

Wastewater Treatment Plant Operator Certification Training



Module 18 The Activated Sludge Process Part IV

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Unit 1 – Nitrification and Denitrification

Learning Objectives

- Explain what nitrogen is and why it needs to be removed from wastewater.
- List five forms of nitrogen.
- Describe nitrogen's effects on receiving water.
- List the various types of nitrogen removal mechanisms and explain how they work.
- In terms of biological nitrification:
 - List the types of suspended growth reactors used.
 - Describe the mixing requirements for suspended growth reactors.
 - List the types of aeration systems used in suspended growth reactors.
 - List and explain the operating parameters required for nitrification in a suspended growth reactor.
- In terms of biological denitrification:
 - List the types of suspended growth reactors used.
 - List and explain the operating parameters required for denitrification in a suspended growth reactor.

Nitrogen

Definition



Inorganic nitrogen is an essential nutrient for plant and algae growth. Certain forms of inorganic nitrogen can be toxic to fish.

Ammonium and Ammonia

- ◆ Ammonium has the chemical formula NH_4^+ and ammonia has the chemical formula NH_3 . These two forms of nitrogen are related by the following equilibrium relationship:
$$\text{NH}_4^+ \leftrightarrow \text{NH}_3 + \text{H}^+$$
- ◆ A given total amount of ammonia nitrogen in a water sample will consist of a fraction of ammonia and ammonium. The fractions of each depend on the pH.
- ◆ As the following figure indicates, most of the ammonia nitrogen in raw domestic wastewater (or any water in the neutral pH range) will be in the form of ammonium.

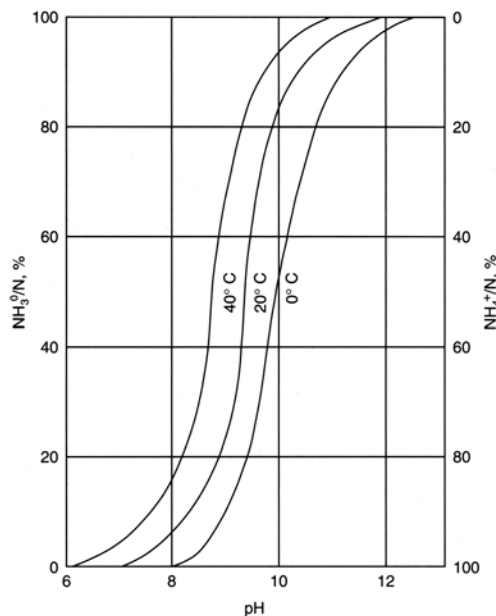


Figure 1.1 The Effect of pH and Temperature on Equilibrium Between Ammonium and Ammonia¹

- ◆ The primary sources of ammonia nitrogen in domestic wastewaters are urea and proteinaceous matter, which are readily converted by bacteria to ammonia. Ammonia nitrogen in domestic wastewater typically ranges in concentration from 12 to 50 mg/L as nitrogen, or "N."

Nitrite

- ◆ The chemical formula for nitrite is NO_2^- .
- ◆ Nitrite is formed from the oxidation of ammonia. *Nitrosomonas* bacteria oxidize ammonia to nitrite in biological wastewater treatment systems.



Oxidation is the addition of oxygen, removal of hydrogen or the removal of electrons from an element or compound.

Nitrate

- ◆ The chemical formula for nitrate is NO_3^- .
- ◆ Nitrate is formed from the oxidation of nitrite. *Nitrobacter* bacteria oxidize nitrite to nitrate in biological wastewater treatment systems. Nitrite and nitrates are not typically found in raw domestic wastewater.

Organic-N

- ◆ Organic-N in domestic wastewaters comes primarily from urea and proteinaceous matter. The organic nitrogen concentration in domestic wastewater ranges from 8 to 35 mg/L as N.

Nitrogen's Effect on Receiving Waters

- ◆ Nitrogen is an essential nutrient for the growth of protista (protozoa, algae and fungi) and plants; however, excessive quantities of nitrogen and certain forms of nitrogen discharged from wastewater treatment plants can adversely affect receiving waters and aquatic species.

Ammonia Toxicity

- ◆ Ammonia concentrations of about 3 mg/L are toxic to fish. Ammonia also imparts an oxygen demand in natural water systems because nitrifying bacteria will consume dissolved oxygen (DO) while oxidizing ammonia to nitrite and nitrate. This can result in low DO conditions that are harmful to fish and other aquatic species.

Oxygen Depletion after Algae/Plant Die-off

- ◆ Excessive nitrogen discharged from a wastewater treatment plant can result in the proliferation of algae (called algal blooms) and certain aquatic plants. This proliferation also results in an increase in the mass of dead algae and plant matter, which become a food source for bacteria. As the bacteria feed on the dead matter, the DO level drops to levels that can no longer support certain species of fish. This process is called eutrophication.

Nitrate in Groundwater

- ◆ Nitrate in excess of 10 mg/L as N in drinking water can cause methemoglobinemia, a condition which impairs the blood's ability to carry oxygen in infants. Nitrates are a concern if a wastewater treatment plant discharges to a stream or lake that is directly used or recharges groundwater used as a drinking water supply.

Chloramines from Disinfection



Chloramines are compounds formed from reactions between chlorine and ammonia in the chlorine disinfection process.

- ◆ Ammonia, as well as nitrite, present in the wastewater prior to chlorination impart a chlorine demand and can make the disinfection process more difficult.

NITROGEN AND NITROGEN REMOVAL MECHANISMS

Nitrogen Removal Mechanisms

Typical nitrogen removal efficiencies for the nitrogen removal processes used in the wastewater treatment industry are shown in the following table.

Table 1.1 The Effect of Various Treatment Operations and Processes on Nitrogen Compounds²

Treatment operation or process	Nitrogen compound			Removal of total nitrogen entering process, % ^b
	Organic nitrogen	NH ₃ -NH ₄ ⁺	NO ₃ ⁻	
Conventional treatment				
Primary	10–20% removed	No effect	No effect	5–10
Secondary	15–50% removed ^c urea → NH ₃ -NH ₄ ⁺ ^d	< 10% removed	Slight effect	10–30
Biological processes				
Bacterial assimilation	No effect	40–70% removed	Slight	30–70
Denitrification	No effect	No effect	80–90% removed	70–95
Harvesting algae	Partial transformation to NH ₃ -NH ₄ ⁺	→ Cells	→ Cells	50–80
Nitrification	Limited effect	→ NO ₃ ⁻	No effect	5–20
Oxidation ponds	Partial transformation to NH ₃ -NH ₄ ⁺	Partial removal by stripping	Partial removal by nitrification/denitrification	20–90
Chemical processes				
Breakpoint chlorination	Uncertain	90–100% removed	No effect	80–95
Chemical coagulation	50–70% removed	Slight effect	Slight effect	20–30
Carbon adsorption	30–50% removed	Slight effect	Slight effect	10–20
Selective ion exchange for ammonium	Slight, uncertain	80–97% removed	No effect	70–95
Selective ion exchange for nitrate	Slight effect	Slight effect	75–90% removed	70–90
Physical operations				
Filtration	30–95% of suspended organic N removed	Slight effect	Slight effect	20–40
Air stripping	No effect	60–95% removed	No effect	50–90
Electrodialysis	100% of suspended organic N removed	30–50% removed	30–50% removed	40–50
Reverse osmosis	60–90% removed	60–90% removed	60–90% removed	80–90

^a Adapted from Ref. 33.

^b Depends on the fraction of influent nitrogen for which the process is effective and other processes in treatment plant.

^c Soluble organic nitrogen, in the form of urea and amino acids, is reduced substantially by secondary treatment.

^d Arrow denotes "conversion to."

Biological Nitrification



Biological nitrification is the process in which *Nitrosomonas* bacteria oxidize ammonia to nitrite and *Nitrobacter* bacteria oxidize nitrite to nitrate.

