation, water pollution can be decreased. It doesn't take much effort, just a little thought.

Sources of water pollution may be divided into two categories.
(i) Point-source pollution, in which contaminants are discharged from a discrete location. Sewage outfalls and oil spills are examples of point-source pollution.

(ii) Non-point-source or diffuse pollution, referring to all of the other discharges that deliver contaminants to water bodies. Acid rain and unconfined runoff from agricultural or urban areas falls under this category.

Sources of Point and Nonpoint Pollution	
POINT SOURCES	NONPOINT SOURCES
• Wastewater effluent, both municipal and industrial • Runoff and leachate from waste disposal sites • Runoff and infiltration from animal feed lots • Runoff from mines, oil fields, and unsewered industrial sites • Storm sewer outfalls from cities with a population of greater than 100,000 • Runoff from construction sites larger than two hectares • Overflows of combined storm and sanitary sewers	• Runoff from agriculture (including return flow from irrigated agriculture) • Runoff from pasture and range • Urban runoff from unsewered areas and sewered areas with a population of less than 100,000 • Septic leachate and runoff from failed septic systems • Runoff from construction sites smaller than two hectares • Runoff from abandoned mines • Atmospheric deposition over a water surface • Activities on land that generate contaminants, such as logging, wetland conversion, construction and development of land or waterways

Both point and nonpoint source pollution can be divided into two categories on basis of the nature of the pollutants-

- Inorganic pollution
- Organic pollution

Table 12.1 General Types of Water Pollutants

Class of pollutant	Significance
Trace Elements	Health, aquatic biota, toxicity
Heavy metals	Health, aquatic biota, toxicity
Organically bound metals	Metal transport
Radionuclides	Toxicity
Inorganic pollutants	Toxicity, aquatic biota
Asbestos	Human health
Algal nutrients	Eutrophication
Acidity, alkalinity, salinity (in excess)	Water quality, aquatic life
Trace organic pollutants	Toxicity
Polychlorinated biphenyls	Possible biological effects
Pesticides	Toxicity, aquatic biota, wildlife
Petroleum wastes	Effect on wildlife, esthetics
Sewage, human and animal wastes	Water quality, oxygen levels
Biochemical oxygen demand	Water quality, oxygen levels
Pathogens	Health effects
Detergents	Eutrophication, wildlife, esthetics
Chemical carcinogens	Incidence of cancer
Sediments	Water quality, aquatic biota, wildlife
Taste, odor, and color	Esthetics

ELEMENTAL POLLUTANTS

Trace element is a term that refers to those elements that occur at very low levels of a few parts per million or less in a given system. The term trace substance is a more general one applied to both elements and chemical compounds.

The following table summarizes the more important trace elements encountered in natural waters. Some of these are recognized as nutrients required for animal and plant life, including some that are essential at low levels but toxic at higher levels.

Important Trace Elements in Natural Waters

Element	Sources	Effects and Significance
Arsenic	Mining byproduct, chemical waste	Toxic[1], possibly carcinogenic
Beryllium	Coal, industrial wastes	Toxic
Boron	Coal, detergents, wastes	Toxic
Chromium	Metal plating	Essential as Cr(III), toxic as Cr(VI)
Copper	Metal plating, mining, industrial waste	Essential trace element, toxic to plants and algae at higher levels
Fluorine (F^-)	Natural geological sources, wastes, water additive	Prevents tooth decay at around 1 mg/L, toxic at higher levels
Iodine (I^-)	Industrial wastes, natural brines, seawater intrusion	Prevents goiter
Iron	Industrial wastes, corrosion, acid mine water, microbial action	Essential nutrient, damages fixtures by staining
Lead	Industrial waste, mining, fuels	Toxic, harmful to wildlife
Manganese	Industrial wastes, acid mine water, microbial action	Toxic to plants, damages fixtures by staining
Mercury	Industrial waste, mining, coal	Toxic, mobilized as methyl mercury compounds by anaerobic bacteria
Molybdenum	Industrial wastes, natural sources	Essential to plants, toxic to animals
Selenium	Natural sources, coal	Essential at lower levels, toxic at higher levels
Zinc	Industrial waste, metal plating, plumbing	Essential element, toxic to plants at higher levels

Some of the **heavy metals** are among the most harmful of the elemental pollutants and are of particular concern because of their toxicities to humans. These elements are, in general, the transition metals, and some of the representative elements, such as lead and tin, in the lower right-hand corner of the periodic table. Heavy metals include essential elements like iron as well as toxic metals like cadmium and mercury. Most of them have a tremendous affinity for sulfur, and disrupt enzyme function by forming bonds with sulfur groups in enzymes. Protein carboxylic acid ($–CO_2H$) and amino ($–NH_2$) groups are also chemically bound by heavy metals.

Some of the **metalloids**, elements on the borderline between metals and nonmetals, are significant water pollutants. Arsenic, selenium, and antimony are of particular interest.

Water quality

The quality of natural water in rivers, lakes and reservoirs and below the ground surface depends on a number of interrelated factors. In its movement on and through the surface of the heart, water has the ability to react with the minerals that occur in the soil and rocks and to dissolve a wide range of materials, so that its natural state is never pure. It always contains a variety of soluble inorganic, soluble organic and organic compounds. In addition to these, water can carry large amounts of insoluble materials that are held in suspension. Both the amounts and type of impurities found in natural water vary from place to place and by time of year and depends on a number of factors. These factors include geology, climate, topography, biological processes and land use. The impurities determine the characteristics of a water body.

The chemical, physical, and biological aspects of water quality are inter-related and must be considered together. For example, higher water temperature reduces the solubility of dissolved oxygen, and may cause a dissolved oxygen shortage that kills more sensitive fish species. The rotting fish and forest residues may contribute to a bacterial bloom that makes some human swimmers or boaters ill. Water quality is highly variable over time due to both natural and human factors. Water temperature, photosynthetic activity, and flows vary with season. Flows, and therefore suspended sediment, can vary daily with rainfall. Nutrient loads can vary with season (homeowners fertilizing in the spring), flow (runoff mechanisms affect pollutant wash off), and human management (nitrogen is released after a clear-cut). A comprehensive characterization of natural water quality therefore requires a large amount of data. Water quality data is expensive and time-consuming to acquire, however, so water quality managers usually deal with a large amount of uncertainty.

Physiochemical parameters

Temperature

Metabolic rate and the reproductive activities of aquatic life are controlled by water temperature. Metabolic activity increases with a rise in temperature, thus increasing a fish's demand for oxygen; however; an increase in stream temperature also causes a decrease in DO, limiting the amount of oxygen available to these aquatic organisms. With a limited

amount of DO available, the fish in this system will become stressed. A rise in temperature can also provide conditions for the growth of disease-causing organisms. Water temperature varies with season, elevation, geographic location, and climatic conditions and is influenced by stream flow, streamside vegetation, groundwater inputs, and water effluent from industrial activities. Water temperatures rise when streamside vegetation is removed. Water temperature also increases when warm water is discharged into streams from industries.

pH

pH is a measure of the amount of free hydrogen ions in water. Specifically, pH is the negative logarithm of the molar concentration of hydrogen ions.

$pH = -\log[H^+]$

for example,	at pH 2,	$[H^+] = 10^{-2}$ or .01
	at pH 10	$[H^+] = 10^{-10}$ or .0000000001
	at pH 4	$[H^+] = 10^{-4}$ or .0001

Because pH is measured on a logarithmic scale, an increase of one unit indicates an increase of ten times the amount of hydrogen ions. A pH of 7 is considered to be neutral. Acidity increases as pH values decrease, and alkalinity increases as pH values increase. Most natural waters are buffered by a carbon-dioxide-bicarbonate system, since the carbon dioxide in the atmosphere serves as a source of carbonic acid.

$$H_2CO_2 = HCO_3 + H^+ \quad , pK \sim 7.5$$

This reaction tends to keep pH of most waters around 7 - 7.5, unless large amounts of acid or base are added to the water. Most streams draining through forest are slightly acidic (6.8 to 6.5) due to organic acids produced by the decaying of organic matter. In waters with high algal concentrations, pH varies diurnally, reaching values as high as 10 during the day when algae are using carbon dioxide in photosynthesis. pH drops during the night when the algae respire and produce carbon dioxide. The pH of water affects the solubility of many toxic and nutritive chemicals; therefore, the availability of these substances to aquatic organisms is affected. As acidity increases, most metals become more water soluble and more toxic. Toxicity of cyanides and sulfides also increases with a decrease in pH (increase in acidity). Ammonia, however, becomes more toxic with only a slight increase in pH. Alkalinity is the capacity to neutralize acids, and the alkalinity of natural water is derived principally from the salts of weak acids. Hydroxide, carbonates, and bicarbonates are the dominant source of natural alkalinity. Reactions of carbon dioxide with calcium or magnesium carbonate in the soil create considerable amounts of bicarbonates in the soil. Organic acids such as humic acid also form salts that increase alkalinity. Alkalinity itself has little public health significance, although highly alkaline waters are unpalatable and can cause gastrointestinal discomfort.

Table 2.1 Effects of pH on fish and aquatic life

pH value		Effects observed under research
Min	Max	
3.8	10.0	Fish eggs could be hatched, but deformed young were often produced.
4.0	10.1	Limits for the most resistant fish species.
4.1	9.5	Range tolerated by trout.
4.3	--	Carp died in five days.
4.5	9.0	Trout eggs and larvae develop normally.
4.6	9.5	Limits for perch.
5.0	--	Limits for stickleback fish.
5.0	9.0	Tolerable range for most fish.
--	8.7	Upper limit for good fishing waters.
5.4	11.4	Fish avoided waters beyond these limits.
6.0	7.2	Optimum (best) range for fish eggs.
1.0	--	Mosquito larvae were destroyed at this pH value.
3.3	4.7	Mosquito larva lived within this range.
7.5	8.4	Best range for the growth of algae.

Dissolved Oxygen

Fish and other aquatic animals depend on dissolved oxygen (the oxygen present in water) to live. The amount of dissolved oxygen in streams is dependent on the water temperature, the quantity of sediment in the stream, the amount of oxygen taken out of the system by respiring and decaying organisms, and the amount of oxygen put back into the system by photosynthesizing plants, stream flow, and aeration. Dissolved oxygen is measured in milligrams per liter (mg/l) or parts per million (ppm). The temperature of stream water influences the amount of dissolved oxygen present; less oxygen dissolves in warm water than cold water. For this reason, there is cause for concern for streams with warm water.

Biochemical Oxygen Demand (BOD)/Chemical Oxygen Demand (COD)

Natural organic detritus and organic waste from waste water treatment plants, failing septic systems, and agricultural and urban runoff, acts as a food source for water-borne bacteria. Bacteria decompose these organic materials using dissolved oxygen, thus reducing the DO present for fish. Biochemical oxygen demand (BOD) is a measure of the amount of oxygen

that bacteria will consume while decomposing organic matter under aerobic conditions. Biochemical oxygen demand is determined by incubating a sealed sample of water for five days and measuring the loss of oxygen from the beginning to the end of the test. The main focus of wastewater treatment plants is to reduce the BOD in the effluent discharged to natural waters. Wastewater treatment plants are designed to function as bacteria farms, where bacteria are fed oxygen and organic waste. The excess bacteria grown in the system are removed as sludge, and this "solid" waste is then disposed of on land. Chemical oxygen demand (COD) does not differentiate between biologically available and inert organic matter, and it is a measure of the total quantity of oxygen required to oxidize all organic material into carbon dioxide and water. COD values are always greater than BOD values, but COD measurements can be made in a few hours while BOD measurements take five days. If effluent with high BOD levels is discharged into a stream or river, it will accelerate bacterial growth in the river and consume the oxygen levels in the river. The oxygen may diminish to levels that are lethal for most fish and many aquatic insects. As the river re-aerates due to atmospheric mixing and as algal photosynthesis adds oxygen to the water, the oxygen levels will slowly increase downstream. The drop and rise in DO levels downstream from a source of BOD is called the DO sag curve.

Electrical Conductivity (EC) and Dissolved Solids

Conductivity is the ability of a substance to conduct electricity. The conductivity of water is a more-or-less linear function of the concentration of dissolved ions. Conductivity itself is not a human or aquatic health concern, but because it is easily measured, it can serve as an indicator of other water quality problems. If the conductivity of a stream suddenly increases, it indicates that there is a source of dissolved ions in the vicinity. Therefore, conductivity measurements can be used as a quick way to locate potential water quality problems. Conductivity is measured in terms of conductivity per unit length, and meters typically use the unit microsiemens/cm. All natural waters contain some dissolved solids due to the dissolution and weathering of rock and soil. Dissolved solids are determined by evaporating a known volume of water and weighing the residue. Some but not the entire dissolved solids act as conductors and contribute to conductance. Waters with high total dissolved solids (TDS) are unpalatable and potentially unhealthy. Water treatment plants use flocculants to aggregate suspended and dissolved solids into particles large enough to settle out of the water column in settling tanks. A flocculent is a chemical that uses double-layer kinetics to attract charged particles.

Nitrates and nitrites

Nitrite and Nitrate are forms of the element Nitrogen, which makes up about 80 percent of the air we breathe. As an essential component of life, nitrogen is recycled continually by plants and animals, and is found in the cells of all living things. Organic nitrogen (nitrogen combined with carbon) is found in proteins and other compounds. Inorganic nitrogen may exist in the free state as a gas, as ammonia (when combined with hydrogen), or as nitrite or nitrate (when combined with oxygen). Nitrites and nitrates are produced naturally as part of the nitrogen cycle, when a bacteria 'production line' breaks down toxic ammonia wastes first into nitrite, and then into nitrate. Nitrites are relatively short-lived because they're

quickly converted to nitrates by bacteria. Nitrites produce a serious illness (brown blood disease) in fish, even though they don't exist for very long in the environment. Nitrites also react directly with hemoglobin in human blood to produce methemoglobin, which destroys the ability of blood cells to transport oxygen. This condition is especially serious for children known as methemoglobinemia or "blue baby" disease. Water with nitrite levels exceeding 1.0 mg/L should not be given to babies. Nitrite concentrations in drinking water seldom exceed 0.1 mg/L. Nitrate is a major ingredient of farm fertilizer and is necessary for crop production. When it rains, varying nitrate amounts wash from farmland into nearby waterways. Nitrates also get into waterways from lawn fertilizer run-off, leaking septic tanks and cesspools, manure from farm livestock, animal wastes (including fish and birds), and discharges from car exhausts. Nitrates stimulate the growth of plankton and water weeds that provide food for fish. This may increase the fish population. However, if algae grow too wildly, oxygen levels will be reduced and fish will die. Nitrates can be reduced to toxic nitrites in the human intestine, and many babies have been seriously poisoned by well water containing high levels of nitrate-nitrogen. Nitrate-nitrogen levels below 90 mg/L and nitrite levels below 0.5 mg/L seem to have no effect on warm-water fish, but salmon and other cold-water fish are more sensitive. The recommended nitrite minimum for salmon is 0.06 mg/L.

Phosphates

The element phosphorus is necessary for plant and animal growth. Nearly all fertilizers contain phosphates (chemical compounds containing the element, phosphorous). When it rains, varying amounts of phosphates wash from farm soils into nearby waterways. Phosphates exist in three forms: orthophosphate, metaphosphate (or polyphosphate) and organically bound phosphate. Phosphates stimulate the growth of plankton and water plants that provide food for fish. This may increase the fish population and improve the waterway's quality of life. If too much phosphate is present, algae and water weeds grow wildly, choke the waterway, and use up large amounts of oxygen. Many fish and aquatic organisms may die. Phosphates come from fertilizers, pesticides, industry, and cleaning compounds. Natural sources include phosphate-containing rocks and solid or liquid wastes. Phosphates enter waterways from human and animal wastes (the human body releases about a pound of phosphorus per year), phosphate-rich rocks, wastes from laundries, cleaning and industrial processes, and farm fertilizers. Phosphates also are used widely in power plant boilers to prevent corrosion and the formation of scale. Phosphates won't hurt people or animals unless they are present in very high concentrations. Even then, they will probably do little more than interfere with digestion. It is doubtful that humans or animals will encounter enough phosphate in natural waters to cause any health problems.

Chlorine

Chlorine is a greenish-yellow gas that dissolves easily in water. It has a pungent, noxious odor that some people can smell at concentrations above 0.3 parts per million. Because chlorine is an excellent disinfectant, it is commonly added to most drinking water supplies. In parts of the world where chlorine is not added to drinking water, thousands of people die each day from waterborne diseases like typhoid and cholera. Chlorine is also used as a

disinfectant in wastewater treatment plants and swimming pools. It is widely used as a bleaching agent in textile factories and paper mills, and it's an important ingredient in many laundry bleaches. Free chlorine (chlorine gas dissolved in water) is toxic to fish and aquatic organisms, even in very small amounts. However, its dangers are relatively short-lived compared to the dangers of most other highly poisonous substances. That is because chlorine reacts quickly with other substances in water (and forms combined chlorine) or dissipates as a gas into the atmosphere. The free chlorine test measures only the amount of free or dissolved chlorine in water. The total chlorine test measures both free and combined forms of chlorine. If water contains a lot of decaying materials, free chlorine can combine with them to form compounds called trihalomethanes or THMs. Some THMs in high concentrations are carcinogenic to people. Unlike free chlorine, THMs are persistent and can pose a health threat to living things for a long time. People who are adding chlorine to water for disinfection must be careful for two reasons:

1) Chlorine gas even at low concentrations can irritate eyes, nasal passages and lungs; it can even kill in a few breaths; and
2) The formation of THM compounds must be minimized because of the long-term health effects.
Less than one-half (0.5) mg/L of free chlorine is needed to kill bacteria without causing water to smell or taste unpleasant. Most people can't detect the presence of chlorine in water at double (1.0 mg/L) that amount. Although 1.0 mg/L chlorine is not harmful to people, it does cause problems for fish if they are exposed to it over a long period of time.

Salinity

High salinity has an impact on people and industries reliant on water from the River system. High levels of salt can reduce crop yields, limit the choice of crops that can be grown and, at higher concentrations over long periods, can kill trees and make the land unsuitable for agricultural purposes. Salinity increases the "hardness" of water, which can mean more soap and detergents have to be used or water softeners installed and maintained. This can also cause scaling in pipes and heaters. In industry, high levels of dissolved salts can cause corrosion, scale, and poor steam quality and increase the need for chemicals for water treatment.

Escherichia coli

Escherichia coli, its full name, is a type of bacteria commonly found in the intestines of animals and humans. *E. coli* has been identified as dangerous to people, producing a powerful toxin that can cause severe illness. It was first recognized in the U.S. in 1982, when an outbreak of severe, bloody diarrhea was traced to contaminated hamburgers, leading the illness to be dubbed "hamburger disease." People who suffer severe E. coli poisoning face a 30 per cent higher risk of high blood pressure or kidney damage, according to a Canadian study released in October 2008. According to the U.S. Environmental Protection Agency, the presence of E. coli in water is a strong indication of recent sewage or animal waste contamination. E. coli comes from human and animal wastes. During precipitation, E. coli may be washed into creeks, rivers, streams, lakes, or

groundwater. When these are used as sources of drinking water – and the water is not treated or inadequately treated – E. coli may end up in drinking water and may cause kidney damage and long-term complications in children. In severe cases, people may die.

Dissolve organic carbon

Dissolve organic carbon (DOC) is the partially decomposed organic matter, is what gives many freshwater bodies their characteristic yellow-brown colour. The concentration and the chemical state of DOC, whether fresh or degraded, are the most important factors that determine how deep sunlight penetrates into a given lake. In effect, DOC therefore acts as the primary sunscreen against UV radiation in the shallows of many lakes.

What is heavy metals?

A heavy metal is any of a number of higher atomic weight elements, which has the properties of a metallic substance at room temperature.

Dissolve metal ions

A heavy metal is a member of a loosely defined subset of elements that exhibit metallic properties. It mainly includes the transition metals, some metalloids, lanthanides, and actinides. Many different definitions have been proposed—some based on density, some on atomic number or atomic weight, and some on chemical properties or toxicity. Heavy metals occur naturally in the ecosystem with large variations in concentration. In modern times, anthropogenic sources of heavy metals, i.e. pollution, have been introduced to the ecosystem. Unlike organic pollutants, heavy metals do not decay and thus pose a different kind of challenge for remediation. One of the largest problems associated with the persistence of heavy metals is the potential for bioaccumulation and biomagnification causing heavier exposure for some organisms than is present in the environment alone. In this study, we discussed a few toxic metals available in the rivers of both developing and developed countries.

Aluminum

Aluminum is a trivalent cation found in its ionic form in most kinds of animal and plant tissues and in natural waters everywhere. It is the third most prevalent element and the most abundant metal in the earth's crust, representing approximately 8% of total mineral components. Due to its reactivity, aluminum in nature is found only in combination with other elements. Urban water supplies may contain a greater concentration because water is usually treated with aluminum before becoming part of the supply. Subsequent purification processes that remove organic compounds take away many of the same compounds that bind the element in its free state, further increasing aluminum concentration. It is the potential inhibitor of some essential elements of characteristics for human health. If a significant load exceeds the body's excretory capacity, the excess is deposited in various tissues, including bone, brain, liver, heart, spleen, and muscle. This accumulation causes morbidity and mortality through various mechanisms.

Copper

Copper is an essential trace mineral that is vitally important for both physical and mental health. However, its importance for health is still largely unappreciated. Copper Toxicity is a condition that is increasingly common in this day and age, due to the widespread occurrence of copper in our food, our hot water pipes, along with the common nutritional deficiencies in Zinc, Manganese and other trace minerals that keep levels of Copper from getting too high. Toxicity of copper to aquatic life is dependent on the alkalinity of water, as copper is generally more toxic to aquatic fauna at lower alkalinities (Train 1979). Overdoses of copper may also lead to neurological complications, hypertension, and liver and kidney dysfunctions (Larocque and Rasmussen 1998; Rao et al. 2001; Krishna and Govil 2004).

Cadmium

High level of cadmium concentration may be due to discharge from industrial waste or by leaching from sewage laden landfills (Singh 2003). High cadmium level may be attributed to large use of PVC plastics, nickelcadmium batteries, insecticides, motor oil, and disposal of sludge in dumpsites (Jarup 2003). Cadmium is highly toxic, producing symptoms such as nausea, vomiting, respiratory difficulties, cramps, and loss of consciousness at high doses. Chronic exposure to metal can lead to anemia, anosmia (loss of sense of small), cardiovascular diseases, renal problems, and hypertension (Mielke et al. 1991; Robards and Worsfold 1991). Friberg (1948) reported the coexistence of renal and lung damage among workers of alkali storage plant.

Cadmium effect on cardiovascular system was explained by linking dietary cadmium to hypertension (Schroeder 1965). Shell fish liver and kidney are the foods that accumulate very high concentration cadmium up to 10 μg/g.

Lead

Lead has a number of uses but many of these are currently being phased out because of growing awareness of its toxicity and of the damage that uncontrolled dispersion in the environment has already caused. Lead is employed in accumulators, ammunitions, piping, paints, in anti-radiation screens and tin-based welding alloys. In the past, lead was added to petrol in the form of tetra-ethyl lead ($PbEt_4$) with an anti-knocking function; however, in developed countries this kind of petrol is currently being phased out for environmental reasons. Lead may also enter the environment as a by-product of mining and of the industrial processing of other metals, such as silver, gold, bismuth, etc. Lead ranks second in the list of prioritized hazardous substances issued by the U.S. ATSDR (Agency for Toxic Substances and Disease Registry) in 1999. The noxious effects of this metal have long been well known, especially as regards acute forms of poisoning. However, as for many other contaminants, the threshold level of safety has been drastically lowered recently. Until approximately 30 years ago, chronic lead poisoning was defined by blood lead levels above 80(gr/dl, while today a lead level of 30(gr/dl in blood is considered excessive and levels at or above 10(gr/dl (0.1 ppm) are considered potentially harmful, particularly in children. Lead is a cumulative poison, initiating hypertension, tiredness, irritability, anemia, behavioral changes, and impairment of intellectual functions in affected patients (Tebbutt

1983). Long-term exposure to lead or its salts (especially soluble salts or the strong oxidant PbO_2) can affect adversely to nervous system and kidneys (Mugica et al. 2002).

Chromium

Chromium salts are used in industrial processes and enter water bodies through discharge of waters. Chromium compounds are often added to cooling water for corrosion control (Nathan 1973).Chromium exists in soil as Cr^{+3} and Cr^{+6} ions is the stable form of chromium. The hexavalent form of chromium is more toxic and also known to be more mobile in the soil environment than the trivalent form (Ramesh and Anbu 1996). Chromium is an essential trace element, required for the metabolism of lipids and proteins and to maintain a normal glucose tolerance factor. High doses of chromium cause liver and kidney damage and chromate dust is carcinogenic (SEGH 2001; Mugica et al. 2002).

Mercury

There are three forms of mercury from a toxicological point of view: inorganic mercury salts; organic mercury compounds; and metallic mercury. Inorganic mercury salts are water soluble, irritate the gut, and cause severe kidney damage. Organic mercury compounds, which are fat soluble, can cross the blood brain barrier and cause neurological damage. Mercury metal poses two dangers. It can be vaporised: the vapour pressure at room temperature is about 100 times the safe amount, so poisoning can occur if mercury metal is spilled into crevices or cracks in the floorboards. Mercury easily crosses into the brain, and causes tremor, depression, and behavioural disturbances. A second danger from metallic mercury is that it is biotransformed into organic mercury, by bacteria at the bottom of lakes. This can be passed along the food chain and eventually to man. It was this process that led to the Japanese tragedy at Minimata Bay in the late 1950s when over 800 people were poisoned. It is the need to reduce mercury contamination of the environment which should encourage us to cut the usage of metallic mercury. However, much more metallic mercury is spilled as waste by the chemical industry than is dropped on the floor in the clinic. Mercury as such is volatile but in aquatic environment under the influence of bacteria and fungi, gets converted into the highly toxic methyl mercury form. These compounds are readily absorbed and concentrated by aquatic plants and animals. Tejam and Halder (1975) reported that fishes from Mumbai and Thane region had 35.56 mg of mercury per gram of fresh weight tissue. Shaw (1987), who reported the effect of chloro alkali factory effluents in Orissa on plants and animal life, has found mercury as main pollutant.

Iron

Iron is an essential nutrient that is vital to the processes by which cells generate energy. Iron is one of the major constituents of the lithosphere and comprises approximately 5% being concentrated mainly in the magmatic rocks. Iron concentration in surface water is extremely variable, reflecting difference in underlying bedrock, erosion to a lesser degree, and industrial and municipal discharges. Iron releases as corrosion products in water and soil environment (Smith 1981). Iron can also be damaging when it accumulates in the body. In fact, iron is a problem nutrient for millions of people. Some people simply don't eat enough iron containing foods to support their health optimally, while others have so much

iron that it threatens their well-being. The principle that too little or too much of a nutrient is harmful seems particularly apropos for iron.

Zinc

Zinc enters the domestic water supply from the corrosion of galvanized iron and dezincification of brass besides industrial waste (Speller 1951). Zinc belongs to a group of trace metals, which are essential for the growth of humans, animals, and plants and are potentially dangerous for the biosphere when present in high concentrations. Zinc is considered to be relatively nontoxic, particularly if taken orally. However, manifestations of overt toxicity symptoms (nausea, vomiting, epigastric pain, lethargy, and fatigue) will occur with extremely high zinc intakes. The main sources of pollution are industries and the use of liquid manure, composted materials, and agrochemicals such as fertilizers and pesticides in agriculture (Romic and Romic 2003).

Both climate change and acidification act to lower DOC concentrations. All Earth's water contains naturally occurring organic molecules, from dissolved sugars to complex contaminants. And all carbon entering surface waters, whether from soils and vegetation or anthropogenic contaminants, must pass through and interact with the DOC pool as it is respired to CO_2 and released to the atmosphere, or transformed to other forms of carbon.

Metalloids

The most significant water pollutant metalloid element is arsenic, a toxic element that has been the chemical villain of more than a few murder plots. Acute arsenic poisoning can result from the ingestion of more than about 100 mg of the element. Chronic poisoning occurs with the ingestion of small amounts of arsenic over a long period of time. There is some evidence that this element is also carcinogenic. Arsenic occurs in the Earth's crust at an average level of 2–5 ppm. The combustion of fossil fuels, particularly coal, introduces large quantities of arsenic into the environment, much of it reaching natural waters. Arsenic occurs with phosphate minerals and enters into the environment along with some phosphorus compounds. Some formerly used pesticides, particularly those from before World War II, contain highly toxic arsenic compounds. The most common of these are lead arsenate, $Pb_3(AsO_4)_2$; sodium arsenite, Na_3AsO_3; and Paris Green, $Cu_3(AsO_3)_2$. Another major source of arsenic is mine tailings. Arsenic produced as a by-product of copper, gold, and lead refining exceeds the commercial demand for arsenic, and it accumulates as waste material. Like mercury, arsenic can be converted by bacteria to more mobile and toxic methyl derivatives according to the following reactions:

$H_3AsO_4 + 2H^+ + 2e^- \rightarrow H_3AsO_3 + H_2O$

$H_3AsO_3 \rightarrow$ Methylcobalamin $CH_3AsO(OH)_2$ Methylarsinic acid

$CH_3AsO(OH)_2 \rightarrow$ Methylcobalamin $(CH_3)_2AsO(OH)$ (Dimethylarsinic acid)

$(CH_3)_2AsO(OH) + 4H^+ + 4e^- \rightarrow (CH_3)_2AsH + 2H_2O$

INORGANIC SPECIES

Inorganic pollutants that contribute acidity, alkalinity, or salinity to water. Cyanide ion, CN-, is probably the most important. Others include ammonia, carbon dioxide, hydrogensulfide, nitrite, and sulfite.

Cyanide

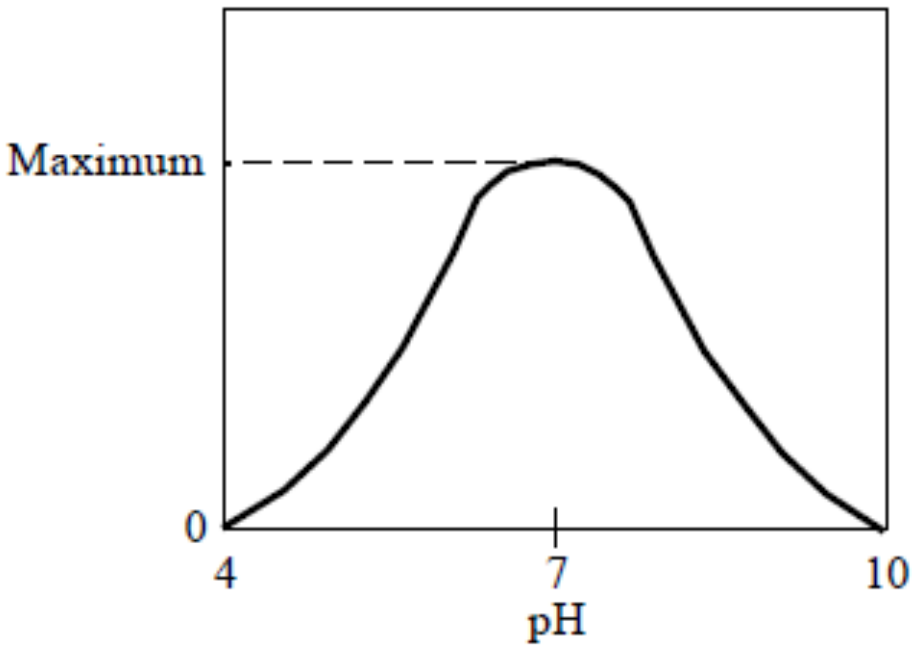
Cyanide, a deadly poisonous substance, exists in water as HCN, a weak acid. The cyanide ion has a strong affinity for many metal ions, forming relatively less-toxic ferrocyanide, $Fe(CN)_6$ with iron(II), for example. Volatile HCN is very toxic and has been used in gas chamber executions in the U.S. Cyanide is widely used in industry, especially for metal cleaning and electroplating. It is also one of the main gas and coke scrubber effluent pollutants from gas works and coke ovens. Cyanide is widely used in certain mineral-processing operations.

In August of 1995, approximately 2.7 billion liters of cyanide-contaminated water mixed with red clay from mine tailings spilled into the Essequibo River from a breached dam at a gold mining operation in the South American country of Guyana. The water contained cyanide at a level of approximately 25 parts per million, which killed all the fish in the small Omai Creek leading from the breached dam to the Essequibo River. No human fatalities or confirmed health effects were reported, however.

Table 12.3 Essential Plant Nutrients: Sources and Functions

Nutrient Source	Source	Function
Macronutrients		
Carbon (CO_2)	Atmosphere, decay	Biomass constituent
Hydrogen	Water	Biomass constituent
Oxygen	Water	Biomass constituent
Nitrogen (NO_3-)	Decay, pollutants, atmosphere	Protein constituent
Phosphorus	Decay, minerals, pollutants	DNA/RNA constituent
Potassium	Minerals, pollutants	Metabolic function
Sulfur (sulfate)	Minerals	Proteins, enzymes
Magnesium	Minerals	Metabolic function
Calcium	Minerals	Metabolic function
B, Cl, Co, Cu, Fe, Mo, Mn, Na, Si, V, Zn	Minerals, pollutants	Metabolic function and/or constituent of enzymes

ACIDITY, ALKALINITY, AND SALINITY?



OXYGEN, OXIDANTS, AND REDUCTANTS

Oxygen is a vitally important species in water. In water, oxygen is consumed rapidly by the oxidation of organic matter, $\{CH_2O\}$:

$$\{CH_2O\} + O_2 \xrightarrow{\text{Microorganisms}} CO_2 + H_2O$$

Unless the water is reaerated efficiently, as by turbulent flow in a shallow stream, it rapidly loses oxygen and will not support higher forms of aquatic life.

In addition to the microorganism-mediated oxidation of organic matter, oxygen in water may be consumed by the biooxidation of nitrogenous material,

$$NH_4^+ + 2O_2 \rightarrow 2H^+ + NO_3^- + H_2O$$

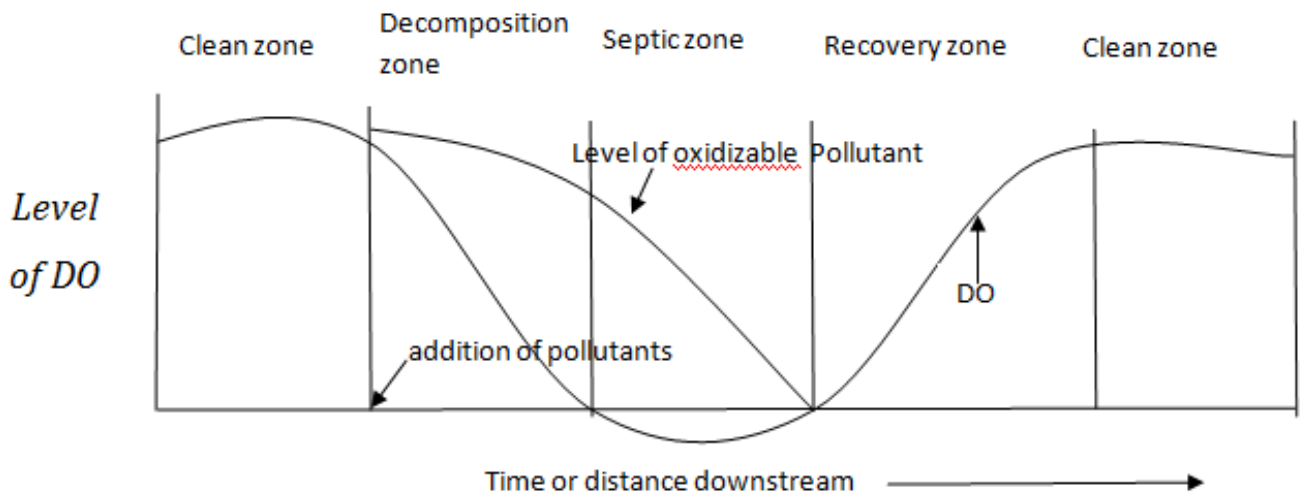
and by the chemical or biochemical oxidation of chemical reducing agents:

$$4Fe^{2+} + O_2 + 10H_2O \rightarrow 4Fe(OH)_3(s) + 8H^+$$
$$2SO_3^{2-} + O_2 \rightarrow 2SO_4^{2-}$$

All these processes contribute to the deoxygenation of water.