- ◆ This process results in the overall conversion of ammonia to nitrate. These microorganisms are autotrophic, which means they derive their carbon source from inorganic carbon, such as carbon dioxide and bicarbonate. Most other types of organisms in activated sludge are heterotrophic, which means they derive their carbon source from the organic matter in the wastewater.
- ◆ Environmental conditions of pH, alkalinity, temperature, dissolved oxygen concentration and organic loading affect the nitrification process in activated sludge plants.

Biological Denitrification



Biological denitrification is the process in which microorganisms reduce nitrate to nitrite and nitrite to nitrogen gas.

- ◆ Heterotrophic bacteria normally present in activated sludge perform this conversion when there is no molecular oxygen or dissolved oxygen, and there is sufficient organic matter. The bacteria derive their oxygen from the oxygen contained in the nitrate. The nitrogen gas produced is in the form of nitric oxide (NO), nitrous oxide (N₂O) or nitrogen gas (N₂).
- ◆ The net removal of nitrogen is accomplished by stripping the nitrogen gas formed during denitrification out of the wastewater in a subsequent aeration process.

Ammonia Stripping



Ammonia stripping is the removal of nitrogen from wastewater when the nitrogen is in gaseous ammonia form.

- ◆ Ammonia is a volatile substance, which means that it has a tendency to leave the wastewater and enter the atmosphere.
- ◆ As discussed previously, ammonia (NH_3) and ammonium (NH_4^+) exist in equilibrium with each other based on the pH. Most of the ammonia-nitrogen in municipal wastewater is in the ammonium form because of its neutral pH range (between 6 and 8). Therefore, chemicals such as lime or sodium hydroxide must be added to raise the pH to the 10.5 to 11.5 range. This will effectively “convert” the ammonium in the wastewater to ammonia.
- ◆ The stripping effect is achieved by introducing the high pH wastewater into the top of a tower packed with fixed media (or “packing”). Air is blown into the bottom of the tower and flows in a countercurrent fashion with the incoming wastewater. The intimate contact between wastewater droplets and fresh air encourages the ammonia to volatilize from the wastewater to the exiting air stream.

Breakpoint Chlorination



Breakpoint chlorination is the chemical oxidation ammonia to nitrogen gas (N_2) by the addition of chlorine. The “breakpoint” is the chlorine dosage, which results in an increase in the free chlorine residual with increasing chlorine dosages.

- ◆ Breakpoint chlorination requires relatively high chlorine dosages per unit of ammonia present in the wastewater. In general, about 10 pounds of chlorine are required to oxidize one pound of ammonia-nitrogen.
- ◆ Because of the high chlorine demand, breakpoint chlorination is not used as the primary ammonia (or nitrogen) removal process. In activated sludge, biological methods, such as nitrification/denitrification, are used to remove the bulk of the nitrogen and breakpoint chlorination is used as a final polishing step to remove the residual nitrogen.

Ion Exchange



Ion exchange is the removal of ions from water and wastewater using vessels packed with natural or synthetic ion exchange resins, which adsorb and removed unwanted ions from the waste stream.

- ◆ The untreated waste typically enters the top of the vessels, flows downward through the resin bed, and exits near the bottom of the vessel. A naturally occurring resin called clinoptilolite is often used for ammonium-nitrogen removal.
- ◆ As a resin bed becomes *exhausted*, or its maximum ion holding capacity has been reached, it is taken offline for regeneration while another freshly regenerated bed is brought back on line. The resin bed can be regenerated by flushing it with a lime or brine solution.
- ◆ The lime solution raises the pH and converts the adsorbed ammonium to ammonia gas, which is carried out of the ion exchange vessel into an air stripper. The air stripper removes the ammonia gas. Brine can also be used to regenerate the resin bed. The use of brine results in an "exchange" of sodium ions for ammonium ions at the resin surface sites.

Land Application



Overland flow systems apply primary or secondary effluent to the surface of gently sloping sections of land with water-tolerant grasses. The wastewater travels over the land and seeps into the grass root zone, where bacteria oxidize the organic matter in the wastewater and convert ammonia nitrogen to nitrate and ultimately to nitrogen gas (denitrification).

- ◆ Most of the treated wastewater is collected in a trench or collection pipe at the bottom of the sloped section of land and the portion that does not run off the land into the collection trench percolates through the soil into the groundwater. The wastewater can be distributed to the land surface by either a sprinkler system or a distribution pipe with equally spaced holes.
- ◆ Nitrogen removal in overland flow systems is adversely affected by low temperatures. These systems can generally be operated year-round in the southern half and west coast of the U.S. Operation in other locations will require sufficient wastewater storage during cold weather (i.e., below 0 °C).

Living Systems

- ◆ Primary domestic wastewater effluent has been effectively treated by living systems consisting of water hyacinth and duckweed plant species. These plants float on the surface of constructed basins and remove nutrients such as nitrogen and phosphorus as well as carbonaceous matter from the wastewater. The water in the basins is typically about two to six feet deep.
- ◆ There are three basic types of water hyacinth treatment systems: aerobic non-aerated, aerobic aerated and facultative anaerobic.
 - Aerobic non-aerated systems are the most common hyacinth system in use today because of its excellent performance, low mosquito potential and low odors.
 - Aerobic aerated systems are used to eliminate mosquito and odor problems and have the ability to treat higher strength wastes with smaller footprints than the other hyacinth systems.
 - Facultative anaerobic systems can handle very high organic loads, but are seldom used because of odor and mosquito generation.
- ◆ Nitrogen removal is achieved by harvesting the floating plants every three to four weeks for hyacinth systems and up to once per week for duckweed systems.
- ◆ Floating aquatic plant systems are capable of removing up to 10 to 20 pounds of nitrogen and phosphorus per acre per day and up to 100 pounds of biochemical oxygen demand (BOD) per acre per day.



Biochemical Oxygen Demand (BOD) is the rate at which organisms use the oxygen in water or wastewater while stabilizing decomposable organic matter under aerobic conditions. In decomposition, organic matter serves as food for the bacteria and energy results from its oxidation.

- ◆ Water hyacinth is sensitive to cold temperatures, so the use of these systems is restricted to warm weather climates. Water hyacinth can tolerate water temperatures as low as 10 °C as long as the air temperature is at least 5 to 10 °C. Duckweed systems can tolerate wastewater temperatures as low as 7 °C and can be used seasonally throughout much of the country and year-round in warmer climates.



Review Exercise

1. List the five types of nitrogen.

a. _____

b. _____

c. _____

d. _____

e. _____

2. List seven nitrogen removal mechanisms.

a. _____

b. _____

c. _____

d. _____

e. _____

f. _____

g. _____

Biological Nitrification



Suspended growth reactors are wastewater treatment processes in which the microorganisms and bacteria treating the wastes are suspended in the wastewater being treated, such as the various modes of the activated sludge treatment process.

Suspended growth reactors are commonly used for the biological conversion of ammonia to nitrate (i.e., biological nitrification). The biological nitrification process can be classified as either single-stage or separate-stage.

- ◆ In the single-stage process, nitrification and carbonaceous oxidation (BOD removal) occur within the same basin, and the BOD₅/TKN (Total Kjeldahl Nitrogen) ratio of the primary effluent is typically greater than 5.



TKN is the sum of organic nitrogen and ammonia nitrogen. The concentration of TKN in typical domestic wastewater ranges from 20 to 85 mg/L as N.

- ◆ In the separate-stage process, carbonaceous oxidation and nitrification occur in separate tanks, and the BOD₅/TKN ratio is typically between 1 and 3.



BOD₅ is the "5-day biochemical oxygen demand." This is the industry standard for measuring the biochemical oxygen demand (BOD) of a sample. BOD is an abbreviation for BOD₅ and the two are often used interchangeably.