The degree of oxygen consumption by microbially mediated oxidation of contaminants in water is called the **biochemical oxygen demand** (or biological oxygen demand), **BOD**. This parameter is commonly measured by determining the quantity of oxygen utilized by suitable aquatic microorganisms during a five-day period. Despite the somewhat arbitrary five-day period, this test remains a respectable measure of the short-term oxygen demand exerted by a pollutant.

The addition of oxidizable pollutants to streams produces a typical oxygen sag curve Initially, a well-aerated, unpolluted stream is relatively free of oxidizable material; the oxygen level is high; and the bacterial population is relatively low. With the addition of oxidizable pollutant, the oxygen level drops because reaeration cannot keep up with oxygen consumption. In the decomposition zone, the bacterial population rises. The septic zone is characterized by a high bacterial population and very low oxygen levels. The septic zone terminates when the oxidizable pollutant is exhausted, and then the recovery zone begins. In the recovery zone, the bacterial population decreases and the dissolved oxygen level increases until the water regains its original condition.



Although BOD is a reasonably realistic measure of water quality insofar as oxygen is concerned, the test for determining it is time-consuming and cumbersome to perform. Total organic carbon (TOC), is frequently measured by catalytically oxidizing carbon in the water and measuring the CO_2 that is evolved. It has become popular because TOC is readily determined instrumentally.

ORGANIC POLLUTANTS

Constituent	Potential sources	Effects in water
Oxygen-demanding substances	Mostly organic materials, particularly human feces	Consume dissolved oxygen
Refractory organics	Industrial wastes, household products	Toxic to aquatic life
Viruses	Human wastes	Cause disease (possibly cancer); major deterrent to sewage recycle through water systems
Detergents	Household detergents	Esthetics, prevent grease and oil removal, toxic to aquatic life
Phosphates	Detergents	Algal nutrients
Grease and oil	Cooking, food processing, industrial wastes	Esthetics, harmful to some aquatic life
Salts	Human wastes, water softeners, industrial wastes	Increase water salinity
Heavy metals	Industrial wastes, chemical laboratories	Toxicity
Chelating agents	Some detergents, industrial wastes	Heavy metal ion solubilization and transport
Solids	All sources	Esthetics, harmful to aquatic life

Pesticides

RADIONUCLIDES IN THE AQUATIC ENVIRONMENT

Radionuclides are produced as fission products of heavy nuclei of such elements as uranium or plutonium. They are also produced by the reaction of neutrons with stable nuclei. Radionuclides are formed in large quantities as waste products in nuclear power generation. Their ultimate disposal is a problem that has caused much controversy regarding the widespread use of nuclear power. Artificially produced radionuclides are also widely used in industrial and medical applications, particularly as “tracers.” With so many possible sources of radionuclides, it is impossible to entirely eliminate radioactive contamination of aquatic systems. Furthermore, radionuclides may enter aquatic systems from natural sources. Therefore, the transport, reactions, and biological

Radionuclides in Water

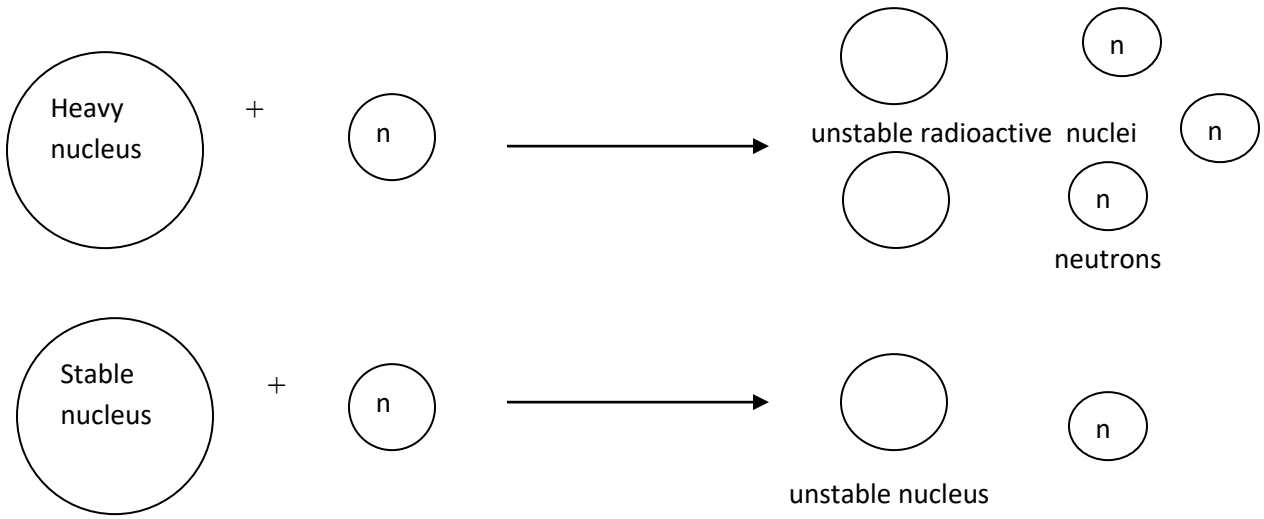
Radionuclide	Half-life	Nuclear reaction, description, source
Naturally occurring and from cosmic reactions		
Carbon-14	5730 y[1]	$^{14}N(n,p)^{14}C$,[2] thermal neutrons from cosmic or nuclear-weapon sources reacting with N_2
Silicon-32	~300 y	$^{40}Ar(p,x)^{32}Si$, nuclear spallation (splitting of the nucleus) of atmospheric argon by cosmic-ray protons
Potassium-40	~1.4×10^9 y	0.0119% of natural potassium including potassium in the body
Naturally occurring from ^{238}U series		
Radium-226	1620 y	Diffusion from sediments, atmosphere
Lead-210	21 y	$^{226}Ra \rightarrow$ 6 steps $\rightarrow {}^{210}Pb$
Thorium-230	75,200 y	$^{238}U \rightarrow$ 3 steps $\rightarrow {}^{230}Th$ produced *in situ*
Thorium-234	24 d	$^{238}U \rightarrow {}^{234}Th$ produced *in situ*
From reactor and weapons fission[3]		
Strontium-90 (28 y)	Iodine-131 (8 d)	Cesium-137 (30 y)
Barium-140 (13 d) > Zirconium-95 (65 d) >Cerium-141 (33d) > Strontium-89 (51 d) > Ruthenium-103 (40 d) > Krypton-85 (10.3 y)		
From nonfission sources		
Cobalt-60	5.25 y	From nonfission neutron reactions in reactors
Manganese-54	310 d	From nonfission neutron reactions in reactors
Iron-55	2.7 y	$^{56}Fe(n,2n)^{55}Fe$, from high-energy neutrons acting on iron in weapons hardware
Plutonium-239	24,300 y	$^{238}U(n,\gamma)^{239}Pu$, neutron capture by uranium

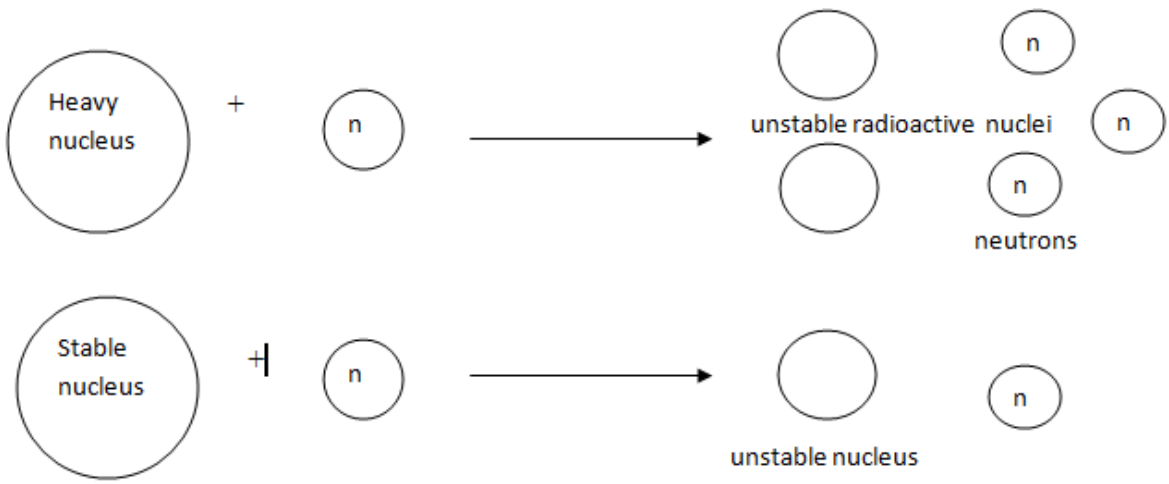
concentration of radionuclides in aquatic ecosystems are of great importance to the environmental chemist.

Radionuclides differ from other nuclei in that they emit **ionizing radiation**— alpha particles, beta particles, and gamma rays. The most massive of these emissions is the **alpha particle**, a helium nucleus of atomic mass 4, consisting of two neutrons and two protons. The symbol for an alpha particle is $_{24}\alpha$. An example of alpha production is found in the radioactive decay of uranium-238:

$$^{238}_{92}\mathrm{U} \rightarrow {}^{234}_{90}\mathrm{Th} + {}^{4}_{2}\propto$$

This transformation occurs when a uranium nucleus, atomic number 92 and atomic mass 238, loses an alpha particle, atomic number 2 and atomic mass 4, to yield a thorium nucleus, atomic number 90 and atomic mass 234.





Beta radiation consists of either highly energetic, negative electrons, which are designated $_{-1}\beta$, $_{0}$ or positive electrons, called positrons, and designated $_{-10}\beta$. A typical beta emitter, chlorine-38, can be produced by irradiating chlorine with neutrons. The chlorine-37 nucleus, natural abundance 24.5%, absorbs a neutron to produce chlorine-38 and gamma radiation:

$$^{37}_{17}\mathrm{Cl} + ^{1}_{0}\mathrm{n} \rightarrow ^{38}_{17}\mathrm{Cl} + \gamma$$

The chlorine-38 nucleus is radioactive and loses a negative **beta particle** to become an argon-38 nucleus:

$$^{38}_{17}\mathrm{Cl} \rightarrow ^{38}_{18}\mathrm{Ar} + ^{0}_{-1}\beta$$

Gamma rays are electromagnetic radiation similar to X-rays, though more energetic. Since the energy of gamma radiation is often a well-defined property of the emitting nucleus, it may be used in some cases for the qualitative and quantitative analysis of radionuclides.

The primary effect of alpha particles, beta particles, and gamma rays upon materials is the production of ions; therefore, they are called **ionizing radiation**. Due to their large size, alpha particles do not penetrate matter deeply, but cause an enormous amount of ionization along their short path of penetration. Therefore, alpha particles present little hazard outside the body, but are

very dangerous when ingested. Although beta particles are more penetrating than alpha particles, they produce much less ionization per unit path length. Gamma rays are much more penetrating than particulate radiation, but cause much less ionization. Their degree of penetration is proportional to their energy.

Half life.

The halflife is the amount of time it takes for half of the atoms in a sample to decay. The halflife for a given isotope is always the same ; it doesn't depend on how many atoms you have or on how long they've been sitting around.

Halflife of beryllium 11 is 13.81 seconds.

Manahan, Stanley E. "WATER TREATMENT"
Fundamentals of Environmental Chemistry
Boca Raton: CRC Press LLC,2001

13 WATER TREATMENT

13.1 WATER TREATMENT AND WATER USE

The treatment of water can be divided into three major categories:

- Purification for domestic use
- Treatment for specialized industrial applications
- Treatment of wastewater to make it acceptable for release or reuse

The type and degree of treatment are strongly dependent upon the source and intended use of the water. Water for domestic use must be thoroughly disinfected to eliminate disease-causing microorganisms, but may contain appreciable levels of dissolved calcium and magnesium (hardness). Water to be used in boilers may contain bacteria but must be quite soft to prevent scale formation. Wastewater being discharged into a large river may require less rigorous treatment than water to be reused in an arid region. As world demand for limited water resources grows, more sophisticated and extensive means will have to be employed to treat water.

Most physical and chemical processes used to treat water involve similar phenomena, regardless of their application to the three main categories of water treatment listed above. Therefore, after introductions to water treatment for municipal use, industrial use, and disposal, each major kind of treatment process is discussed as it applies to all of these applications.

13.2 MUNICIPAL WATER TREATMENT

The modern water treatment plant is often called upon to perform wonders with the water fed to it. The clear, safe, even tasteful water that comes from a faucet may have started as a murky liquid pumped from a polluted river laden with mud and swarming with bacteria. Or, its source may have been well water, much too hard for domestic use and containing high levels of stain-producing dissolved iron and man-

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ganese. The water treatment plant operator's job is to make sure that the water plant product presents no hazards to the consumer.

A schematic diagram of a typical municipal water treatment plant is shown in Figure 13.1. This particular facility treats water containing excessive hardness and a high level of iron. The raw water taken from wells first goes to an aerator. Contact of the water with air removes volatile solutes such as hydrogen sulfide, carbon dioxide, methane, and volatile odorous substances such as methane thiol (CH_3SH) and bacterial metabolites. Contact with oxygen also aids iron removal by oxidizing soluble iron(II) to insoluble iron(III). The addition of lime as CaO or $Ca(OH)_2$ after aeration raises the pH and results in the formation of precipitates containing the hardness ions Ca^{2+} and Mg^{2+}. These precipitates settle from the water in a primary basin. Much of the solid material remains in suspension and requires the addition of coagulants (such as iron(III) and aluminum sulfates, which form gelatinous metal hydroxides) to settle the colloidal particles. Activated silica or synthetic polyelectrolytes may also be added to stimulate coagulation or flocculation. The settling occurs in a secondary basin after the addition of carbon dioxide to lower the pH. Sludge from both the primary and secondary basins is pumped to a sludge lagoon. The water is finally chlorinated, filtered, and pumped to the city water mains.

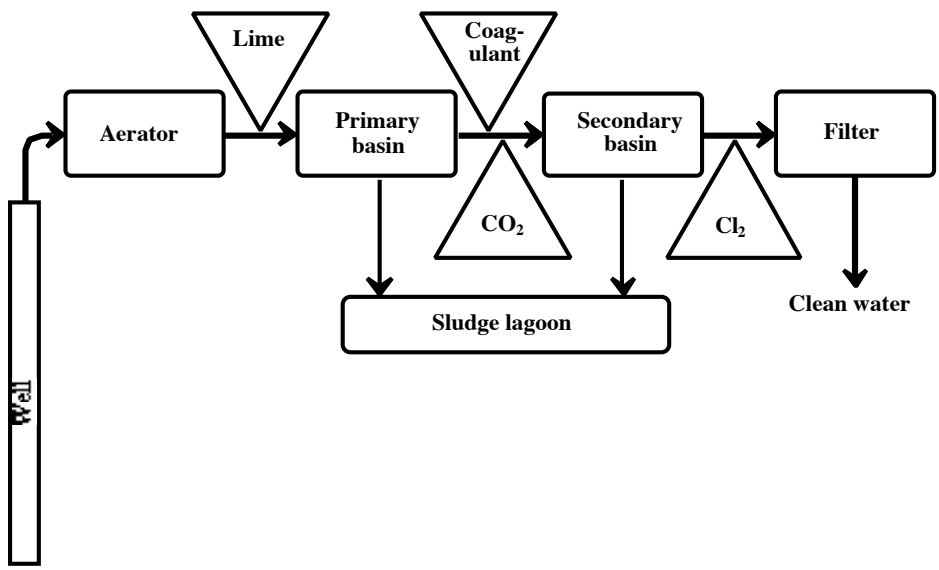

Figure 13.1 Schematic of a municipal water treatment plant.

13.3 TREATMENT OF WATER FOR INDUSTRIAL USE

Water is widely used in various process applications in industry. Other major industrial uses are boiler feedwater and cooling water. The kind and degree of treatment of water in these applications depends upon the end use. As examples, although cooling water may require only minimal treatment, removal of corrosive substances and scale-forming solutes is essential for boiler feedwater, and water used in food processing must be free of pathogens and toxic substances. Improper treatment of water for industrial use can cause problems such as corrosion, scale formation,

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reduced heat transfer in heat exchangers, reduced water flow, and product contamination. These effects may cause reduced equipment performance or equipment failure, increased energy costs due to inefficient heat utilization or cooling, increased costs for pumping water, and product deterioration. Obviously, the effective treatment of water at minimum cost for industrial use is a very important area of water treatment.

Numerous factors must be taken into consideration in designing and operating an industrial water treatment facility. These include the following:

- Water requirement
- Quantity and quality of available water sources
- Sequential use of water (successive uses for applications requiring progressively lower water quality)
- Water recycle
- Discharge standards

The various specific processes employed to treat water for industrial use are discussed in later sections of this chapter. **External treatment**, usually applied to the plant's entire water supply, uses processes such as aeration, filtration, and clarification to remove material that might cause problems from water. Such substances include suspended or dissolved solids, hardness, and dissolved gases. Following this basic treatment, the water can be divided into different streams, some to be used without further treatment, and the rest to be treated for specific applications.

Internal treatment is designed to modify the properties of water for specific applications. Examples of internal treatment include the following:

- Reaction of dissolved oxygen with hydrazine or sulfite
- Addition of chelating agents to react with dissolved Ca^{2+} and prevent formation of calcium deposits
- Addition of precipitants, such as phosphate used for calcium removal
- Treatment with dispersants to inhibit scale
- Addition of inhibitors to prevent corrosion
- Adjustment of pH
- Disinfection for food processing uses or to prevent bacterial growth in cooling water

13.4 SEWAGE TREATMENT

Typical municipal sewage contains oxygen-demanding materials, sediments, grease, oil, scum, pathogenic bacteria, viruses, salts, algal nutrients, pesticides, refractory organic compounds, heavy metals, and an astonishing variety of flotsam ranging from children's socks to sponges. It is the job of the waste-treatment plant to remove as much of this material as possible.

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Several characteristics are used to describe sewage. These include turbidity (international turbidity units), suspended solids (ppm), total dissolved solids (ppm), acidity (H^+ ion concentration or pH), and dissolved oxygen (in ppm O_2). Biochemical oxygen demand is used as a measure of oxygen-demanding substances.

Current processes for the treatment of wastewater can be divided into three main categories of primary treatment, secondary treatment, and tertiary treatment, each of which is discussed separately. Also discussed are total wastewater treatment systems, based largely upon physical and chemical processes

Waste from a municipal water system is normally treated in a **publicly owned treatment works**, **POTW**. In the United States these systems are allowed to discharge only effluents that have attained a certain level of treatment, as mandated by Federal law.