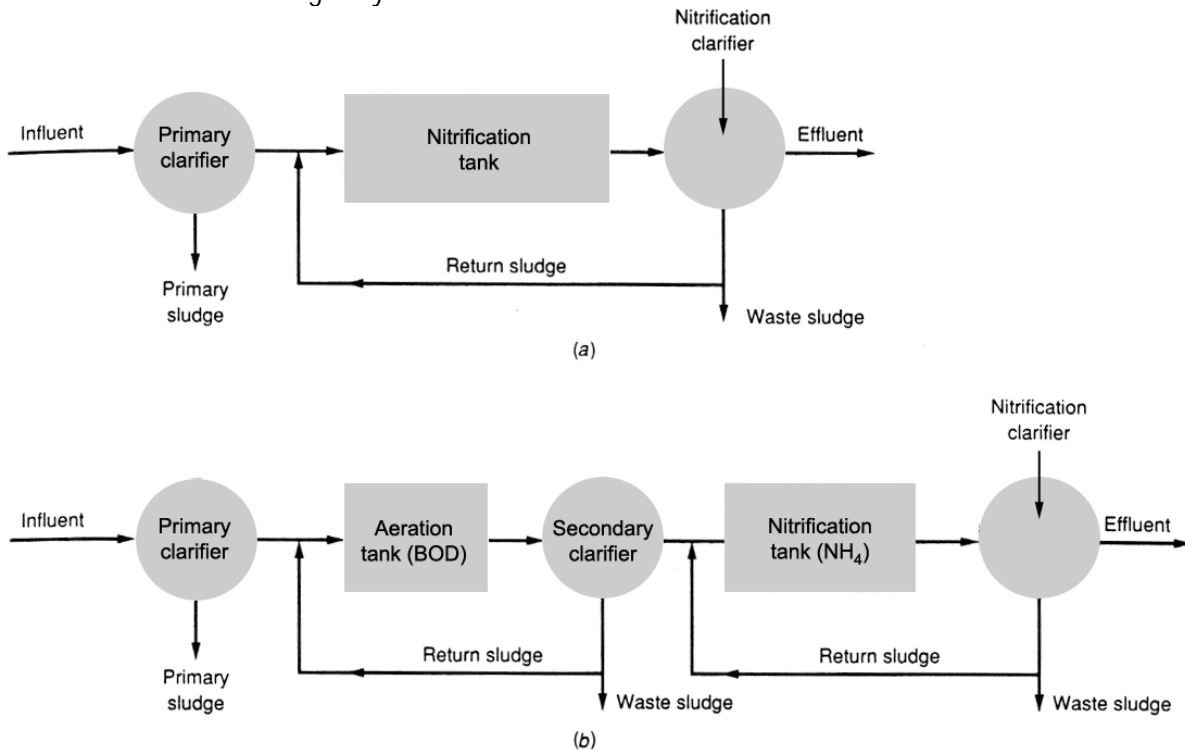


Figure 1.2 Single-stage and Separate-stage Biochemical Nitrification Processes³

Types of Suspended Growth Reactors

There are a variety of operational configurations for suspended growth reactors, but not all of them are suitable for biological nitrification.

Conventional or Plug Flow

- ◆ The long, narrow aeration basins associated with conventional activated sludge systems work well for nitrification because their plug flow hydraulic characteristic allow precise control of the hydraulic detention time, an important operational control parameter in nitrification. Care must be taken to prevent the pH level from dropping too low, as ammonia oxidation results in the consumption of alkalinity.

Complete-Mix

- ◆ In complete-mix systems, conditions eliminate problems associated with uneven distribution of dissolved oxygen and organic matter. These systems are used for nitrification, but they can be more sensitive than conventional systems to pH drops due to nitrification.

Contact Stabilization

- ◆ Most of the biomass in contact stabilization suspended growth reactors is kept in an aerated tank separate from the aeration tank. This can result in an inadequate amount of nitrifying bacteria in the aeration tank. These systems also have small aeration tanks, which have hydraulic detention times which are too short for significant nitrification to occur. Contact stabilization plants are not well suited to nitrification.

Extended Aeration

- ◆ Extended aeration plants will perform the best in regards to achieving nitrification because of their long aeration and mean cell residence times (MCRTs). The relevance of these parameters to nitrification will be discussed later in this unit.



Mean Cell Residence Time (MCRT) is the average length of time a bacterial cell remains in the system.

Step-Feed

- ◆ Step-feed aeration involves applying primary effluent at several points along the aeration tank. It can be used to provide partial, but not complete, nitrification because the detention times for the portion of influent applied at the end of the aeration tank are too low for complete nitrification to occur.

Batch Reactors

- ◆ Batch reactors, such as a sequencing batch reactor (SBR), are well suited for nitrification.

Mixing Requirements

Mixing requirements for biological nitrification and carbonaceous oxidation are the same. In other words, complete-mix basins require the entire contents of the basin to be completely mixed, while conventional plug flow basins should have minimal mixing in the direction of flow. Mixing in complete-mix basins is typically achieved through the use of mechanical aerators.

Ideal plug flow reactors have no mixing in the direction of, or perpendicular to, the flow direction. Real plug flow reactors, however, experience minor mixing in both directions due to turbulence caused by the diffused aerators.

Regardless of the type of aeration basin (i.e., complete-mix or plug flow), enough mixing must occur to prevent solids from settling on the bottom of the basin.

Types of Aeration Systems

The aeration systems used for nitrification are the same systems used in carbonaceous oxidation. The two types of aeration systems typically used are surface aerators and diffused air.

Operating Parameters to be Monitored for Nitrification

Nitrifying bacteria are present in all activated sludge systems, but they are slow-growing and have different environmental requirements than carbon-oxidizing bacteria. Environmental conditions suitable for nitrification are established by adjusting operating parameters, such as the MCRT, dissolved oxygen concentration, hydraulic retention time, Mixed Liquor Volatiles Suspended Solids (MLVSS), pH and temperature. Typical values for some of these parameters are shown in the following table.

Table 1.2 Typical Values for Operating Parameters⁴

Treatment process	Type of reactor	Design parameter				
		t_c , d ^a	θ , h ^a	MLVSS, mg/L	pH	Temperature coefficient ^b
Single-stage nitrification	Plug-flow	8–20	6–15	2,000–3,500	7.0–8.0 ^c	1.08–1.10
Denitrification ^d	Plug-flow	1–5	0.2–2	1,000–2,000 ^e	6.5–7	1.14–1.16

^a Indicated values for t_c and θ are for 20°C.

^b Temperature coefficient to be used in the equation $K_T = K_{20} \theta^{T-20}$

^c Lower values have been reported.

^d Methanol requirement can be computed using Eq. 11-18.

^e Higher values may be observed depending on the degree of solids carryover.

Note: mg/L = g/m³

MLSS/MLVSS



Mixed Liquor Suspended Solids (MLSS) are the suspended solids in the mixed liquor of an aeration tank.



Mixed Liquor Volatile Suspended Solids (MLVSS) are the organic or volatile suspended solids in the mixed liquor of an aeration tank. This volatile portion is used as a measure or indication of the microorganisms present.

- ◆ Biological nitrification requires MLSS/MLVSS concentrations similar to those in conventional activated sludge systems. A typical range in MLVSS is 2,000 to 3,500 mg/L.
- ◆ The MLVSS concentration is integrally related to the MCRT, which is a critical operational parameter in nitrification. Therefore, the MLVSS will need to be adjusted (by wasting) to achieve the desired MCRT.
- ◆ The MLVSS concentration for nitrification systems is higher than the typical MLVSS range of 1,000 to 2,000 mg/L for denitrification systems. Denitrification will be discussed in detail later in this unit.

pH

The optimal pH range for nitrification is 7.8 to 8.2; however, nitrification can occur with pH in the range of 6.5 to 9.0. The following figure demonstrates the effect of pH on the rate of nitrification at 20°C. The amount of alkalinity in the wastewater can have a significant impact on the pH level.