Primary Waste Treatment

Primary treatment of wastewater consists of the removal of insoluble matter such as grit, grease, and scum from water. The first step in primary treatment normally is screening. Screening removes or reduces the size of trash and large solids that get into the sewage system. These solids are collected on screens and scraped off for subsequent disposal. Most screens are cleaned with power rakes. Comminuting devices shred and grind solids in the sewage. Particle size can be reduced to the extent that the particles can be returned to the sewage flow.

Grit in wastewater consists of such materials as sand and coffee grounds that do not biodegrade well and generally have a high settling velocity. **Grit removal** is practiced to prevent its accumulation in other parts of the treatment system, to reduce clogging of pipes and other parts, and to protect moving parts from abrasion and wear. Grit normally is allowed to settle in a tank under conditions of low flow velocity, and it is then scraped mechanically from the bottom of the tank.

Primary sedimentation removes both settleable and floatable solids. During primary sedimentation there is a tendency for flocculent particles to aggregate for better settling, a process that may be aided by the addition of chemicals. The material that floats in the primary settling basin is known collectively as grease. In addition to fatty substances, the grease consists of oils, waxes, free fatty acids, and insoluble soaps containing calcium and magnesium. Normally, some of the grease settles with the sludge and some floats to the surface, where it can be removed by a skimming device.

Secondary Waste Treatment by Biological Processes

The most obvious harmful effect of biodegradable organic matter in wastewater is BOD, consisting of a biochemical oxygen demand for dissolved oxygen by microorganism-mediated degradation of the organic matter. **Secondary wastewater treatment** is designed to remove BOD, usually by taking advantage of the same kind of biological processes that would otherwise consume oxygen in water receiving the wastewater. Secondary treatment by biological processes takes many forms but consists basically of the action of microorganisms provided with added oxygen degrading organic material in solution or in suspension until the BOD of the

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waste has been reduced to acceptable levels. The waste is oxidized biologically under conditions controlled for optimum bacterial growth, and at a site where this growth does not influence the environment.

One of the simplest biological waste treatment processes is the **trickling filter** (Fig. 13.2) in which wastewater is sprayed over rocks or other solid support material covered with microorganisms. The structure of the trickling filter is such that contact of the wastewater with air is allowed and degradation of organic matter occurs by the action of the microorganisms.

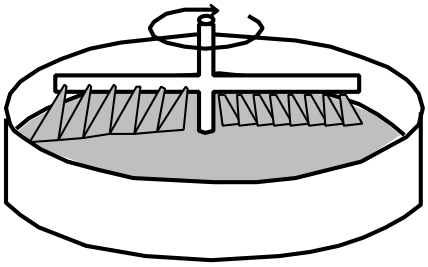

Figure 13.2 Trickling filter for secondary waste treatment.

Rotating biological reactors (**contactors**), another type of treatment system, consist of groups of large plastic discs mounted close together on a rotating shaft. The device is positioned such that at any particular instant half of each disc is immersed in wastewater and half exposed to air. The shaft rotates constantly, so that the submerged portion of the discs is always changing. The discs, usually made of high-density polyethylene or polystyrene, accumulate thin layers of attached biomass, which degrades organic matter in the sewage. Oxygen is absorbed by the biomass and by the layer of wastewater adhering to it during the time that the biomass is exposed to air.

Both trickling filters and rotating biological reactors are examples of fixed-film biological (FFB) or attached growth processes. The greatest advantage of these processes is their low energy consumption. The energy consumption is minimal because it is not necessary to pump air or oxygen into the water, as is the case with the popular activated sludge process described below. The trickling filter has long been a standard means of wastewater treatment, and a number of wastewater treatment plants use trickling filters at present.

The **activated sludge process**, Figure 13.3, is probably the most versatile and effective of all wastewater treatment processes. Microorganisms in the aeration tank convert organic material in wastewater to microbial biomass and CO_2. Organic nitrogen is converted to ammonium ion or nitrate. Organic phosphorus is converted to orthophosphate. The microbial cell matter formed as part of the waste degradation processes is normally kept in the aeration tank until the microorganisms are past the log phase of growth (Section 6.3), at which point the cells flocculate relatively well to form settleable solids. These solids settle out in a settler and a fraction of them is discarded. Part of the solids, the return sludge, is recycled to the head of the aeration tank and comes into contact with fresh sewage. The combination of a high concentration of "hungry" cells in the return sludge and a rich food source in the influent sewage provides optimum conditions for the rapid degradation of organic matter.

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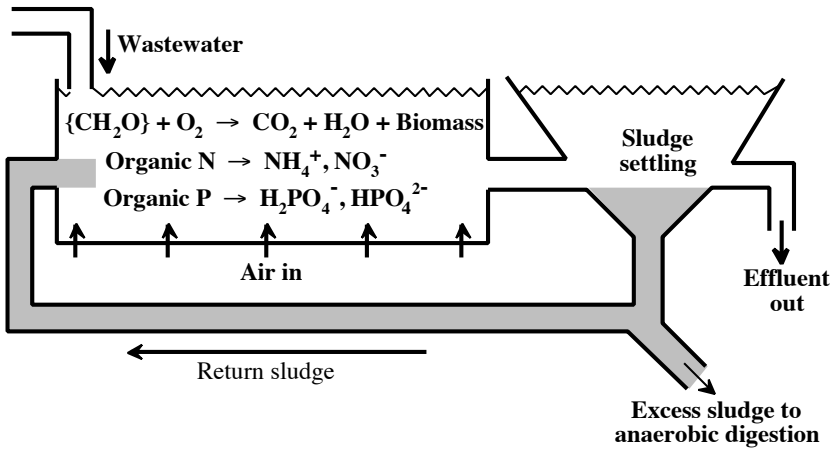

Figure 13.3 Activated sludge process.

The degradation of organic matter that occurs in an activated sludge facility also occurs in streams and other aquatic environments. However, in general, when a degradable waste is put into a stream, it encounters only a relatively small population of microorganisms capable of carrying out the degradation process. Thus, several days may be required for the buildup of a sufficient population of organisms to degrade the waste. In the activated sludge process, continual recycling of active organisms provides the optimum conditions for waste degradation, and a waste may be degraded within the very few hours that it is present in the aeration tank.

The activated sludge process provides two pathways for the removal of BOD, as illustrated schematically in Figure 13.4. BOD can be removed by (1) oxidation of organic matter to provide energy for the metabolic processes of the microorganisms, and (2) synthesis, incorporation of the organic matter into cell mass. In the first pathway, carbon is removed in the gaseous form as CO_2. The second pathway provides for removal of carbon as a solid in biomass. That portion of the carbon converted to CO_2 is vented to the atmosphere and does not present a disposal problem. The disposal of waste sludge, however, is a problem, primarily because it is only about 1% solids and contains many undesirable components. Normally, partial water removal is accomplished by drying on sand filters, vacuum filtration, or centrifugation. The dewatered sludge can be incinerated or used as landfill. To a certain extent, sewage

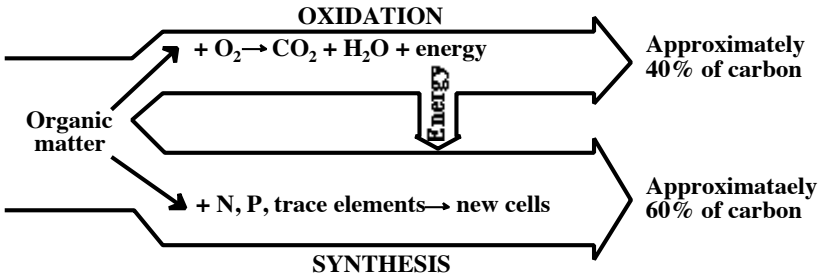

Figure 13.4 Pathways for the removal of BOD in biological wastewater treatment.

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sludge can be digested in the absence of oxygen by methane-producing anaerobic bacteria to produce methane and carbon dioxide

$$2\{CH_2O\} \rightarrow CH_4 + CO_2 \tag{13.4.1}$$

reducing both volatile-matter content and sludge volume by about 60%. A carefully designed plant can produce enough methane to provide for all of its power needs.

One of the most desirable means of sludge disposal is to use it to fertilize and condition soil. However, care has to be taken that excessive levels of heavy metals are not applied to the soil as sludge contaminants. Problems with various kinds of sludges resulting from water treatment are discussed further in Section 13.10.

Activated sludge wastewater treatment is the most common example of an aerobic suspended culture process. Many factors must be considered in the design and operation of an activated sludge wastewater treatment system.[1] These include parameters involved with the process modeling and kinetics. The microbiology of the system must be considered. In addition to BOD removal, phosphorus and nitrogen removal must also be taken into account. Oxygen transfer and solids separation are important. Industrial wastes and the fates and effects of industrial chemicals (xenobiotics) must also be considered.

Nitrification (the microbially mediated conversion of ammonium nitrogen to nitrate; see Section 6.11) is a significant process that occurs during biological waste treatment. Ammonium ion is normally the first inorganic nitrogen species produced in the biodegradation of nitrogenous organic compounds. It is oxidized, under the appropriate conditions, first to nitrite by *Nitrosomonas* bacteria, then to nitrate by *Nitrobacter*:

$$2NH_4^+ + 3O_2 \rightarrow 4H^+ + 2NO_2^- + 2H_2O \tag{13.4.2}$$

$$2NO_2^- + O_2 \rightarrow 2NO_3^- \tag{13.4.3}$$

These reactions occur in the aeration tank of the activated sludge plant and are favored in general by long retention times, low organic loadings, large amounts of suspended solids, and high temperatures. Nitrification can reduce sludge settling efficiency because the denitrification reaction

$$4NO_3^- + 5\{CH_2O\} + 4H^+ \rightarrow 2N_2(g) + 5CO_2(g) + 7H_2O \tag{13.4.4}$$

occurring in the oxygen-deficient settler causes bubbles of N_2 to form on the sludge floc (aggregated sludge particles), making it so buoyant that it floats to the top. This prevents settling of the sludge and increases the organic load in the receiving waters. Under the appropriate conditions, however, advantage can be taken of this phenomenon to remove nutrient nitrogen from water (see Section 13.9).

Tertiary Waste Treatment

Unpleasant as the thought may be, many people drink used water—water that has been discharged from a municipal sewage treatment plant or from some

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industrial process. This raises serious questions about the presence of pathogenic organisms or toxic substances in such water. Because of high population density and heavy industrial development, the problem is especially acute in Europe, where some municipalities process 50% or more of their water from "used" sources. Obviously, there is a great need to treat wastewater in a manner that makes it amenable to reuse. This requires treatment beyond the secondary processes.

Tertiary waste treatment (sometimes called **advanced waste treatment**) is a term used to describe a variety of processes performed on the effluent from secondary waste treatment.[2] The contaminants removed by tertiary waste treatment fall into the general categories of (1) suspended solids, (2) dissolved organic compounds, and (3) dissolved inorganic materials, including the important class of algal nutrients. Each of these categories presents its own problems with regard to water quality. Suspended solids are primarily responsible for residual biological oxygen demand in secondary sewage effluent waters. The dissolved organics are the most hazardous from the standpoint of potential toxicity. The major problem with dissolved inorganic materials is that presented by algal nutrients, primarily nitrates and phosphates. In addition, potentially hazardous toxic metals may be found among the dissolved inorganics.

In addition to these chemical contaminants, secondary sewage effluent often contains a number of disease-causing microorganisms, requiring disinfection in cases where humans may later come into contact with the water. Among the bacteria that may be found in secondary sewage effluent are organisms causing tuberculosis, dysenteric bacteria (*Bacillus dysenteriae*, *Shigella dysenteriae*, *Shigella paradysenteriae*, *Proteus vulgaris*), cholera bacteria (*Vibrio cholerae*), bacteria causing mud fever (*Leptospira icterohemorrhagiae*), and bacteria causing typhoid fever (*Salmonella typhosa*, *Salmonella paratyphi*). In addition, viruses causing diarrhea, eye infections, infectious hepatitis, and polio may be encountered. Ingestion of sewage still causes disease, even in more-developed nations.

Physical-Chemical Treatment of Municipal Wastewater

Complete physical-chemical wastewater treatment systems offer both advantages and disadvantages relative to biological treatment systems. The capital costs of physical-chemical facilities can be less than those of biological treatment facilities, and they usually require less land. They are better able to cope with toxic materials and overloads. However, they require careful operator control and consume relatively large amounts of energy.

Basically, a physical-chemical treatment process involves:

- Removal of scum and solid objects
- Clarification, generally with addition of a coagulant, and frequently with the addition of other chemicals (such as lime for phosphorus removal)
- Filtration to remove filterable solids
- Activated carbon adsorption
- Disinfection

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The basic steps of a complete physical-chemical wastewater treatment facility are shown in Figure 13.5.

During the early 1970s, it appeared likely that physical-chemical treatment would largely replace biological treatment. However, higher chemical and energy costs since then have slowed the development of physical-chemical facilities.

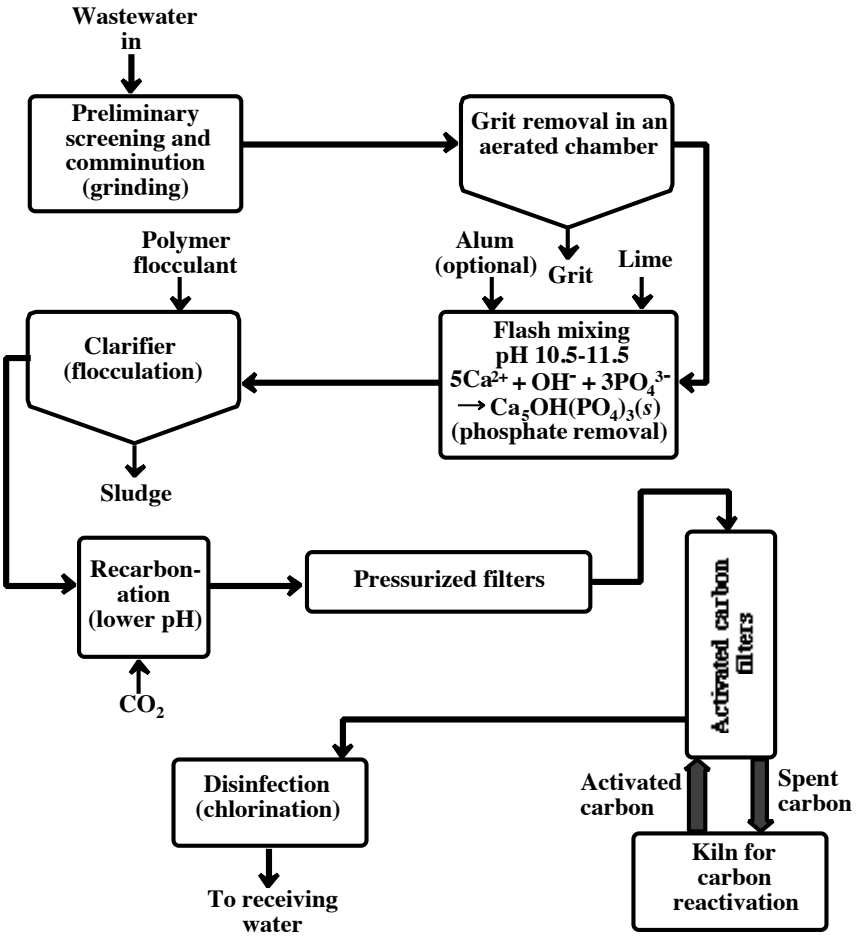

Figure 13.5 Major components of a complete physical-chemical treatment facility for municipal wastewater.

13.5 INDUSTRIAL WASTEWATER TREATMENT

Before treatment, industrial wastewater should be characterized fully and the biodegradability of wastewater constituents determined. The options available for the treatment of wastewater are summarized briefly in this section and discussed in greater detail in later sections.

One of two major ways of removing organic wastes is biological treatment by an activated sludge or related process (see Section 13.4 and Figure 13.3). It may be necessary to acclimate microorganisms to the degradation of constituents that are not

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normally biodegradable. Consideration needs to be given to possible hazards of biotreatment sludges, such as those containing excessive levels of heavy metal ions. The other major process for the removal of organics from wastewater is sorption by activated carbon (see Section 13.8), usually in columns of granular activated carbon. Activated carbon and biological treatment can be combined with the use of powdered activated carbon in the activated sludge process. The powdered activated carbon sorbs some constituents that may be toxic to microorganisms and is collected with the sludge. A major consideration with the use of activated carbon to treat wastewater is the hazard that spent activated carbon can present from the wastes it retains. These hazards may include those of toxicity or reactivity, such as those posed by wastes from the manufacture of explosives sorbed to activated carbon. Regeneration of the carbon is expensive and can be hazardous in some cases.

Wastewater can be treated by a variety of chemical processes, including acid/base neutralization, precipitation, and oxidation/reduction. Sometimes these steps must precede biological treatment; for example, acidic or alkaline wastewater must be neutralized for microorganisms to thrive in it. Cyanide in the wastewater can be oxidized with chlorine and organics with ozone, hydrogen peroxide promoted with ultraviolet radiation, or dissolved oxygen at high temperatures and pressures. Heavy metals can be precipitated with base, carbonate, or sulfide.

Wastewater can be treated by several physical processes. In some cases, simple density separation and sedimentation can be used to remove water-immiscible liquids and solids. Filtration is frequently required, and flotation by gas bubbles generated on particle surfaces may be useful. Wastewater solutes can be concentrated by evaporation, distillation, and membrane processes, including reverse osmosis, hyperfiltration, and ultrafiltration. Organic constituents can be removed by solvent extraction, air stripping, or steam stripping.

Synthetic resins are useful for removing some pollutant solutes from wastewater. Organophilic resins have proven useful for the removal of alcohols; aldehydes; ketones; hydrocarbons; chlorinated alkanes, alkenes, and aryl compounds; esters, including phthalate esters; and pesticides. Cation exchange resins are effective for the removal of heavy metals.

13.6 REMOVAL OF SOLIDS

Relatively large solid particles are removed from water by simple **settling** and **filtration**. A special type of filtration procedure known as **microstraining** is especially effective in the removal of the very small particles. These filters are woven from stainless steel wire so fine that it is barely visible. This enables preparation of filters with openings only 60–70 μm across. These openings may be reduced to 5–15 μm by partial clogging with small particles, such as bacterial cells. The cost of this treatment is likely to be substantially lower than the costs of competing processes. High flow rates at low back pressures are normally achieved.

The removal of colloidal solids from water usually requires **coagulation**. Salts of aluminum and iron are the coagulants most often used in water treatment. Of these, alum or filter alum is most commonly used. This substance is a hydrated aluminum sulfate, $Al_2(SO_4)_3 \cdot 18H_2O$. When this salt is added to water, the aluminum ion hydrolyzes by reactions that consume alkalinity in the water, such as:

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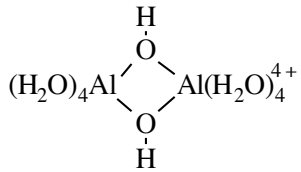
$$Al(H_2O)_6^{3+} + 3HCO_3^- \rightarrow Al(OH)_3(s) + 3CO_2 + 6H_2O \qquad (13.6.1)$$

The gelatinous hydroxide thus formed carries suspended material with it as it settles. Furthermore, it is likely that positively charged hydroxyl-bridged dimers such as



and higher polymers are formed that interact specifically with colloidal particles, bringing about coagulation. Sodium silicate partially neutralized by acid aids coagulation, particularly when used with alum. Metal ions in coagulants also react with virus proteins and destroy viruses in water.

Anhydrous iron(III) sulfate added to water forms iron(III) hydroxide in a reaction analogous to Reaction 13.6.1. An advantage of iron(III) sulfate is that it works over a wide pH range of approximately 4–11. Hydrated iron(II) sulfate, or copperas, $FeSO_4 \cdot 7H_2O$, is also commonly used as a coagulant. It forms a gelatinous precipitate of hydrated iron(III) oxide; in order to function, it must be oxidized to iron(III) by dissolved oxygen in the water at a pH higher than 13.5, or by chlorine, which can oxidize iron(II) at lower pH values.

Natural and synthetic polyelectrolytes are used in flocculating particles. Among the natural compounds so used are starch and cellulose derivatives, proteinaceous materials, and gums composed of polysaccharides. More recently, selected synthetic polymers, including neutral polymers and both anionic and cationic polyelectrolytes that are effective flocculants have come into use.

Coagulation-filtration is a much more effective procedure than filtration alone for the removal of suspended material from water. As the term implies, the process consists of the addition of coagulants that aggregate the particles into larger-size particles, followed by filtration. Either alum or lime, often with added polyelectrolytes, is most commonly employed for coagulation .

The filtration step of coagulation-filtration is usually performed on a medium such as sand or anthracite coal. Often, to reduce clogging, several media with progressively smaller interstitial spaces are used. One example is the **rapid sand filter**, which consists of a layer of sand supported by layers of gravel particles, the particles becoming progressively larger with increasing depth. The substance that actually filters the water is coagulated material that collects in the sand. As more material is removed, the buildup of coagulated material eventually clogs the filter and must be removed by back-flushing.

An important class of solids that must be removed from wastewater consists of suspended solids in secondary sewage effluent that arise primarily from sludge that was not removed in the settling process. These solids account for a large part of the BOD in the effluent and may interfere with other aspects of tertiary waste treatment, such as by clogging membranes in reverse osmosis water treatment processes. The quantity of material involved may be rather high. Processes designed to remove suspended solids often will remove 10–20 mg/L of organic material from secondary sewage effluent. In addition, a small amount of the inorganic material is removed.

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13.7 REMOVAL OF CALCIUM AND OTHER METALS

Calcium and magnesium salts, which generally are present in water as bicarbonates or sulfates, cause water hardness. One of the most common manifestations of water hardness is the insoluble "curd" formed by the reaction of soap with calcium or magnesium ions. The formation of these insoluble soap salts is discussed in Section 12.10. Although ions that cause water hardness do not form insoluble products with detergents, they do adversely affect detergent performance. Therefore, calcium and magnesium must be complexed or removed from water for detergents to function properly.

Another problem caused by hard water is the formation of mineral deposits. For example, when water containing calcium and bicarbonate ions is heated, insoluble calcium carbonate is formed:

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3(s) + CO_2(g) + H_2O \qquad (13.7.1)$$

This product coats the surfaces of hot water systems, clogging pipes and reducing heating efficiency. Dissolved salts such as calcium and magnesium bicarbonates and sulfates can be especially damaging in boiler feedwater. Clearly, the removal of water hardness is essential for many uses of water.

Several processes are used for softening water. On a large scale, such as in community water-softening operations, the lime-soda process is used. This process involves the treatment of water with lime, $Ca(OH)_2$, and soda ash, Na_2CO_3. Calcium is precipitated as $CaCO_3$ and magnesium as $Mg(OH)_2$. When the calcium is present primarily as "bicarbonate hardness," it can be removed by the addition of $Ca(OH)_2$ alone:

$$Ca^{2+} + 2HCO_3^- + Ca(OH)_2 \rightarrow 2CaCO_3(s) + 2H_2O \qquad (13.7.2)$$

When bicarbonate ion is not present at substantial levels, a source of CO_3^{2-} must be provided at a high enough pH to prevent conversion of most of the carbonate to bicarbonate. These conditions are obtained by the addition of Na_2CO_3. For example, calcium present as the chloride can be removed from water by the addition of soda ash:

$$Ca^{2+} + 2Cl^- + 2Na^+ + CO_3^{2-} \rightarrow CaCO_3(s) + 2Cl^- + 2Na^+ \qquad (13.7.3)$$

Note that the removal of bicarbonate hardness results in a net removal of soluble salts from solution, whereas removal of nonbicarbonate hardness involves the addition of at least as many equivalents of ionic material as are removed.

The precipitation of magnesium as the hydroxide requires a higher pH than the precipitation of calcium as the carbonate:

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2(s) \qquad (13.7.4)$$

The high pH required can be provided by the basic carbonate ion from soda ash:

$$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^- \qquad (13.7.5)$$

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Some large-scale lime-soda softening plants make use of the precipitated calcium carbonate product as a source of additional lime. The calcium carbonate is first heated to at least 825°C to produce quicklime, CaO:

$$CaCO_3 + \text{heat} \rightarrow CaO + CO_2(g) \tag{13.7.6}$$

The quicklime is then slaked with water to produce calcium hydroxide:

$$CaO + H_2O \rightarrow Ca(OH)_2 \tag{13.7.7}$$

The water softened by lime-soda softening plants usually suffers from two defects. First, because of super-saturation effects, some $CaCO_3$ and $Mg(OH)_2$ usually remain in solution. If not removed, these compounds will precipitate at a later time and cause harmful deposits or undesirable cloudiness in water. The second problem results from the use of highly basic sodium carbonate, which gives the product water an excessively high pH, up to pH 11. To overcome these problems, the water is recarbonated by bubbling CO_2 into it. The carbon dioxide converts the slightly soluble calcium carbonate and magnesium hydroxide to their soluble bicarbonate forms:

$$CaCO_3(s) + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^- \tag{13.7.8}$$

$$Mg(OH)_2(s) + 2CO_2 \rightarrow Mg^{2+} + 2HCO_3^- \tag{13.7.9}$$

The CO_2 also neutralizes excess hydroxide ion:

$$OH^- + CO_2 \rightarrow HCO_3^- \tag{13.7.10}$$

The pH generally is brought within the range 7.5-8.5 by recarbonation, commonly using CO_2 from the combustion of carbonaceous fuel. Scrubbed stack gas from a power plant frequently is utilized. Water adjusted to a pH, alkalinity, and Ca^{2+} concentration very close to $CaCO_3$ saturation is labeled *chemically stabilized*. It neither precipitates $CaCO_3$ in water mains, which can clog the pipes, nor dissolves protective $CaCO_3$ coatings from the pipe surfaces. Water with Ca^{2+} concentration much below $CaCO_3$ saturation is called an *aggressive* water.

Calcium can be removed from water very efficiently by the addition of orthophosphate:

$$5Ca^{2+} + 3PO_4^{3-} + OH^- \rightarrow Ca_5OH(PO_4)_3(s) \tag{13.7.11}$$

It should be pointed out that the chemical formation of a slightly soluble product for the removal of undesired solutes such as hardness ions, phosphate, iron, and manganese must be followed by sedimentation in a suitable apparatus. Frequently, coagulants must be added, and filtration employed for complete removal of these sediments.

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Water can be purified by ion exchange, the reversible transfer of ions between aquatic solution and a solid material capable of bonding ions. The removal of NaCl from solution by two ion exchange reactions is a good illustration of this process. First, the water is passed over a solid cation exchanger in the hydrogen form, represented by $H^{+-}\{Cat(s)\}$:

$$H^{+-}\{Cat(s)\} + Na^+ + Cl^- \rightarrow Na^{+-}\{Cat(s)\} + H^+ + Cl^- \quad (13.7.12)$$

Next, the water is passed over an anion exchanger in the hydroxide ion form, represented by $OH^{-+}\{An(s\}$:

$$OH^{-+}\{An(s)\} + H^+ + Cl^- \rightarrow Cl^{-+}\{An(s)\} + H_2O \quad (13.7.13)$$

Thus, the cations in solution are replaced by hydrogen ion and the anions by hydroxide ion, yielding water as the product.

The softening of water by ion exchange does not require the removal of all ionic solutes, just those cations responsible for water hardness. Generally, therefore, only a cation exchanger is necessary. Furthermore, the sodium rather than the hydrogen form of the cation exchanger is used, and the divalent cations are replaced by sodium ion. Sodium ion at low concentrations is harmless in water to be used for most purposes, and sodium chloride is a cheap and convenient substance with which to recharge the cation exchangers.

A number of materials have ion-exchanging properties. Among the minerals especially noted for their ion-exchange properties are the aluminum silicate minerals, or **zeolites**. An example of a zeolite that has been used commercially in water softening is glauconite, $K_2(MgFe)_2Al_6(Si_4O_{10})_3(OH)_{12}$. Synthetic zeolites have been prepared by drying and crushing the white gel produced by mixing solutions of sodium silicate and sodium aluminate.

The discovery in the mid-1930s of synthetic ion exchange resins composed of organic polymers with attached functional groups marked the beginning of modern ion-exchange technology. Structural formulas of typical synthetic ion exchangers are shown in Figures 13.6 and 13.7. The cation exchanger shown in Figure 13.6 is called a **strongly acidic cation exchanger** because the parent $-SO_3^-H^+$ group is a strong acid. When the functional group binding the cation is the $-CO_2^-$ group, the exchange resin is called a **weakly acidic cation exchanger**, because the $-CO_2H$ group is a weak acid. Figure 13.7 shows a **strongly basic anion exchanger** in which the functional group is a quaternary ammonium group, $-N^+(CH_3)_3$. In the hydroxide form, $-N^+(CH_3)_3OH^-$, the hydroxide ion is readily released, so the exchanger is classified as **strongly basic**.

The water-softening capability of a cation exchanger is shown in Figure 13.6, where sodium ion on the exchanger is exchanged for calcium ion in solution. The same reaction occurs with magnesium ion. Water softening by cation exchange is widely used, effective, and economical. However, it does cause some deterioration of wastewater quality arising from the contamination of wastewater by sodium chloride. Such contamination results from the periodic need to regenerate a water softener with sodium chloride in order to displace calcium and magnesium ions from the resin and replace these hardness ions with sodium ions:

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$$Ca^{2+}\,{}^{-}\{Cat(s)\}_2 + 2Na^+ + 2Cl^- \rightarrow 2Na^+\,{}^{-}\{Cat(s)\} + Ca^{2+} + 2Cl^- \qquad (13.7.14)$$

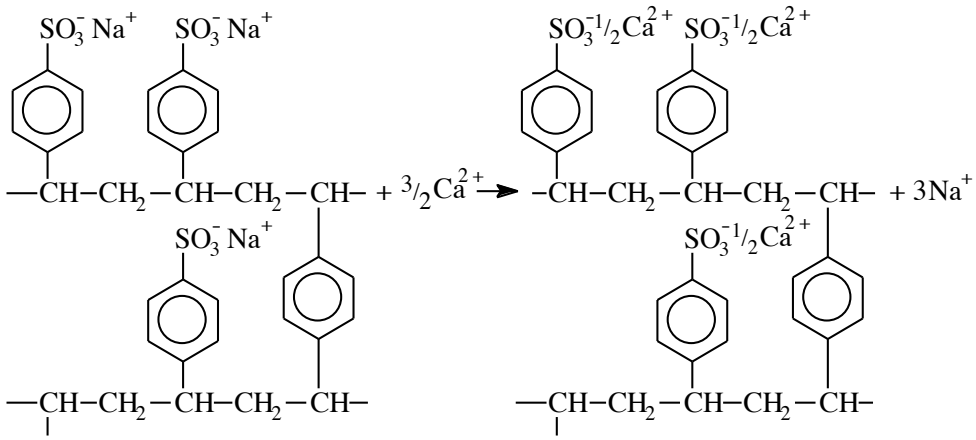

Figure 13.6. Strongly acidic cation exchanger. Sodium exchange for calcium in water is shown.

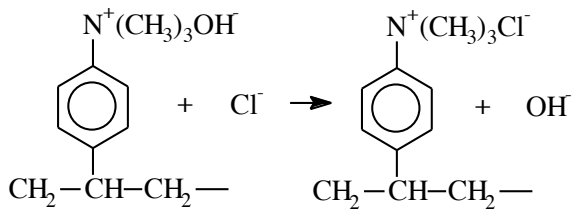

Figure 13.7 Strongly basic anion exchanger. Chloride exchange for hydroxide ion is shown.

During the regeneration process, a large excess of sodium chloride must be used — several pounds for a home water softener. Appreciable amounts of dissolved sodium chloride can be introduced into sewage by this route.

Strongly acidic cation exchangers are used for the removal of water hardness. Weakly acidic cation exchangers having the $-CO_2H$ group as a functional group are useful for removing alkalinity. Alkalinity generally is manifested by bicarbonate ion, a species that is a sufficiently strong base to neutralize the acid of a weak acid cation exchanger:

$$2R\text{-}CO_2H + Ca^{2+} + 2HCO_3^- \rightarrow [R\text{-}CO_2^-]_2Ca^{2+} + 2H_2O + 2CO_2 \qquad (13.7.15)$$

However, weak bases such as sulfate ion or chloride ion are not strong enough to remove hydrogen ion from the carboxylic acid exchanger. An additional advantage of these exchangers is that they can be regenerated almost stoichiometrically with dilute strong acids, thus avoiding the potential pollution problem caused by the use of excess sodium chloride to regenerate strongly acidic cation changers.

Chelation or, as it is sometimes known, *sequestration*, is an effective method of softening water without actually having to remove calcium and magnesium from solution. A complexing agent is added that greatly reduces the concentrations of free hydrated cations, as shown by some of the example calculations in Chapter 3. For example, chelating calcium ion with excess EDTA anion (Y^{4-}),

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$$Ca^{2+} + Y^{4-} \rightarrow CaY^{2-} \quad (13.7.16)$$

reduces the concentration of hydrated calcium ion, preventing the precipitation of calcium carbonate:

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3(s) \quad (13.7.17)$$

Polyphosphate salts, EDTA, and NTA (see Chapter 3) are chelating agents commonly used for water softening. Polysilicates are used to complex iron.

Removal of Iron and Manganese

Soluble iron and manganese are found in many groundwaters because of reducing conditions that favor the soluble +2 oxidation state of these metals (see Chapter 4). Iron is the more commonly encountered of the two metals. In groundwater, the level of iron seldom exceeds 10 mg/L, and that of manganese is rarely higher than 2 mg/L. The basic method for removing both of these metals depends upon oxidation to higher insoluble oxidation states. The oxidation is generally accomplished by aeration. The rate of oxidation is pH-dependent in both cases, with a high pH favoring more rapid oxidation. The oxidation of soluble Mn(II) to insoluble MnO_2 is a complicated process. It appears to be catalyzed by solid MnO_2, which is known to adsorb Mn(II). This adsorbed Mn(II) is slowly oxidized on the MnO_2 surface.

Chlorine and potassium permanganate are sometimes employed as oxidizing agents for iron and manganese. There is some evidence that organic chelating agents with reducing properties hold iron(II) in a soluble form in water. In such cases, chlorine is effective because it destroys the organic compounds and enables the oxidation of iron(II).

In water with a high level of carbonate, $FeCO_3$ and $MnCO_3$ may be precipitated directly by raising the pH above 13.5 by the addition of sodium carbonate or lime. This approach is less popular than oxidation, however.

Relatively high levels of insoluble iron(III) and manganese(IV) frequently are found in water as colloidal material, which is difficult to remove. These metals can be associated with humic colloids or "peptizing" organic material that binds to colloidal metal oxides, stabilizing the colloid.

Heavy metals such as copper, cadmium, mercury, and lead are found in wastewaters from a number of industrial processes. Because of the toxicity of many heavy metals, their concentrations must be reduced to very low levels prior to release of the wastewater. A number of approaches are used in heavy-metals removal.

Lime treatment, discussed earlier in this section for calcium removal, precipitates heavy metals as insoluble hydroxides, basic salts, or coprecipitated with calcium carbonate or iron(III) hydroxide. This process does not completely remove mercury, cadmium, or lead, so their removal is aided by addition of sulfide (most heavy metals are sulfide-seekers):

$$Cd^{2+} + S^{2-} \rightarrow CdS(s) \quad (13.7.18)$$

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Heavy chlorination is frequently necessary to break down metal-solubilizing ligands (see Chapter 3). Lime precipitation does not normally permit recovery of metals and is sometimes undesirable from the economic viewpoint.

Electrodeposition (reduction of metal ions to metal by electrons at an electrode), *reverse osmosis* (see Section 13.9), and *ion exchange* are frequently employed for metal removal. Solvent extraction using organic-soluble chelating substances is also effective in removing many metals. **Cementation**, a process by which a metal deposits by reaction of its ion with a more readily oxidized metal, can be employed:

$$Cu^{2+} + Fe \text{ (iron scrap)} \rightarrow Fe^{2+} + Cu \tag{13.7.19}$$

Activated carbon adsorption effectively removes some metals from water at the part per million level. Sometimes a chelating agent is sorbed to the charcoal to increase metal removal.

Even when not specifically designed for the removal of heavy metals, most waste-treatment processes remove appreciable quantities of the more troublesome heavy metals encountered in wastewater. Biological waste treatment effectively removes metals from water. These metals accumulate in the sludge from biological treatment, so sludge disposal must be given careful consideration.