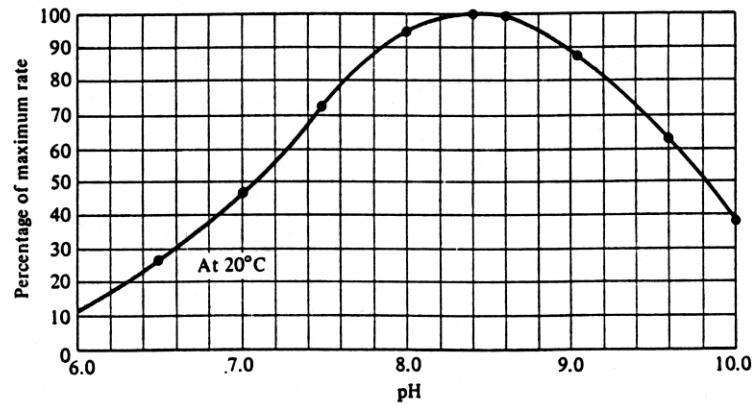


Figure 1.3 The Effect of pH on the Rate of Nitrification⁵

Alkalinity

1. Alkalinity is a measure of the wastewater's ability to neutralize an acid. The overall chemical equation for the nitrification process is as follows:
$$\text{NH}_4^+ + 1.83\text{O}_2 + 1.98\text{HCO}_3^- \rightarrow 0.021\text{C}_5\text{H}_7\text{O}_2\text{N} + 0.98\text{NO}_3^- + 1.04\text{H}_2\text{O} + 1.88\text{H}_2\text{CO}_3$$
2. From this equation, we determine that bacteria consume 7.14 mg/L (or pounds) of alkalinity (as CaCO_3) for every mg/L (or pounds) of ammonia-nitrogen ($\text{NH}_4^+\text{-N}$) oxidized.
3. Domestic wastewater typically contains sufficient alkalinity so that nitrification does not create pH problems. Effluent alkalinity should be monitored daily to ensure that a minimum level of 50 mg/L alkalinity (as CaCO_3) is maintained. An alkalinity concentration below 50 mg/L may result in pH levels below 7.0, which will adversely affect nitrification.
4. Wastewaters low in alkalinity (below 50 mg/L as CaCO_3) that results in pH levels inhibitory to nitrification may require the addition of an alkaline solution such as lime or soda ash. Some industrial wastewaters require the addition of alkalinity to sustain nitrification.



Calculation

Example: Township WWTF, which processes 1.0 MGD, is required to nitrify to meet the 2.0 mg/L ammonia discharge limit stated in their NPDES permit. A table reflecting average daily influent alkalinity and ammonia concentrations and the average daily ammonia removal requirement is presented in the table below. Using the equation provided, determine how many pounds of alkalinity are available for nitrification.

	Alkalinity	Ammonia
	mg/L	mg/L
Influent	210	50.0
Final Effluent Requirement	50	2.0
Available for Nitrification	160	---
Removal Requirement	---	48.0

Flow (MG) x concentration (mg/L) x 8.34 = lbs

1.0 MG x 160 mg/L alkalinity x 8.34 = 1,334 lbs alkalinity

Now, determine how many pounds of alkalinity are required for nitrification. Hint: Approx. 7.2 lbs of alkalinity is required for every pound of ammonia-nitrogen oxidized.

	Alkalinity		Ammonia	
	mg/L	lbs	mg/L	lbs
Influent	210	---	50.0	---
Final Effluent Requirement	50	---	2.0	---
Available for Nitrification	160	1,334	---	---
Removal Requirement	---	--	48.0	400

400 lbs ammonia removed x 7.2 lbs alkalinity = 2,880 lbs of alkalinity are required.

Based on this information, will the addition of alkalinity be required in order to achieve complete nitrification and if so how much?

2,880 lbs alkalinity required – 1,334 lbs alkalinity available = 1,546 lbs alkalinity needed.

Answer: Yes. At least 1,546 lbs of alkalinity will need to be added.



Calculation

Capital City WWTF, which processes 2.0 MGD, is required to nitrify to meet the 2.0 mg/L ammonia discharge limit stated in their NPDES permit. A table reflecting average daily influent alkalinity and ammonia concentrations and the average daily ammonia removal requirement is presented in the table below.

	Alkalinity	Ammonia
	mg/L	mg/L
Influent	415	52.0
Final Effluent Requirement	50	2.0
Available for Nitrification	365	---
Removal Requirement	---	50.0

Using the equation provided, determine how many pounds of alkalinity are available for nitrification, the pounds of ammonia removed and the pounds of alkalinity required for nitrification. Based on this information, will the addition of alkalinity be required in order to achieve complete nitrification and if so how much?

$$\text{Flow (MG)} \times \text{concentration (mg/L)} \times 8.34 = \text{lbs}$$

Temperature

5. Temperature has a significant effect on the rate of nitrification.

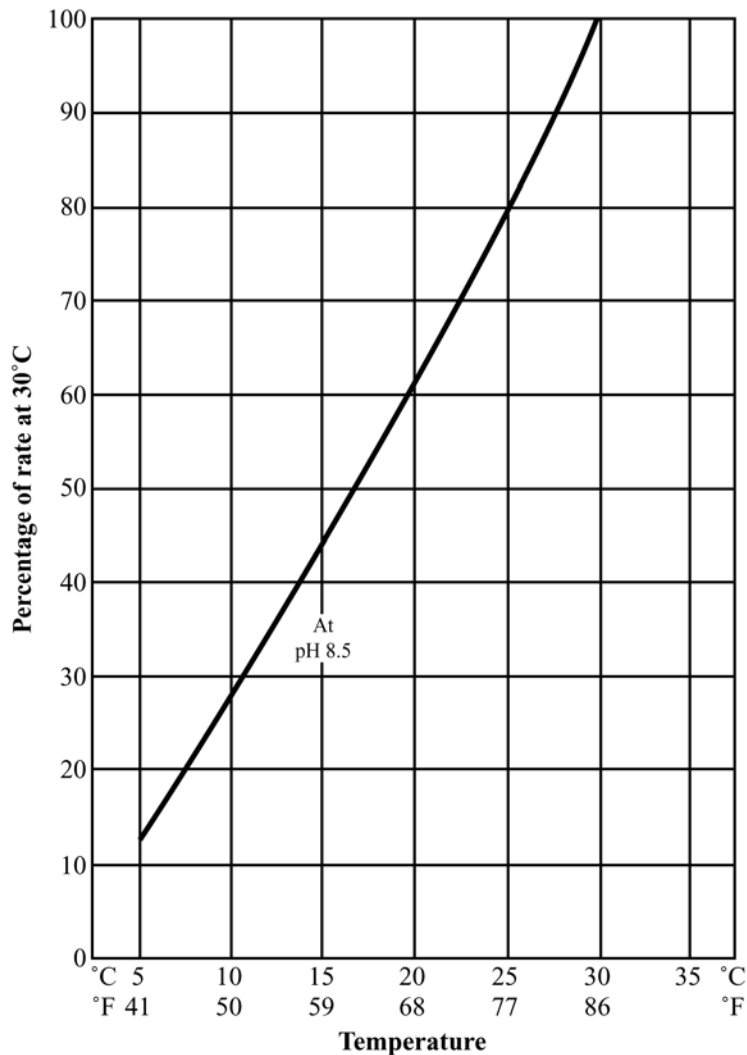


Figure 1.4 The Effect of Temperature on the Rate of Nitrification⁶

- ◆ The optimal temperature for nitrification is 60 to 95 °F (15 to 30 °C). Nitrification during the winter may require up to five times the detention time used during the summer.
- ◆ Since the temperature cannot be controlled, other parameters are adjusted to compensate for the slower nitrification rates caused by reduced temperatures. Increasing the MCRT by reducing the wasting rate, increasing the MLVSS and increasing the pH are ways to achieve complete nitrification during cold weather months. During warm weather conditions, lower pH and MLVSS concentrations will be required to achieve complete nitrification.

Dissolved Oxygen

- ◆ The dissolved oxygen (DO) concentration is one of the primary operational control parameters for biological nitrification. The oxidation of ammonia to nitrate by nitrifying bacteria requires approximately 4.6 milligrams of oxygen per milligram of ammonia oxidized. Nitrifying bacteria require dissolved DO concentrations of 2 to 4 mg/L. These DO concentrations should be maintained at all times throughout the nitrification basin. DO concentrations below 0.2 mg/L will inhibit the nitrification process.
- ◆ Because of the DO requirements, activated sludge processes are typically better suited for nitrification than systems that use lower concentrations of oxygen, such as lagoons.

Mean Cell Residence Time (MCRT)

- ◆ Mean cell residence time (MCRT) and the dissolved oxygen level are the two primary operational control parameters for biological nitrification. Single-stage biological nitrification typically requires a MCRT of 8-20 days.

Hydraulic Retention Time



Hydraulic retention time (HRT) is the average time a water molecule spends in a vessel. The theoretical HRT is equal to the volume of the vessel divided by the flow rate.

Single-stage biological nitrification typically requires an HRT of 6-15 hours.

BOD₅/TKN Ratio

- ◆ The efficiency of biological nitrification systems depends on the ratio of the BOD₅ concentration to the Total Kjeldahl Nitrogen (TKN) concentration of the wastewater entering the nitrification tank.
- ◆ The amount of nitrifying bacteria is presented in Table 1.3 as a percentage of the total biomass in the aeration tank.
- ◆ To determine the concentration of nitrifying bacteria, in mg/l, in the MLVSS you multiply the MLVSS (mg/l) by the nitrifier fraction.

Table 1.3 The Relationship Between Amount of Nitrifying Bacteria Present and BOD₅/TKN Ratio⁷

BOD₅/TKN ratio	Nitrifier fraction	BOD₅/TKN ratio	Nitrifier fraction
0.5	0.35	5	0.054
1	0.21	6	0.043
2	0.12	7	0.037
3	0.083	8	0.033
4	0.064	9	0.029

BOD:N:P Ratio

- ◆ Microorganisms in activated sludge treatment systems require an adequate supply of carbon (or BOD), nitrogen (or TKN) and phosphorus to survive and reproduce. The generally accepted ratio of BOD to nitrogen to phosphorus (BOD:N:P) for BOD reduction is 100:5:1. This ratio may be considerably different for nitrification due to the relationship between the nitrifier fraction and the BOD₅/TKN ratio discussed previously.
- ◆ For example, operating with a 100:5:1 ratio of BOD₅ to nitrogen to phosphorus is equivalent to a BOD₅/TKN ratio of 20, which would result in a very low concentration of nitrifying bacteria (i.e., off the chart on the previous table). Operating a 10:20:0.2 BOD:N:P ratio (0.5 BOD₅/TKN ratio) may be more appropriate for separate-stage nitrification processes.
- ◆ Laboratory analysis of BOD₅, TKN and phosphorus should be performed on a daily basis to check the BOD₅:TKN:phosphorus ratio. A supplemental source of phosphorus, such as phosphate fertilizer, might need to be added to the aeration tank if the phosphorus concentration is too low.

Biological Denitrification

Denitrification occurs when heterotrophic bacteria consume a carbon source under anoxic conditions in the presence of nitrate.



An **anoxic** environment is an environment in which there is very little to no free dissolved oxygen but where oxygen is present combined with other molecules, such as nitrate.

Under these conditions, the bacteria strip oxygen from nitrate, thus converting the nitrate to nitrogen gas. Denitrification of wastewater can be accomplished using a variety of different suspended growth reactor configurations. As in BOD removal and nitrification activated sludge systems, plug flow and complete-mix reactors are used for denitrification systems. In general, denitrification systems can be classified as either single- or separate-sludge systems.

Single Sludge Systems

- ◆ In single sludge systems, nitrification and denitrification occur within the same basin as shown in the bottom two diagrams in Figure 1.10. There is only one sludge recycle stream and one sludge wasting stream in single-sludge systems. Single sludge systems can be further divided into post-denitrification and pre-denitrification systems.

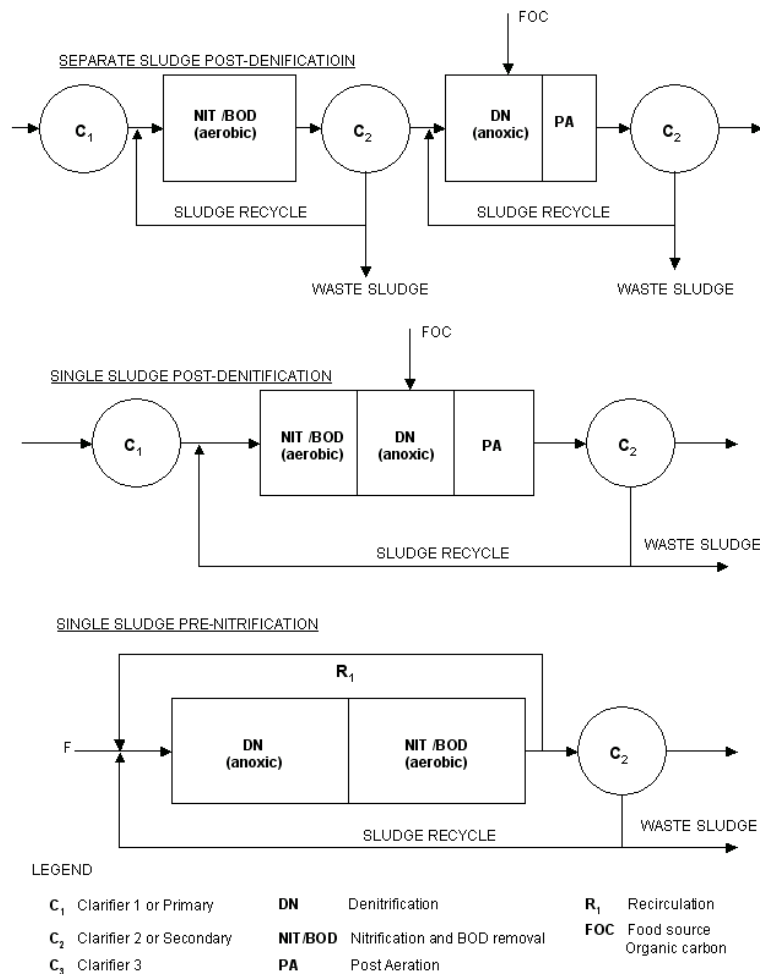


Figure 1.10 Single Sludge Systems

Post-denitrification Systems

- ◆ In post-denitrification systems, as seen in the middle diagram in the previous figure, BOD and nitrification occur first in an aerobic environment, followed by denitrification in an anoxic environment.
- ◆ Aerobic and anoxic conditions are controlled by the placement of aeration devices. For example, in a plug flow reactor, diffused aerators would be placed along the aerobic zone and no aerators would be placed in the anoxic zone.
- ◆ Post-denitrification systems have a post-aeration zone following the anoxic zone to strip the nitrogen gas from the wastewater.
- ◆ Since most of the carbon source is consumed in the BOD/nitrification stage, a supplemental carbon source, typically methanol is added to the denitrification zone to support denitrifying bacteria. Denitrifying bacteria require a methanol-to-nitrogen ratio of about 3:1.

Pre-denitrification Systems

- ◆ In pre-denitrification systems, as seen in the third diagram in previous figure, raw wastewater or primary effluent first passes through an anoxic denitrification zone and then proceeds to an aerobic combined nitrification/BOD removal zone.
- ◆ Nitrate generated from the aerobic zone is recycled to the anoxic zone, where it is converted to nitrogen gas. The nitrogen gas generated in the anoxic zone is stripped out of the wastewater in the aerobic zone.
- ◆ Some pre-denitrification systems have additional anoxic and aerobic zones following the initial aerobic zone to remove the nitrate that is not recycled back to the anoxic zone. Systems using the additional anoxic and aerobic zones are referred to as the four-stage Bardenpho process.
- ◆ Methanol is not typically used in pre-denitrification systems because the organic carbon in the influent to the anoxic zone is sufficient for the denitrifying bacteria.

Separate Sludge Systems

- ◆ In separate-sludge systems, there are separate sludge recycle and waste streams for the nitrification/BOD removal and denitrification stages. A typical separate-sludge system is shown in the first diagram in the previous figure.
- ◆ Methanol is added to the denitrification stage as a supplemental carbon source because most of the carbon in the raw wastewater is removed in the nitrification/BOD removal stage. A post-aeration step follows the anoxic denitrification zone to strip the nitrogen gas from the wastewater.