Various physical-chemical treatment processes effectively remove heavy metals from wastewaters. One such treatment is lime precipitation followed by activated-carbon filtration. Activated-carbon filtration may also be preceded by treatment with iron(III) chloride to form an iron(III) hydroxide floc, which is an effective heavy metals scavenger. Similarly, alum, which forms aluminum hydroxide, may be added prior to activated-carbon filtration.

The form of the heavy metal has a strong effect upon the efficiency of metal removal. For instance, chromium(VI) is normally more difficult to remove than chromium(III). Chelation may prevent metal removal by solubilizing metals (see Chapter 3).

In the past, removal of heavy metals has been largely a fringe benefit of wastewater treatment processes. Currently, however, more consideration is being given to design and operating parameters that specifically enhance heavy-metals removal as part of wastewater treatment.

13.8 REMOVAL OF DISSOLVED ORGANICS

Very low levels of exotic organic compounds in drinking water are suspected of contributing to cancer and other maladies. Water disinfection processes, which by their nature involve chemically rather severe conditions, particularly of oxidation, have a tendency to produce **disinfection by-products**. Some of these are chlorinated organic compounds produced by chlorination of organics in water, especially humic substances. Removal of organics to very low levels prior to chlorination has been found to be effective in preventing trihalomethane formation. Another major class of disinfection by-products consists of organooxygen compounds such as aldehydes, carboxylic acids, and oxoacids.

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A variety of organic compounds survive, or are produced by, secondary wastewater treatment and should be considered as factors in discharge or reuse of the treated water. Almost half of these are humic substances (see Section 3.17) with a molecular-weight range of 1000–5000. Among the remainder are found ether-extractable materials, carbohydrates, proteins, detergents, tannins, and lignins. The humic compounds, because of their high molecular weight and anionic character, influence some of the physical and chemical aspects of waste treatment. The ether-extractables contain many of the compounds that are resistant to biodegradation and are of particular concern regarding potential toxicity, carcinogenicity, and mutagenicity. In the ether extract are found many fatty acids, hydrocarbons of the *n*-alkane class, naphthalene, diphenylmethane, diphenyl, methylnaphthalene, isopropylbenzene, dodecylbenzene, phenol, phthalates, and triethylphosphate.

The standard method for the removal of dissolved organic material is adsorption on activated carbon, a product that is produced from a variety of carbonaceous materials including wood, pulp-mill char, peat, and lignite.[3] The carbon is produced by charring the raw material anaerobically below 600°C, followed by an activation step consisting of partial oxidation. Carbon dioxide can be employed as an oxidizing agent at 600–700°C.

$$CO_2 + C \rightarrow 2CO \tag{13.8.1}$$

or the carbon can be oxidized by water at 800–900°C:

$$H_2O + C \rightarrow H_2 + CO \tag{13.8.2}$$

These processes develop porosity, increase the surface area, and leave the C atoms in arrangements that have affinities for organic compounds.

Activated carbon comes in two general types: granulated activated carbon, consisting of particles 0.1–1 mm in diameter, and powdered activated carbon, in which most of the particles are 50–100 μm in diameter.

The exact mechanism by which activated carbon holds organic materials is not known. However, one reason for the effectiveness of this material as an adsorbent is its tremendous surface area. A solid cubic foot of carbon particles can have a combined pore and surface area of approximately 10 square miles!

Although interest is increasing in the use of powdered activated carbon for water treatment, currently granular carbon is more widely used. It can be employed in a fixed bed, through which water flows downward. Accumulation of particulate matter requires periodic backwashing. An expanded bed in which particles are kept slightly separated by water flowing upward can be used with less chance of clogging.

Economics require regeneration of the carbon. Regeneration can be accomplished by heating carbon to 950°C in a steam-air atmosphere. This process oxidizes adsorbed organics and regenerates the carbon surface, with an approximately 10% loss of carbon.

Removal of organics can also be accomplished by adsorbent synthetic polymers. Such polymers as Amberlite XAD-4 have hydrophobic surfaces and strongly attract relatively insoluble organic compounds, such as chlorinated pesticides. The porosity of these polymers is up to 50% by volume, and the surface area may be as high as 850 m^2/g. They are readily regenerated by solvents such as isopropanol and acetone.

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Under appropriate operating conditions, these polymers remove virtually all nonionic organic solutes; for example, phenol at 250 mg/L is reduced to less than 0.1 mg/L by appropriate treatment with Amberlite XAD-4. The use of adsorbent polymers is more expensive than that of activated carbon, however.

Oxidation of dissolved organics holds some promise for their removal. Ozone, hydrogen peroxide, molecular oxygen (with or without catalysts), chlorine and its derivatives, permanganate, or ferrate (iron(VI)) can be used as oxidants. Electrochemical oxidation may be possible in some cases. High-energy electron beams produced by high-voltage electron accelerators also have the potential to destroy organic compounds.

Removal of Herbicides

Because of their widespread application and persistence, herbicides have proven to be particularly troublesome in some drinking water sources. Herbicide levels vary with season, related to times that they are applied to control weeds. The more soluble ones, such as chlorophenoxy esters, are most likely to enter drinking water sources. One of the most troublesome is atrazine, which is often manifested by its metabolite desethylatrazine. Activated carbon treatment is the best means of removing herbicides and their metabolites from drinking water sources.[4] A problem with activated carbon is that of **preloading**, in which natural organic matter in the water loads up the carbon and hinders uptake of pollutant organics such as herbicides. Pretreatment to remove such organic matter, such as flocculation and precipitation of humic substances, can significantly increase the efficacy of activated carbon for the removal of herbicides and other organics.

13.9 REMOVAL OF DISSOLVED INORGANICS

For complete water recycling to be feasible, inorganic-solute removal is essential. The effluent from secondary waste treatment generally contains 300–400 mg/L more dissolved inorganic material than does the municipal water supply. It is obvious, therefore, that 100% water recycling without removal of inorganics would cause the accumulation of an intolerable level of dissolved material. Even when water is not destined for immediate reuse, the removal of the inorganic nutrients phosphorus and nitrogen is highly desirable to reduce eutrophication downstream. In some cases, the removal of toxic trace metals is needed.

One of the most obvious methods for removing inorganics from water is distillation. However, the energy required for distillation is generally quite high, so that distillation is not generally economically feasible. Furthermore, volatile materials such as ammonia and odorous compounds are carried over to a large extent in the distillation process unless special preventive measures are taken. Freezing produces a very pure water, but is considered uneconomical with present technology. This leaves membrane processes as the most cost-effective means of removing inorganic materials from water. Membrane processes considered most promising for bulk removal of inorganics from water are electrodialysis, ion exchange, and reverse osmosis. (Other membrane processes used in water purification are nanofiltration, ultrafiltration,[5] microfiltration, and dialysis.)

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Electrodialysis

Electrodialysis consists of applying a direct current across a body of water separated into vertical layers by membranes alternately permeable to cations and anions.[6] Cations migrate toward the cathode and anions toward the anode. Cations and anions both enter one layer of water, and both leave the adjacent layer. Thus, layers of water enriched in salts alternate with those from which salts have been removed. The water in the brine-enriched layers is recirculated to a certain extent to prevent excessive accumulation of brine. The principles involved in electrodialysis treatment are shown in Figure 13.8.

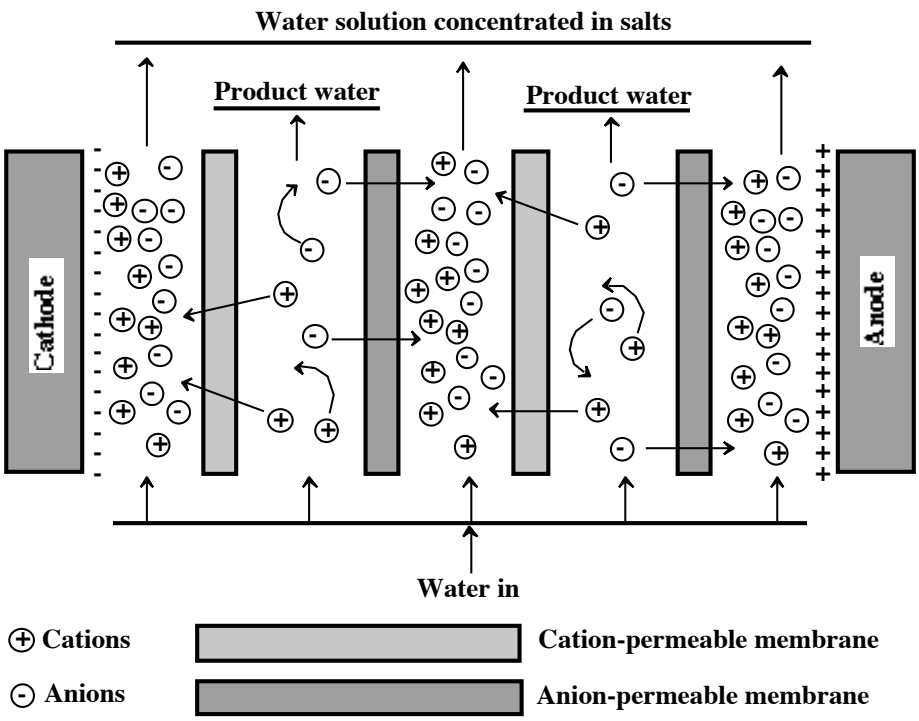

Figure 13.8 Electrodialysis apparatus for the removal of ionic material from water.

Fouling caused by various materials can cause problems with reverse osmosis treatment of water. Although the relatively small ions constituting the salts dissolved in wastewater readily pass through the membranes, large organic ions (proteins, for example) and charged colloids migrate to the membrane surfaces, often fouling or plugging the membranes and reducing efficiency. In addition, growth of microorganisms on the membranes can cause fouling.

Experience with pilot plants indicates that electrodialysis has the potential to be a practical and economical method to remove up to 50% of the dissolved inorganics from secondary sewage effluent after pretreatment to eliminate fouling substances. Such a level of efficiency would permit repeated recycling of water through municipal water systems without dissolved inorganic materials reaching unacceptably high levels.

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Ion Exchange

The ion exchange method for softening water is described in detail in Section 13.7. The ion exchange process used for removal of inorganics consists of passing the water successively over a solid cation exchanger and a solid anion exchanger, which replace cations and anions by hydrogen ion and hydroxide ion, respectively, so that each equivalent of salt is replaced by a mole of water. For the hypothetical ionic salt MX, the reactions are the following where $^{-}\{Cat(s)\}$ represents the solid cation exchanger and $^{+}\{An(s)\}$ represents the solid anion exchanger:

$$H^{+}\,{}^{-}\{Cat(s)\} + M^{+} + X^{-} \rightarrow M^{+}\,{}^{-}\{Cat(s)\} + H^{+} + X^{-} \tag{13.9.1}$$

$$OH^{-}\,{}^{+}\{An(s)\} + H^{+} + X^{-} \rightarrow X^{-}\,{}^{+}\{An(s)\} + H_2O \tag{13.9.2}$$

The cation exchanger is regenerated with strong acid and the anion exchanger with strong base.

Demineralization by ion exchange generally produces water of a very high quality. Unfortunately, some organic compounds in wastewater foul ion exchangers, and microbial growth on the exchangers can diminish their efficiency. In addition, regeneration of the resins is expensive, and the concentrated wastes from regeneration require disposal in a manner that will not damage the environment.

Reverse Osmosis

Reverse osmosis, Figure 13.9, is a very useful and well-developed technique for the purification of water.[7] Basically, it consists of forcing pure water through a semipermeable membrane that allows the passage of water but not of other material. This process, which is not simply sieve separation or ultrafiltration, depends on the preferential sorption of water on the surface of a porous cellulose acetate or polyamide membrane. Pure water from the sorbed layer is forced through pores in the membrane under pressure. If the thickness of the sorbed water layer is d, the pore diameter for optimum separation should be 2d. The optimum pore diameter depends upon the thickness of the sorbed pure water layer and may be several times the diameters of the solute and solvent molecules.

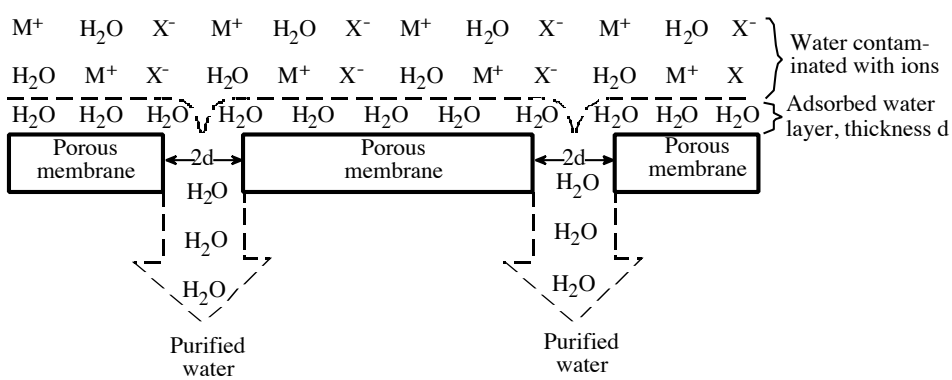

Figure 13.9 Solute removal from water by reverse osmosis.

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Phosphorus Removal

Advanced waste treatment normally requires removal of phosphorus to reduce algal growth. Algae may grow at PO_4^{3-} levels as low as 0.05 mg/L. Growth inhibition requires levels well below 0.5 mg/L. Since municipal wastes typically contain approximately 25 mg/L of phosphate (as orthophosphates, polyphosphates, and insoluble phosphates), the efficiency of phosphate removal must be quite high to prevent algal growth. This removal may occur in the sewage treatment process (1) in the primary settler; (2) in the aeration chamber of the activated sludge unit; or (3) after secondary waste treatment.

Activated sludge treatment removes about 20% of the phosphorus from sewage. Thus, an appreciable fraction of largely biological phosphorus is removed with the sludge. Detergents and other sources contribute significant amounts of phosphorus to domestic sewage and considerable phosphate ion remains in the effluent. However, some wastes, such as carbohydrate wastes from sugar refineries, are so deficient in phosphorus that supplementation of the waste with inorganic phosphorus is required for proper growth of the microorganisms degrading the wastes.

Under some sewage plant operating conditions, much greater than normal phosphorus removal has been observed. In such plants, characterized by high dissolved oxygen and high pH levels in the aeration tank, removal of 60–90% of the phosphorus has been attained, yielding two or three times the normal level of phosphorus in the sludge. In a conventionally operated aeration tank of an activated sludge plant, the CO_2 level is relatively high because of release of the gas by the degradation of organic material. A high CO_2 level results in a relatively low pH, due to the presence of carbonic acid. The aeration rate is generally not maintained at a very high level because oxygen is transferred relatively more efficiently from air when the dissolved oxygen levels in water are relatively low. Therefore, the aeration rate normally is not high enough to sweep out sufficient dissolved carbon dioxide to bring its concentration down to low levels. Thus, the pH generally is low enough that phosphate is maintained primarily in the form of the $H_2PO_4^-$ ion. However, at a higher rate of aeration in a relatively hard water, the CO_2 is swept out, the pH rises, and reactions such as the following occur:

$$5Ca^{2+} + 3HPO_4^{2-} + H_2O \rightarrow Ca_5OH(PO_4)_3(s) + 4H^+ \qquad (13.9.3)$$

The precipitated hydroxyapatite or other form of calcium phosphate is incorporated in the sludge floc. Reaction 13.9.3 is strongly hydrogen ion-dependent, and an increase in the hydrogen ion concentration drives the equilibrium back to the left. Thus, under anaerobic conditions when the sludge medium becomes more acidic due to higher CO_2 levels, the calcium returns to solution.

Chemically, phosphate is most commonly removed by precipitation. Some common precipitants and their products are shown in Table 13.1. Precipitation processes are capable of at least 90–95% phosphorus removal at reasonable cost.Lime, $Ca(OH)_2$, is the chemical most commonly used for phosphorus removal:

$$5Ca(OH)_2 + 3HPO_4^{2-} \rightarrow Ca_5OH(PO_4)_3(s) + 3H_2O + 6OH^- \qquad (13.9.4)$$

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Table 13.1 Chemical Precipitants for Phosphate and Their Products

Precipitant(s)	Products
$Ca(OH)_2$	$Ca_5OH(PO_4)_3$ (hydroxyapatite)
$Ca(OH)_2 + NaF$	$Ca_5F(PO_4)_3$ (fluorapatite)
$Al_2(SO_4)_3$	$AlPO_4$
$FeCl_3$	$FePO_4$
$MgSO_4$	$MgNH_4PO_4$

Lime has the advantages of low cost and ease of regeneration. The efficiency with which phosphorus is removed by lime is not as high as would be predicted by the low solubility of hydroxyapatite, $Ca_5OH(PO_4)_3$. Some of the possible reasons for this are slow precipitation of $Ca_5OH(PO_4)_3$, formation of nonsettling colloids; precipitation of calcium as $CaCO_3$ in certain pH ranges, and the fact that phosphate may be present as condensed phosphates (polyphosphates), which form soluble complexes with calcium ion.

Phosphate can be removed from solution by adsorption on some solids, particularly activated alumina, Al_2O_3. Removals of up to 99.9% of orthophosphate have been achieved with this method.

Nitrogen Removal

Next to phosphorus, nitrogen is the algal nutrient most commonly removed as part of advanced wastewater treatment. The techniques most often used for nitrogen removal are summarized in Table 13.2. Nitrogen in municipal wastewater generally is present as organic nitrogen or ammonia. Ammonia is the primary nitrogen product produced by most biological waste treatment processes. This is because it is expensive to aerate sewage sufficiently to oxidize the ammonia to nitrate through the action of nitrifying bacteria. If the activated sludge process is operated under conditions such that the nitrogen is maintained in the form of ammonia, the latter may be stripped in the form of NH_3 gas from the water by air. For ammonia stripping to work, the ammoniacal nitrogen must be converted to volatile NH_3 gas, which requires a pH substantially higher than the pK_a of the NH_4^+ ion. In practice, the pH is raised to approximately 11.5 by the addition of lime (which also serves to remove phosphate). The ammonia is stripped from the water by air.