Operational Parameters

As with conventional activated sludge and nitrification systems, certain environmental conditions must be satisfied in order to achieve denitrification. These environmental conditions are controlled by adjusting operational parameters, such as the amount of available carbon, free oxygen concentration, hydraulic retention time, and mean cell retention time.

A summary of typical values for some of the operational parameters for denitrification is shown in the following table.

Table 1.8 Values for Operational Parameters for Denitrification⁸

Treatment process	Type of reactor	Design parameter				
		θ_c , d ^a	θ , h ^a	MLVSS, mg/L	pH	Temperature coefficient ^b
Single-stage nitrification	Plug-flow	8–20	6–15	2,000–3,500	7.0–8.0 ^c	1.08–1.10
Denitrification ^d	Plug-flow	1–5	0.2–2	1,000–2,000 ^e	6.5–7	1.14–1.16

^a Indicated values for θ_c and θ are for 20°C.

^b Temperature coefficient to be used in the equation $K_T = K_{20} \theta^{T-20}$

^c Lower values have been reported.

^d Methanol requirement can be computed using Eq. 11-18.

^e Higher values may be observed depending on the degree of solids carryover.

Note: mg/L = g/m³

Temperature

- ◆ Denitrification is a biological process and is therefore dependent on the wastewater temperature. The rate of denitrification increases with increasing temperature.
- ◆ The effect of temperature on the denitrification rate can be seen from the following relationship. In this relationship, the growth rate at 20°C is used as the baseline.

$$P = 0.25 T^2$$

where

P = percent of denitrification growth rate at 20°C
T = wastewater temperature, °C



Climates with large temperature variations can have a significant impact on denitrification. For example, the denitrification reactor volume at 10 °C would be about four times the volume required at 20 °C to achieve the same degree of nitrification. Why do you think this is the case?

Carbon Source

- ◆ Denitrifying bacteria require an adequate supply of carbon as they break down nitrate into oxygen and nitrogen gas. The general rule of thumb is that the wastewater to be denitrified should have a methanol-to-nitrogen (nitrate) ratio of 3:1. As discussed previously, methanol is typically added to the denitrification stages in single-sludge post-denitrification and separate-sludge systems.
- ◆ Nitrate concentrations in the influent to the denitrification stages should be monitored daily so that the methanol dose can be adjusted if necessary. Methanol addition is typically required if the total effluent nitrogen limit is less than 7.5 mg/L.

Oxygen

- ◆ The absence of free oxygen is crucial to the denitrification process. The rate of denitrification and the specific growth rate of denitrifying bacteria will decrease linearly, starting at 0.3 mg/L, with increasing dissolved oxygen (DO) concentration and will reach zero when the DO concentration reaches 1 mg/L. The concentration of free oxygen is minimized by not aerating the wastewater in the denitrification stages.

Mixing

- ◆ Mixing requirements for denitrification and conventional activated sludge systems are the same and depend on the type of reactor used. For example, ideal plug flow reactors require minimal mixing along the direction of flow and complete mixing perpendicular to the flow, whereas ideal complete-mix reactors require complete mixing throughout the reactor. Both types of reactors are used for denitrification systems.

Hydraulic Retention Time (HRT)

- ◆ HRT is the theoretical average length of time a water molecule remains in a basin and is equal to the volume of the basin divided by the flow rate through the basin.
- ◆ The required HRT for denitrification depends on the denitrification rate, which depends on several parameters, such as the wastewater temperature, DO concentration, nitrate concentration and organic carbon concentration.
- ◆ As explained earlier, lower temperatures result in decreased denitrification rates, which require longer HRTs to achieve the same degree of denitrification. Typical HRTs for separate-sludge denitrification systems range from 0.2 to 2 hours.

Sludge Age



Sludge age, or **MCRT**, is the average length of time a bacterial cell remains in the system. The typical MCRT for separate-sludge denitrification systems ranges from 1 to 5 days.

Nitrogen Gas Separation Step

- ◆ Biological denitrification will result in the conversion of nitrate to nitrogen gas. In order to complete the nitrogen removal process, the nitrogen gas must be stripped from the wastewater. This is typically done in an aerated chamber following the anoxic, or denitrification, zone.

**Key Points for Unit 1 – Nitrification and Denitrification.**

- Nitrogen discharges can create an environment that promotes plant and algae growth and some forms of nitrogen ammonia can be toxic to fish.
- It may be necessary to reduce the total nitrogen content of wastewater effluent before it is released.
- Total nitrogen reduction can be accomplished using biological, chemical or physical methods depending on the nature of the nitrogen compounds in the wastewater.
- The presence of ammonia and nitrite in wastewater greatly increases the amount of chlorine dosage needed to reach the chlorine breakpoint.
- Temperature, pH, alkalinity, dissolved oxygen concentrations and organic loading can have significant impacts on wastewater processes.
- DO concentrations below 0.2 mg/L will inhibit the nitrification process.
- The absence of free oxygen (an anoxic environment) is crucial to the denitrification process.
- Wastewater treatment processes can be designed using living plants such as hyacinth and duck weed.
- Methanol can be added to wastewater to provide a source of carbon if needed to support the denitrification process.

**Exercise for Unit 1 – Nitrification and Denitrification**

1. MCRT is the abbreviation for _____.
2. The two types of aeration systems used in nitrification processes are _____ and _____.
3. The optimal pH range for biological nitrification is _____ to _____.
4. Nitrification in the winter months may require up to five times the detention time used during the summer.
 - a. True
 - b. False
5. Single stage biological nitrification typically requires a MCRT of _____ to _____ days.
6. For biological nitrification to proceed efficiently, there must be an adequate supply of carbon, nitrogen, and phosphorous in the wastewater. If the phosphorus level is too low, it may be remedied by adding a phosphate fertilizer to the aeration tank.
 - a. True
 - b. False
7. In a denitrification process, it may be necessary to add a carbon source such as methanol if the total effluent nitrogen limit is less than _____ mg/L.
8. List the four types of suspended growth biological nitrification reactors that are commonly used.
 - a. _____
 - b. _____
 - c. _____
 - d. _____

9. Given the following data, determine how many pounds of alkalinity are available for nitrification, the pounds of ammonia removed and the pounds of alkalinity required for nitrification. Based on this information, is there adequate alkalinity to achieve complete nitrification?

Influent flow = 1.5 MGD

Influent ammonia nitrogen = 40 mg/L

Effluent ammonia nitrogen = 2 mg/L

Alkalinity available for nitrification = 160 mg/L

¹ John G.M. Gonzales, "Chapter 6: Nitrogen Removal," in *Advanced Waste Treatment*, (Sacramento, CA: California State University, Sacramento Foundation, 1998), p. 508.

² George Tchobanoglous and Frank Burton, *Wastewater Engineering: Treatment, Disposal, Reuse*, 3rd Edition, (New York, NY: Irwin/McGraw-Hill, 1991), pp. 692-693.

³ Tchobanoglous, p. 697.

⁴ Tchobanoglous, p. 722.

⁵ John William Clark, Warren Viessman, Jr., and Mark J. Hammer, *Water Supply and Pollution Control*, (New York, NY: IEP-A Dun-Donnelley Publisher, 1977), p. 741.

⁶ Clark et al, p. 740.

⁷ Tchobanoglous, p. 697.

⁸ Tchobanoglous, p. 722.

Unit 2 – Biological Phosphorus Removal

Learning Objectives

- Explain what phosphorus is and why it needs to be removed from wastewater.
- List three forms of phosphorus.
- Explain the effect of phosphorus on receiving water.
- List three phosphorus removal mechanisms and explain how they work.

What is Phosphorus?

Along with nitrogen, phosphorus is an essential nutrient for algae and plant growth.

Three Forms of Phosphorus

Orthophosphates

- ◆ Orthophosphates come in the form of PO_4^{3-} , HPO_4^{2-} , H_2PO_4^- , and H_3PO_4 .
- ◆ In the neutral pH range, most of the orthophosphate will be in the form of H_2PO_4^- and HPO_4^{2-} .
- ◆ Phosphorus in the orthophosphate form is readily metabolized by bacteria and algae without further breakdown.

Polyphosphate (P_2O_7)

- ◆ Polyphosphates are complex molecules consisting of two or more phosphorus atoms, oxygen atoms and sometimes hydrogen atoms.
- ◆ Polyphosphates must be hydrolyzed (broken down) to the orthophosphate form before they can be readily metabolized by microorganisms.

Organically Bound Phosphorus

- ◆ Organically-bound phosphorus is phosphorus contained in cellular tissue and other organic matter.
- ◆ Like polyphosphates, organically-bound phosphorus must undergo hydrolysis before it can be readily metabolized by microorganisms.
- ◆ The typical domestic raw wastewater contains from 4 to 15 mg/L of total phosphorus, with greater than 60% of the total phosphorus in the inorganic form (i.e., orthophosphates and polyphosphates).

Effects of Phosphorus on Receiving Water

Phosphorus is usually the limiting nutrient, which means that there is usually plenty of nitrogen in aquatic environments to support the growth of excess algae, but a shortage of phosphorus prevents the excessive growth.

Phosphorus discharges to surface waters from wastewater treatment plants (and non-point source runoff) can result in the proliferation of algae. Excessive algae can cause taste and odor problems in drinking water supplies. Decaying algae can deplete the dissolved oxygen level, which can kill fish and other aquatic wildlife.

Biological Phosphorus Removal – A/O Process – Mainstream Treatment



The **A/O process** is a proprietary biological treatment process for phosphorus removal.

- ◆ Biological phosphorus removal is accomplished by the absorption of orthophosphates, polyphosphates and organic phosphorus in untreated wastewater into bacterial cell tissue and subsequently removing the cell tissue from the wastewater.
- ◆ Absorbing phosphorus into bacterial cell tissue is accomplished by subjecting the bacteria to alternating anaerobic and aerobic (or oxic) environments. In response to the alternating anaerobic and oxic environments, the bacteria absorb and store more phosphorus than they would under normal aerobic conditions.



Anaerobic is a condition in which both dissolved oxygen and molecularly bound oxygen, such as in nitrate, is absent.

- ◆ Phosphorus-accumulating bacteria are heterotrophic, meaning they derive their carbon source from organic matter. They are also facultative, meaning they can survive in both aerobic and anaerobic environments. In order to survive in anaerobic environments, phosphorus-accumulating bacteria use stored polyphosphates as their energy source. During this survival process, stored polyphosphates are converted to and released as soluble phosphates. When these bacteria are subsequently subjected to aerobic conditions, they rapidly uptake soluble phosphates to replenish their phosphorus stores. This is called “luxury uptake.”

The introduction of dissolved oxygen, or molecularly bound oxygen such as nitrate, into the anaerobic environment will inhibit the release, and subsequent uptake, of phosphorus.

- ◆ A process flow schematic of the A/O process is shown in the following figure:

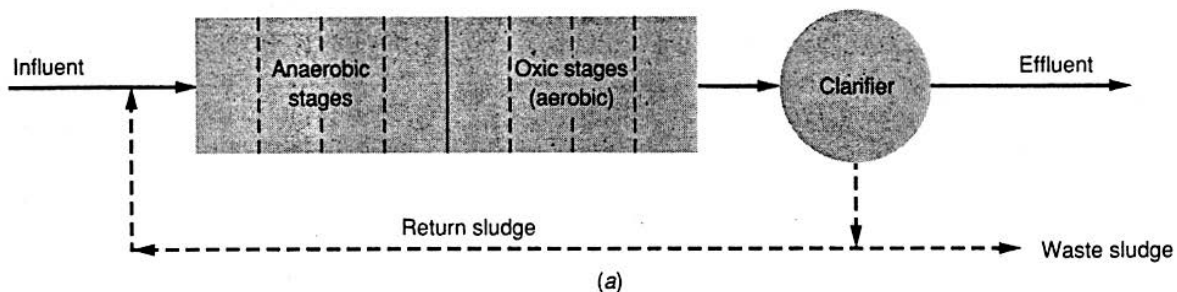


Figure 2.1 The A/O Process¹

- ◆ In the A/O process, influent wastewater first passes through an anaerobic stage, where phosphorus-accumulating bacteria release stored phosphorus into the wastewater in the form of soluble phosphates. Released phosphorus and soluble phosphorus from the influent are absorbed by the phosphorus-accumulating bacteria in the aerobic stage. Phosphorus is ultimately removed from the wastewater by wasting the sludge from the secondary clarifier.

PHOSPHORUS REMOVAL MECHANISMS

- ◆ The A/O process is a “mainstream” phosphorus removal process because phosphorus removal occurs along the main plant flow stream as opposed to a sidestream. The lime precipitation, or PhoStrip process, is an example of a “sidestream” phosphorus removal process and will be discussed in the next section.
- ◆ Typical design information for the A/O process is shown in the following table:

Table 2.1 Design Information for the A/O Process²

Design parameter	Units	Process		
		A/O	PhoStrip	Sequencing batch reactor
Food-to-microorganism ratio (F/M)	lb BOD/ lb MLVSS · d	0.2 – 0.7	0.1 – 0.5	0.15 – 0.5
Solids retention time, θ_c	d	2–25	10–30	
MLSS	mg/L	2,000–4,000	600–5,000	2,000–3,000
Hydraulic retention time, θ	h			
Anaerobic zone		0.5–1.5	8–12	1.8–3
Aerobic zone		1–3	4–10	1.0–4
Return activated sludge	% of influent	25–40	20–50	
Internal recycle	% of influent		10–20 ^b	

^a Adapted from Ref. 41.

^b Stripper underflow.

- ◆ The phosphorus removal efficiency of the A/O process depends primarily on the ratio of the BOD concentration to the phosphorus concentration in the influent. Effluent soluble phosphorus concentrations as low as 1 mg/L are possible when this ratio exceeds 10:1.

Lime Precipitation – PhoStrip Process – Sidestream Treatment

The PhoStrip process is a proprietary biological phosphorus removal process. A process flow schematic of the PhoStrip process is shown in the following figure.