Nitrification followed by denitrification is arguably the most effective technique for the removal of nitrogen from wastewater. The first step is an essentially complete conversion of ammonia and organic nitrogen to nitrate under strongly aerobic conditions, achieved by more extensive than normal aeration of the sewage:

$$NH_4^+ + 2O_2 \text{ (Nitrifying bacteria)} \rightarrow NO_3^- + 2H^+ + H_2O \qquad (13.9.5)$$

The second step is the reduction of nitrate to nitrogen gas. This reaction is also bacterially catalyzed and requires a carbon source and a reducing agent such as methanol, CH_3OH.[8]

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Table 13.2 Common Processes for the Removal of Nitrogen from Wastewater[1]

Process	Principles and conditions
Air stripping ammonia	Ammonium ion is the initial product of biodegradation of nitrogen waste. It is removed by raising the pH to approximately 11 with lime, and stripping ammonia gas from the water by air in a stripping tower. Scaling, icing, and air pollution are the main disadvantages.
Ammonium ion exchange	Clinoptilolite, a natural zeolite, selectively removes ammonium ion by ion exchange: $Na^+\{^-\text{clinoptilolite}\} + NH_4^+ \rightarrow NH_4^+\{^-\text{clinoptilolite}\} + Na^+$. The ion exchanger is regenerated with sodium or calcium salts.
Biosynthesis	The production of biomass in the sewage treatment system and its subsequent removal from the sewage effluent result in a net loss of nitrogen from the system.
Nitrification-denitrification	This approach involves the conversion of ammoniacal nitrogen to nitrate by bacteria under aerobic conditions, $2NH_4^+ + 3O_2 \xrightarrow{\textit{Nitrosomonas}} 4H^+ + 2NO_2^- + 2H_2O$ $2NO_2^- + O_2 \xrightarrow{\textit{Nitrobacter}} 2NO_3^-$ followed by production of elemental nitrogen (denitrification): $4NO_3^- + 5\{CH_2O\} + 4H^+ \xrightarrow[\text{bacteria}]{\text{Denitrifying}} 2N_2(g) + 5CO_2(g) + 7H_2O$ Typically, denitrification is carried out in an anaerobic column with added methanol as a food source (microbial reducing agent).
Chlorination	Reaction of ammonium ion and hypochlorite (from chlorine) results in denitrification by chemical reactions: $NH_4^+ + HOCl \rightarrow NH_2Cl + H_2O + H^+$ $2NH_2Cl + HOCl \rightarrow N_2(g) + 3H^+ + 3\ Cl^-\ H_2O$

$$6NO_3^- + 5CH_3OH + 6H^+ \text{ (Denitrifying bacteria)} \rightarrow 3N_2(g) + 5CO_2 + 13H_2O \qquad (13.9.6)$$

The denitrification process shown in Reaction 13.9.6 can be carried out either in a tank or on a carbon column. In pilot plant operation, conversions of 95% of the ammonia to nitrate and 86% of the nitrate to nitrogen have been achieved. Although methanol is shown in the reaction as a source of reducing agent for the microbial reduction of nitrate, other organic substances can be used as well. Ethanol from the fermentation of otherwise waste carbohydrates would serve as a reducing substance.

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13.10 SLUDGE

Perhaps the most pressing water treatment problem at this time has to do with sludge collected or produced during water treatment. Finding a safe place to put the sludge or a use for it has proven troublesome, and the problem is aggravated by the growing numbers of water treatment systems.

Some sludge is present in wastewater prior to treatment and can be collected from it. Such sludge includes human wastes, garbage grindings, organic wastes and inorganic silt and grit from storm water runoff, and organic and inorganic wastes from commercial and industrial sources. There are two major kinds of sludge generated in a waste treatment plant. The first of these is organic sludge from activated sludge, trickling filter, or rotating biological reactors. The second is inorganic sludge from the addition of chemicals, such as in phosphorus removal (see Section 13.9).

Most commonly, sewage sludge is subjected to anaerobic digestion in a digester designed to allow bacterial action to occur in the absence of air. This reduces the mass and volume of sludge and ideally results in the formation of a stabilized humus. Disease agents are also destroyed in the process.

Following digestion, sludge is generally conditioned and thickened to concentrate and stabilize it and make it more dewaterable. Relatively inexpensive processes, such as gravity thickening, may be employed to get the moisture content down to about 95%. Sludge can be further conditioned chemically by the addition of iron or aluminum salts, lime, or polymers.

Sludge dewatering is employed to convert the sludge from an essentially liquid material to a damp solid containing not more than about 85% water. This can be accomplished on sludge drying beds consisting of layers of sand and gravel. Mechanical devices can also be employed, including vacuum filtration, centrifugation, and filter presses. Heat can be used to aid the drying process.

Ultimately, disposal of the sludge is required.Two of the main alternatives for sludge disposal are land spreading and incineration.

Rich in nutrients, waste sewage sludge contains around 5% N, 3% P, and 0.5% K on a dry-weight basis and can be used to fertilize and condition soil. The humic material in the sludge improves the physical properties and cation-exchange capacity of the soil. Possible accumulation of heavy metals is of some concern insofar as the use of sludge on cropland is concerned. Sewage sludge is an efficient heavy-metals scavenger and may contain elevated levels of zinc, copper, nickel, and cadmium These and other metals tend to remain immobilized in soil by chelation with organic matter, adsorption on clay minerals, and precipitation as insoluble compounds such as oxides or carbonates. However, increased application of sludge on cropland has caused distinctly elevated levels of zinc and cadmium in both leaves and grain of corn. Therefore, caution has been advised in heavy or prolonged application of sewage sludge to soil. Prior control of heavy-metal contamination from industrial sources has greatly reduced the heavy-metal content of sludge and enabled it to be used more extensively on soil.

An increasing problem in sewage treatment arises from sludge sidestreams. These consist of water removed from sludge by various treatment processes. Sewage treatment processes can be divided into mainstream treatment processes (primary clarification, trickling filter, activated sludge, and rotating biological reactor) and

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sidestream processes. During sidestream treatment, sludge is dewatered, degraded, and disinfected by a variety of processes, including gravity thickening, dissolved air flotation, anaerobic digestion, aerobic digestion, vacuum filtration, centrifugation, belt-filter press filtration, sand-drying-bed treatment, sludge-lagoon settling, wet air oxidation, pressure filtration, and Purifax treatment. Each of these produces a liquid byproduct sidestream that is circulated back to the mainstream. These add to the biochemical oxygen demand and suspended solids of the mainstream.

A variety of chemical sludges are produced by various water treatment and industrial processes. Among the most abundant of such sludges is alum sludge produced by the hydrolysis of Al(III) salts used in the treatment of water, which creates gelatinous aluminum hydroxide:

$$Al^{3+} + 3OH^{-}(aq) \rightarrow Al(OH)_3(s) \tag{13.10.1}$$

Alum sludges normally are 98% or more water and are very difficult to dewater.

Both iron(II) and iron(III) compounds are used for the removal of impurities from wastewater by precipitation of $Fe(OH)_3$. The sludge contains $Fe(OH)_3$ in the form of soft, fluffy precipitates that are difficult to dewater beyond 10 or 12% solids.

The addition of either lime, $Ca(OH)_2$, or quicklime, CaO, to water is used to raise the pH to about 11.5 and cause the precipitation of $CaCO_3$, along with metal hydroxides and phosphates. Calcium carbonate is readily recovered from lime sludges and can be recalcined to produce CaO, which can be recycled through the system.

Metal hydroxide sludges are produced in the removal of metals such as lead, chromium, nickel, and zinc from wastewater by raising the pH to such a level that the corresponding hydroxides or hydrated metal oxides are precipitated. The disposal of these sludges is a substantial problem because of their toxic heavy-metal content. Reclamation of the metals is an attractive alternative for these sludges.

Pathogenic (disease-causing) microorganisms may persist in the sludge left from the treatment of sewage. Many of these organisms present potential health hazards, and there is risk of public exposure when the sludge is applied to soil. Therefore, it is necessary both to be aware of pathogenic microorganisms in municipal wastewater treatment sludge and to find a means of reducing the hazards caused by their presence.

The most significant organisms in municipal sewage sludge include (1) indicators of fecal pollution, including fecal and total coliform; (2) pathogenic bacteria, including *Salmonellae* and *Shigellae*; (3) enteric (intestinal) viruses, including enterovirus and poliovirus; and (4) parasites, such as *Entamoeba histolytica* and *Ascaris lumbricoides*.

Several methods are recommended to significantly reduce levels of pathogens in sewage sludge. Aerobic digestion involves aerobic agitation of the sludge for periods of 40 to 60 days (longer times are employed with low sludge temperatures). Air drying involves draining and/or drying of the liquid sludge for at least 3 months in a layer 20–25 cm thick. This operation can be performed on underdrained sand beds or in basins. Anaerobic digestion involves maintenance of the sludge in an anaerobic state for periods of time ranging from 60 days at 20°C to 15 days at temperatures exceeding 35°C. Composting involves mixing dewatered sludge cake with bulking

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agents subject to decay, such as wood chips or shredded municipal refuse, and allowing the action of bacteria to promote decay at temperatures ranging up to 45–65°C. The higher temperatures tend to kill pathogenic bacteria. Finally, pathogenic organisms can be destroyed by lime stabilization in which sufficient lime is added to raise the pH of the sludge to 12 or higher.

13.11 WATER DISINFECTION

Chlorine is the most commonly used disinfectant employed for killing bacteria in water. When chlorine is added to water, it rapidly hydrolyzes according to the reaction

$$Cl_2 + H_2O \rightarrow H^+ + Cl^- + HOCl \tag{13.11.1}$$

which has the following equilibrium constant:

$$K = \frac{[H^+][Cl^-][HOCl]}{[Cl_2]} = 4.5 \times 10^{-4} \tag{13.11.2}$$

Hypochlorous acid, HOCl, is a weak acid that dissociates according to the reaction,

$$HOCl \leftrightarrow H^+ + OCl^- \tag{13.11.3}$$

with an ionization constant of 2.7×10^{-8}. From the above it can be calculated that the concentration of elemental Cl_2 is negligible at equilibrium above pH 3 when chlorine is added to water at levels below 1.0 g/L.

Sometimes, hypochlorite salts are substituted for chlorine gas as a disinfectant. Calcium hypochlorite, $Ca(OCl)_2$, is commonly used. The hypochlorites are safer to handle than gaseous chlorine.

The two chemical species formed by chlorine in water, HOCl and OCl^-, are known as **free available chlorine**. Free available chlorine is very effective in killing bacteria. In the presence of ammonia, monochloramine, dichloramine, and trichloramine are formed:

$$NH_4^+ + HOCl \rightarrow NH_2Cl \text{ (monochloramine)} + H_2O + H^+ \tag{13.11.4}$$

$$NH_2Cl + HOCl \rightarrow NHCl_2 \text{ (dichloramine)} + H_2O \tag{13.11.5}$$

$$NHCl_2 + HOCl \rightarrow NCl_3 \text{ (trichloramine)} + H_2O \tag{13.11.6}$$

The chloramines are called **combined available chlorine**. Chlorination practice frequently provides for formation of combined available chlorine which, although a weaker disinfectant than free available chlorine, is more readily retained as a disinfectant throughout the water distribution system. Too much ammonia in water is considered undesirable because it exerts excess demand for chlorine.

At sufficiently high Cl:N molar ratios in water containing ammonia, some HOCl and OCl^- remain unreacted in solution, and a small quantity of NCl_3 is formed. The ratio at which this occurs is called the **breakpoint**. Chlorination beyond the break-

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point ensures disinfection. It has the additional advantage of destroying the more common materials that cause odor and taste in water.

At moderate levels of NH_3-N (approximately 20 mg/L), when the pH is between 5.0 and 8.0, chlorination with a minimum 8:1 weight ratio of Cl to NH_3-nitrogen produces efficient denitrification:

$$NH_4^+ + HOCl \rightarrow NH_2Cl + H_2O + H^+ \quad (13.11.4)$$

$$2NH_2Cl + HOCl \rightarrow N_2(g) + 3H^+ + 3Cl^- + H_2O \quad (13.11.7)$$

This reaction is used to remove pollutant ammonia from wastewater. However, problems can arise from chlorination of organic wastes. Typical of such by-products is chloroform, produced by the chlorination of humic substances in water.

Chlorine is used to treat water other than drinking water. It is employed to disinfect effluent from sewage treatment plants, as an additive to the water in electric power plant cooling towers, and to control microorganisms in food processing.

Chlorine Dioxide

Chlorine dioxide, ClO_2, is an effective water disinfectant that is of particular interest because, in the absence of impurity Cl_2, it does not produce impurity trihalomethanes in water treatment. In acidic and neutral water, respectively, the two half-reactions for ClO_2 acting as an oxidant are the following:

$$ClO_2 + 4H^+ + 5e^- \leftrightarrow Cl^- + 2H_2O \quad (13.11.8)$$

$$ClO_2 + e^- \leftrightarrow ClO_2^- \quad (13.11.9)$$

In the neutral pH range, chlorine dioxide in water remains largely as molecular ClO_2 until it contacts a reducing agent with which to react. Chlorine dioxide is a gas that is violently reactive with organic matter and explosive when exposed to light. For these reasons, it is not shipped, but is generated on-site by processes such as the reaction of chlorine gas with solid sodium hypochlorite:

$$2NaClO_2(s) + Cl_2(g) \leftrightarrow 2ClO_2(g) + 2NaCl(s) \quad (13.11.10)$$

A high content of elemental chlorine in the product may require its purification to prevent unwanted side-reactions from Cl_2.

As a water disinfectant, chlorine dioxide does not chlorinate or oxidize ammonia or other nitrogen-containing compounds. Some concern has been raised over possible health effects of its main degradation byproducts, ClO_2^- and ClO_3^-.

Ozone

Ozone is sometimes used as a disinfectant in place of chlorine, particularly in Europe. Figure 13.10 shows the main components of an ozone water treatment system. Basically, air is filtered, cooled, dried, and pressurized, then subjected to an electrical discharge of approximately 20,000 volts. The ozone produced is then pumped into a contact chamber, where water contacts the ozone for 10–15 minutes.

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Concern over possible production of toxic organochlorine compounds by water chlorination processes has increased interest in ozonation. Furthermore, ozone is more destructive to viruses than is chlorine. Unfortunately, the solubility of ozone in water is relatively low, which limits its disinfective power.

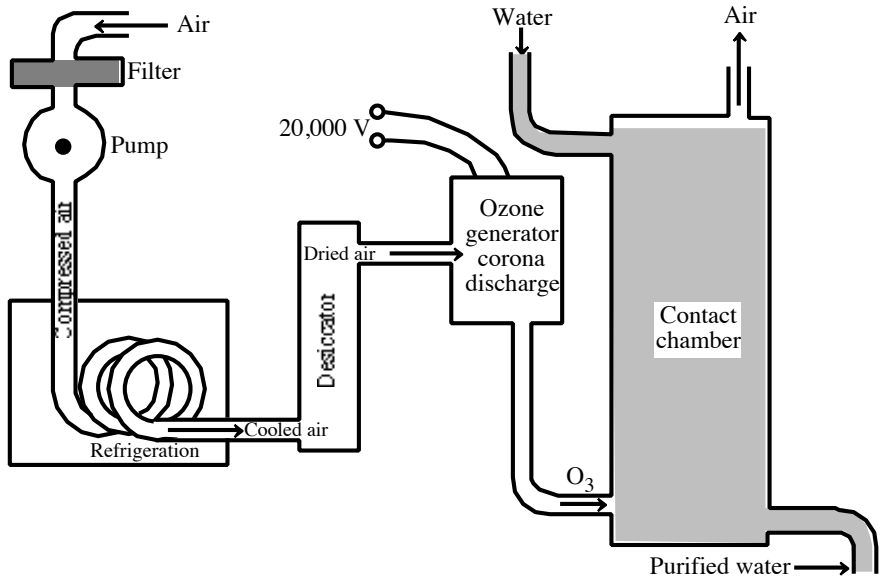

Figure 13.10 A schematic diagram of a typical ozone water-treatment system.

A major consideration with ozone is the rate at which it decomposes spontaneously in water, according to the overall reaction,

$$2O_3 \rightarrow 3O_2(g) \qquad (13.11.11)$$

Because of the decomposition of ozone in water, some chlorine must be added to maintain disinfectant throughout the water distribution system.

Iron(VI) in the form of ferrate ion, FeO_4^{2-}, is a strong oxidizing agent with excellent disinfectant properties. It has the additional advantage of removing heavy metals, viruses, and phosphate. It may well find limited application for disinfection in the future.

13.12 NATURAL WATER PURIFICATION PROCESSES

Virtually all of the materials that waste-treatment processes are designed to eliminate can be absorbed by soil or degraded in soil. In fact, most of these materials can serve to add fertility to soil. Wastewater can provide the water that is essential to plant growth. The mineralization of biological wastes in wastewater provides phosphorus, nitrogen and potassium usually provided by fertilizers. Wastewater also contains essential trace elements and vitamins. Stretching the point a bit, the degradation of organic wastes provides the CO_2 essential for photosynthetic production of plant biomass.

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Soil may be viewed as a natural filter for wastes. Most organic matter is readily degraded in soil and, in principle, soil constitutes an excellent primary, secondary, and tertiary treatment system for water. Soil has physical, chemical, and biological characteristics that can enable wastewater detoxification, biodegradation, chemical decomposition, and physical and chemical fixation. A number of soil characteristics are important in determining its use for land treatment of wastes. These characteristics include physical form, ability to retain water, aeration, organic content, acid-base characteristics, and oxidation-reduction behavior. Soil is a natural medium for a number of living organisms that may can an effect upon biodegradation of wastewaters, including those that contain industrial wastes. Of these, the most important are bacteria, including those from the genera *Agrobacterium*, *Arthrobacteri*, *Bacillus*, *Flavobacterium*, and *Pseudomonas*. Actinomycetes and fungi are important in decay of vegetable matter and may be involved in biodegradation of wastes. Other unicellular organisms that may be present in or on soil are protozoa and algae. Soil animals, such as earthworms, affect soil parameters such as soil texture. The growth of plants in soil may have an influence on its waste treatment potential in such aspects as uptake of soluble wastes and erosion control.

Early civilizations, such as the Chinese, used human organic wastes to increase soil fertility, and the practice continues today. The ability of soil to purify water was noted well over a century ago. In 1850 and 1852, J. Thomas Way, a consulting chemist to the Royal Agricultural Society in England, presented two papers to the Society entitled "Power of Soils to Absorb Manure." Mr. Way's experiments showed that soil is an ion exchanger. Much practical and theoretical information on the ion exchange process resulted from his work.

If soil treatment systems are not properly designed and operated, odor can become an overpowering problem. The author of this book is reminded of driving into a small town, recalled from some years before as a very pleasant place, and being assaulted with a virtually intolerable odor. The disgruntled residents pointed to a large spray irrigation system on a field in the distance—unfortunately upwind—spraying liquified pig manure as part of an experimental feedlot waste treatment operation. The experiment was not deemed a success and was discontinued by the investigators, presumably before they met with violence from the local residents.

Industrial Wastewater Treatment by Soil

Wastes that are amenable to land treatment are biodegradable organic substances, particularly those contained in municipal sewage and in wastewater from some industrial operations, such as food processing. However, through acclimation over a long period of time, soil bacterial cultures may develop that are effective in degrading normally recalcitrant compounds that occur in industrial wastewater. Acclimated microorganisms are found particularly at contaminated sites, such as those where soil has been exposed to crude oil for many years.

A variety of enzyme activities are exhibited by microorganisms in soil that enable them to degrade synthetic substances. Even sterilized soil may show enzyme activity due to extracellular enzymes secreted by microorganisms in soil. Some of these enzymes are hydrolase enzymes (see Chapter 21), such as those that catalyze the hydrolysis of organophosphate compounds as shown by the reaction,

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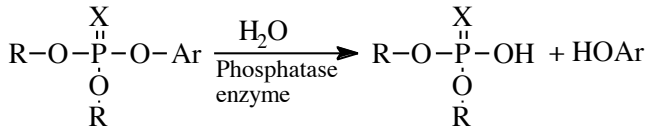
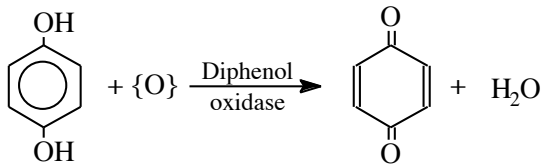


(13.12.1)

where R is an alkyl group, Ar is a substituent group that is frequently aryl, and X is either S or O. Another example of a reaction catalyzed by soil enzymes is the oxidation of phenolic compounds by diphenol oxidase:



(13.12.2)

Land treatment is most used for petroleum-refining wastes and is applicable to the treatment of fuels and wastes from leaking underground storage tanks. It can also be applied to biodegradable organic chemical wastes, including some organohalide compounds. Land treatment is not suitable for the treatment of wastes containing acids, bases, toxic inorganic compounds, salts, heavy metals, and organic compounds that are excessively soluble, volatile, or flammable.

13.13 WATER REUSE AND RECYCLING

Water reuse and recycling are becoming much more common as demands for water exceed supply. **Unplanned reuse** occurs as the result of waste effluents entering receiving waters or groundwater and subsequently being taken into a water distribution system. A typical example of unplanned water reuse occurs in London, which withdraws water from the Thames River that may have been through other water systems at least once, and which uses groundwater sources unintentionally recharged with sewage effluents from a number of municipalities. **Planned reuse** utilizes wastewater treatment systems deliberately designed to bring water up to standards required for subsequent applications. The term **direct reuse** refers to water that has retained its identity from a previous application; reuse of water that has lost its identity is termed **indirect reuse**. The distinction also needs to be made between recycling and reuse. **Recycling** occurs internally before water is ever discharged. An example is condensation of steam in a steam power plant followed by return of the steam to boilers. **Reuse** occurs, for example, when water discharged by one user is taken as a water source by another user.

Reuse of water continues to grow because of two major factors. The first of these is lack of supply of water. The second is that widespread deployment of modern water treatment processes significantly enhances the quality of water available for reuse. These two factors come into play in semi-arid regions in countries with advanced technological bases. For example, Israel, which is dependent upon irrigation for essentially all its agriculture, reuses about 2/3 of the country's sewage effluent for irrigation, whereas the U.S., where water is relatively more available, uses only about 2–3% of its water for this purpose.

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Since drinking water and water used for food processing require the highest quality of all large applications, intentional reuse for potable water is relatively less desirable, though widely practiced unintentionally or out of necessity. This leaves three applications with the greatest potential for reuse:

- Irrigation for cropland, golf courses, and other applications requiring water for plant and grass growth. This is the largest potential application for reused water and one that can take advantage of plant nutrients, particularly nitrogen and phosphorus, in water.
- Cooling and process water in industrial applications. For some industrial applications, relatively low-quality water can be used and secondary sewage effluent is a suitable source.
- Groundwater recharge. Groundwater can be recharged with reused water either by direct injection into an aquifer or by applying the water to land, followed by percolation into the aquifer. The latter, especially, takes advantage of biodegradation and chemical sorption processes to further purify the water.

It is inevitable that water recycling and reuse will continue to grow. This trend will increase the demand for water treatment, both qualitatively and quantitatively. In addition, it will require more careful consideration of the original uses of water to minimize water deterioration and enhance its suitability for reuse.

CHAPTER SUMMARY

The chapter summary below is presented in a programmed format to review the main points covered in this chapter. It is used most effectively by filling in the blanks, referring back to the chapter as necessary. The correct answers are given at the end of the summary.

The major categories for water treatment are [1]_____ _____ _____. Sources of water treated for municipal use include [2]_____. External treatment of water for industrial use is usually applied to [3]_____ _____ whereas internal treatment is designed to [4]_____ _____. Removal of [5]_____ _____ is essential for the treatment of boiler feedwater. [6]_____ _____ must be removed from water used in food processing. Current processes for the treatment of wastewater (sewage) may be divided into the three main categories of [7]_____ _____. Primary treatment of water is designed to remove [8]_____. The major constituent removed from water by secondary wastewater treatment is [9]_____ _____. Generally regarded as the most versatile and effective means of secondary wastewater treatment, the [10]_____ process uses a [11]_____ in an aerated tank to remove

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BOD from water. The reaction by which sewage sludge may be digested in the absence of oxygen by methane-producing anaerobic bacteria is [12]_____ _____ and it reduces [13]_____ _____ by about 60%. Tertiary waste treatment normally is applied to [14]_____ _____, and the three general kinds of contaminants that it removes are [15]_____ _____. Five major operations in a physical-chemical wastewater treatment process are [16]_____ _____ _____. Two factors that have prevented development of physical-chemical wastewater treatment are [17]_____. Some physical processes used in industrial wastewater treatment are [18]_____ _____ _____. Before colloidal solids can be removed by filtration, they usually must be subjected to [19]_____. A reaction by which water becomes softened when heated is [20]_____ _____. The reaction by which water containing "bicarbonate hardness," can be treated by addition of lime is [21]_____. _____. When bicarbonate ion is not present at substantial levels, softening water by $CaCO_3$ removal requires [22]_____ _____. Two reactions involving a solid ion exchanger by which hardness may be removed from water are [23]_____ _____ _____. The basic method for removing both soluble iron and manganese from water is [24]_____ _____. The removal of mercury, cadmium, or lead by lime treatment is aided by addition of [25]_____. The standard method of removing organic compounds from water is [26]_____ _____. Some methods for removing dissolved inorganic material from water are [27]_____ _____. A water purification process that consists of forcing pure water through a semipermeable membrane that allows the passage of water but not of other material is [28]_____ _____. Phosphorus is removed in advanced wastewater treatment to [29]_____. Phosphorus removal is usually accomplished by addition of [30]_____ for which the reaction is [31]_____. At a very high aeration rate in an activated sludge treatment process, phosphate is commonly removed because [32]_____ _____. The two overall biological reactions by which nitrogen, originally present as NH_4^+, can be removed from water are [33]_____ _____ and [34]_____. Anaerobic digestion of sewage sludge in a digester serves to [35]_____ _____. major plant nutrients contained in

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sewage sludge are [36]_____
_____. Sludge created by the water treatment reacation $Al^{3+} + 3OH^{-}(s) \rightarrow Al(OH)_3(aq)$ is known as alum sludge and causes problems because it is [37]_____. The most significant classes of organisms in municipal sludge are [38]_____
_____
_____.
The most commonly used water disinfectant is [39]_____ which reacts with water according to the reaction [40]_____. Free available chlorine consists of [41]_____ in water, and combined available chlorine consists of [42]_____. Chlorine dioxide is of particular interest for water disinfection because it does not produce [43]_____
_____. An oxidizing disinfectant that does not contain chlorine is [44]_____ produced by [45]_____. Soil has physical, chemical, and biological characteristics that can enable [46]_____
_____
_____ of impurities in wastewater. The soil characteristics that are important in determining its use for land treatment of wastes are [47]_____
_____
_____. Acclimated microorganisms adapted to degradation of organic compounds are found most commonly at [48]_____
_____.

Answers to Chapter Summary

1. purification for domestic use, treatment for specialized industrial applications, treatment of wastewater to make it acceptable for release or reuse
2. river water and well water
3. the plant's entire water supply
4. modify the properties of water for specific applications
5. corrosive substances and scale-forming solutes
6. Pathogens and toxic substances
7. primary treatment, secondary treatment, and tertiary treatment
8. insoluble matter such as grit, grease, and scum from water
9. biochemical oxygen demand
10. activated sludge
11. suspension of microorganisms
12. $2\{CH_2O\} \rightarrow CH_4 + CO_2$
13. both the volatile-matter content and the volume of the sludge
14. a variety of processes performed on the effluent from secondary waste treatment
15. suspended solids, dissolved organic compounds, and dissolved inorganic materials
16. removal of scum and solid objects, clarification, generally with addition of a coagulant, and frequently with the addition of other chemicals (such as lime for phosphorus removal), filtration to remove filterable solids, activated carbon adsorption, disinfection
17. high costs of chemicals and energy

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18. density separation, filtration, flotation, evaporation, distillation, reverse osmosis, hyperfiltration, ultrafiltration, solvent extraction, air stripping, or steam stripping
19. coagulation
20. $Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3(s) + CO_2(g) + H_2O$
21. $Ca^{2+} + 2HCO_3^- + Ca(OH)_2 \rightarrow 2CaCO_3(s) + 2H_2O$
22. a source of CO_3^{2-} at a relatively high enough pH
23. $H^{+-}\{Cat(s)\} + Na^+ + Cl^- \rightarrow Na^{+-}\{Cat(s)\} + H^+ + Cl^-$ and $OH^{-+}\{An(s)\} + H^+ + Cl^- \rightarrow Cl^{-+}\{An(s)\} + H_2O$
24. oxidation to higher insoluble oxidation states
25. sulfide
26. activated carbon sorption
27. distillation, electrodialysis, ion exchange, reverse osmosis, nanofiltration, ultrafiltration, microfiltration, and dialysis
28. reverse osmosis
29. reduce algal growth
30. lime
31. $5Ca(OH)_2 + 3HPO_4^{2-} \rightarrow Ca_5OH(PO_4)_3(s) + 3H_2O + 6OH^-$
32. the CO_2 is swept out, the pH rises, and reactions occur such as $5Ca^{2+} + 3HPO_4^{2-} + H_2O \rightarrow Ca_5OH(PO_4)_3(s) + 4H^+$
33. $NH_4^+ + 2O_2$ (Nitrifying bacteria) $\rightarrow NO_3^- + 2H^+ + H_2O$
34. $6NO_3^- + 5CH_3OH + 6H^+$ (Denitrifying bacteria) $\rightarrow 3N_2(g) + 5CO_2 + 13H_2O$
35. reduce the mass and volume of sludge and destroys disease agent
36. 5% N, 3% P, and 0.5% K on a dry-weight basis
37. very difficult to dewater
38. indicators of fecal pollution, pathogenic bacteria, enteric viruses, and parasites
39. Cl_2
40. $Cl_2 + H_2O \rightarrow H^+ + Cl^- + HOCl$
41. HOCl and OCl^-
42. the chloramines
43. trihalomethanes
44. ozone
45. an electrical discharge through dry air
46. detoxification, biodegradation, chemical decomposition, and physical and chemical fixation
47. physical form, ability to retain water, aeration, organic content, acid-base characteristics, and oxidation-reduction behavior
48. sites contaminated with the kinds of wastes degraded

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QUESTIONS AND PROBLEMS

1. During municipal water treatment, air is often mixed intimately with the water, that is, it is aerated. What kinds of undesirable contaminants would this procedure remove from water?
2. What is the purpose of the return sludge step in the activated sludge process?
3. What are the two processes by which the activated sludge process removes soluble carbonaceous material from sewage?
4. Why might hard water be desirable as a medium if phosphorus is to be removed by an activated sludge plant operated under conditions of high aeration?
5. How does reverse osmosis differ from a simple sieve separation or ultrafiltration process?
6. How many liters of methanol would be required daily to remove the nitrogen from a 200,000-L/day sewage treatment plant producing an effluent containing 50 mg/L of nitrogen? Assume that the nitrogen has been converted to NO_3^- in the plant. The denitrifying reaction is Reaction 13.9.6.

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7. Discuss some of the advantages of physical-chemical treatment of sewage as opposed to biological wastewater treatment. What are some disadvantages?

8. Why is recarbonation necessary when water is softened by the lime-soda process?

9. Assume that a waste contains 300 mg/L of biodegradable $\{CH_2O\}$ and is processed through a 200,000-L/day sewage-treatment plant that converts 40% of the waste to CO_2 and H_2O. Calculate the volume of air (at 25°, 1 atm) required for this conversion. Assume that the O_2 is transferred to the water with 20% efficiency.

10. If all of the $\{CH_2O\}$ in the plant described in Question 9 could be converted to methane by anaerobic digestion, how many liters of methane (STP) could be produced daily?

11. Assuming that aeration of water does not result in the precipitation of calcium carbonate, of the following, which one would not be removed by aeration: hydrogen sulfide, carbon dioxide, volatile odorous bacterial metabolites, alkalinity, iron?

12. In which of the following water supplies would moderately high water hardness be most detrimental: municipal water; irrigation water; boiler feedwater; drinking water (in regard to potential toxicity).

13. Which solute in water is commonly removed by the addition of sulfite or hydrazine?

14. A wastewater containing dissolved Cu^{2+} ion is to be treated to remove copper. Which of the following processes would *not* remove copper in an insoluble form; lime precipitation; cementation; treatment with NTA; ion exchange; reaction with metallic Fe.

15. Match each water contaminant in the left column with its preferred method of removal in the right column.

A. Mn^{2+}	1. Activated carbon
B. Ca^{2+} and HCO_3^-	2. Raise pH by addition of Na_2CO_3
C. Trihalomethane compounds	3. Addition of lime
D. Mg^{2+}	4. Oxidation

16. A cementation reaction employs iron to remove Cd^{2+} present at a level of 350 mg/L from a wastewater stream. Given that the atomic weight of Cd is 112.4 and that of Fe is 55.8, how many kg of Fe are consumed in removing all the Cd from 4.50×10^6 liters of water?

17. Consider municipal drinking water from two different kinds of sources, one a flowing, well-aerated stream with a heavy load of particulate matter, and the other an anaerobic groundwater. Describe possible differences in the water treatment strategies for these two sources of water.

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18. In treating water for industrial use, consideration is often given to "sequential use of the water." What is meant by this term? Give some plausible examples of sequential use of water.

19. Active biomass is used in the secondary treatment of municipal wastewater. Describe three ways of supporting a growth of the biomass, contacting it with wastewater, and exposing it to air.

20. Using appropriate chemical reactions for illustration, show how calcium present as the dissolved HCO_3^- salt in water is easier to remove than other forms of hardness, such as dissolved $CaCl_2$.

21. Suggest a source of microorganisms to use in a waste-treatment process. Where should an investigator look for microorganisms to use in such an application? What are some kinds of wastes for which soil is particularly unsuitable as a treatment medium?

22. An *increase* in which of the following *decreases* the rate of oxidation of iron(II) to iron(III) in water? [Fe(II)]; pH; $[H^+]$; $[O_2]$; $[OH^-]$.

23. Label each of the following as external treatment (ex) or internal treatment (in): ( ) aeration, ( ) addition of inhibitors to prevent corrosion ( ) adjustment of pH ( ), filtration, ( ) clarification ( ) removal of dissolved oxygen by reaction with hydrazine or sulfite, ( ) disinfection for food processing

24. Label each of the following as primary treatment (pr), secondary treatment (sec), or tertiary treatment (tert): screening, comminuting, ( ) grit removal, ( ) BOD removal, ( ) activated carbon filtration removal of dissolved organic compounds, ( ) removal of dissolved inorganic materials

25. Both activated-sludge waste treatment and natural processes in streams and bodies of water remove degradable material by biodegradation. Explain why activated-sludge treatment is so much more effective.

26. Of the following, the one that does not belong with the rest is ( ) removal of scum and solid objects, ( ) clarification, ( ) filtration, ( ) degradation with activated sludge, ( ) activated carbon adsorption, ( ) disinfection.

27. Explain why complete physical-chemical wastewater-treatment systems are better than biological systems in dealing with toxic substances and overloads.

28. What are the two major ways in which dissolved carbon (organic compounds) are removed from water in industrial wastewater treatment. How do these two approaches differ fundamentally?

29. What is the reaction for the hydrolysis of aluminum ion in water? How is this reaction used for water treatment?

30. Explain why coagulation is used with filtration.

31. What are two major problems that arise from the use of excessively hard water?

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32. Show with chemical reactions how the removal of bicarbonate hardness with lime results in a net removal of ions from solution, whereas removal of nonbicarbonate hardness does not.
33. What two purposes are served by adding CO_2 to water that has been subjected to lime-soda softening?
34. Why is cation exchange normally used without anion exchange for softening water?
35. Show with chemical reactions how oxidation is used to remove soluble iron and manganese from water.
36. Show with chemical reactions how lime treatment, sulfide treatment, and cementation are used to remove heavy metals from water.
37. How is activated carbon prepared? What are the chemical reactions involved? What is remarkable about the surface area of activated carbon?
38. How is the surface of the membrane employed involved in the process of reverse osmosis?
39. Describe with a chemical reaction how lime is used to remove phosphate from water. What are some other chemicals that can be used for phosphate removal?
40. Why is nitrification required as a preliminary step in removal of nitrogen from water by biological denitrification?
41. What are some possible beneficial uses for sewage sludge? What are some of its characteristics that may make such uses feasible?
42. Distinguish between free available chlorine and combined available chlorine in water disinfection.
43. Give one major advantage and one major disadvantage of using chlorine dioxide for water disinfection.
44. Give one major advantage and one major disadvantage of using ozone dioxide for water disinfection.
45. Discuss how soil may be viewed as a natural filter for wastes. How does soil aid waste treatment? How can waste treatment be of benefit to soil in some cases?

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