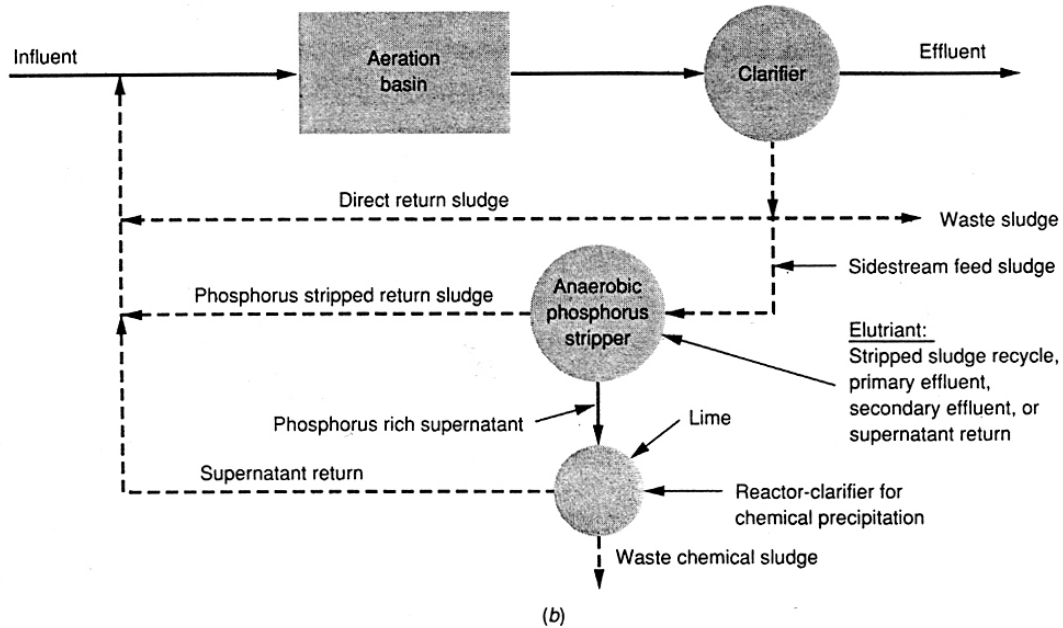


Figure 2.2 The PhoStrip Process³

- ◆ The PhoStrip process is a “sidestream” phosphorus removal process because phosphorus removal occurs in a sidestream as opposed to the main treatment plant flow.
- ◆ The process works as follows:
 - Influent enters an aeration basin where phosphorus-accumulating bacteria uptake soluble phosphates. The bacteria are then separated from the wastewater in the secondary clarifier.
 - A portion of the sludge from the secondary clarifier is recycled back to the aeration basin and the remaining sludge is directed to an anaerobic basin where stored phosphorus is released.
 - Phosphorus stripped sludge is returned to the beginning of the aeration basin and the phosphorus-rich supernatant from the anaerobic basin is directed to a reactor-clarifier.
 - Lime is added to the reactor-clarifier to precipitate the soluble phosphorus.
 - Phosphorus precipitate is wasted from the reactor clarifier and the supernatant from the clarifier is returned to the influent of the aeration basin.

- ◆ Typical design parameters for the PhoStrip process are shown in the following table:

Table 2.2 Design Information for PhoStrip Process⁴

Design parameter	Units	Process		
		A/O	PhoStrip	Sequencing batch reactor
Food-to-microorganism ratio (F/M)	lb BOD/ lb MLVSS · d	0.2 – 0.7	0.1 – 0.5	0.15 – 0.5
Solids retention time, θ_c	d	2–25	10–30	
MLSS	mg/L	2,000–4,000	600–5,000	2,000–3,000
Hydraulic retention time, θ	h			
Anaerobic zone		0.5–1.5	8–12	1.8–3
Aerobic zone		1–3	4–10	1.0–4
Return activated sludge	% of influent	25–40	20–50	
Internal recycle	% of influent		10–20 ^b	

^a Adapted from Ref. 41.

^b Stripper underflow.

- ◆ The PhoStrip process is capable of producing an effluent total phosphorus concentration of less than 1.5 mg/L.

Aluminum Sulfate or Ferric Chloride Flocculation and Precipitation

- ◆ Coagulation is achieved by the addition of a chemical that neutralizes the negative surface charge of suspended particles. The neutralized surface charge allows suspended particles to come together rather than be repelled from each other.
- ◆ Flocculation is achieved by gently mixing coagulated wastewater to promote the agglomeration of smaller particles into larger particles.
- ◆ Sedimentation occurs when the flocculated particles agglomerate into particles large enough to settle by gravity.
- ◆ Often, a sufficient quantity of coagulant, such as alum or ferric chloride, is added in the coagulation stage to precipitate a target compound, such as soluble phosphates. The target compounds, such as soluble phosphorus, are also removed by adsorption onto metal hydroxide precipitates formed during the coagulation and flocculation stages.
- ◆ Chemicals commonly used for phosphorus removal include lime and metal salts, such as aluminum sulfate (or alum) and ferric chloride. Polymers are commonly used in conjunction with metal salts as flocculation aids.

Phosphorus Removal Using Lime

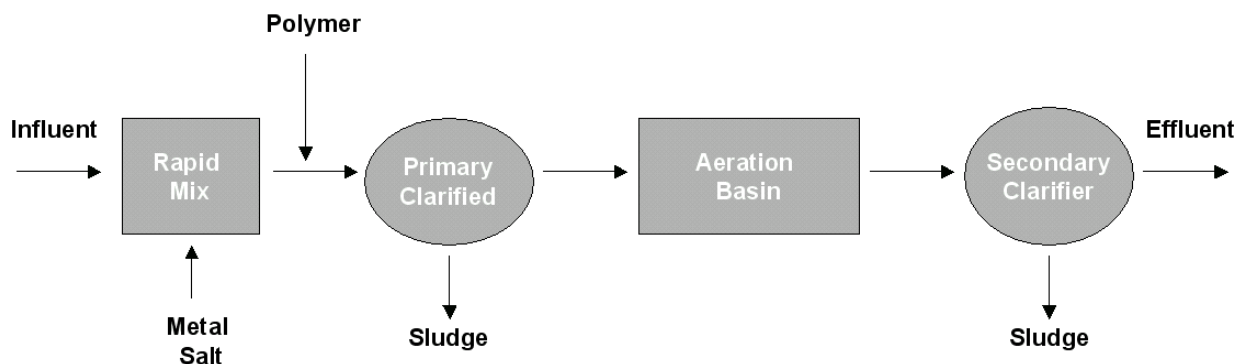
- ◆ In order to remove phosphorus using lime, a sufficient quantity of lime must be added to the wastewater to raise the pH to about 11. This is because the lime will first react with the alkalinity in the wastewater to form calcium carbonate before it reacts with soluble phosphates.
- ◆ Therefore, lime dosages for phosphorus removal typically depend on the alkalinity, not on the phosphorus concentration. Lime dosages typically range from 1.4 to 1.5 times the total alkalinity expressed as CaCO_3 .
- ◆ The high pH involved in lime precipitation makes lime treatment in or immediately after the aeration tank undesirable. The pH is typically lowered following lime precipitation by injecting carbon dioxide into the wastewater.

Phosphorus Removal Using Metal Salts

- ◆ Metal salts commonly used for phosphorus removal include:
 - Aluminum sulfate (or alum).
 - Ferric chloride.
 - Ferric sulfate.
 - Ferrous sulfate.

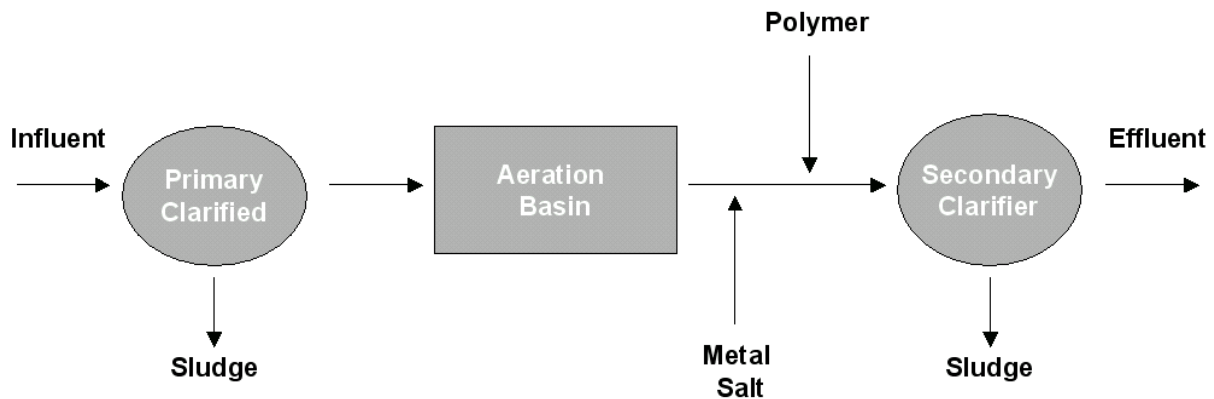
- ◆ Metal salts can be applied for phosphorus removal at the following locations within the plant:
 - Primary sedimentation facilities.
 - Secondary treatment facilities (i.e., aeration tank).
 - Secondary clarifiers.

- ◆ Metal salts added to primary sedimentation facilities will remove soluble phosphates via formation of metal-phosphorus precipitates, but will also remove particulate phosphorus, suspended solids and BOD.
 - Polymer is sometimes added after metal salt addition to aid the settling process.
 - Typical metal salt dosages range from one to three moles of metal ions to 1 mole of phosphate ion, resulting in phosphorus removals as high as 95%.
 - The addition of metal salts will consume alkalinity, so the pH may drop too low if insufficient alkalinity is present. Optimal pH for phosphate precipitation is in the 5 to 7 range from aluminum and iron salts.

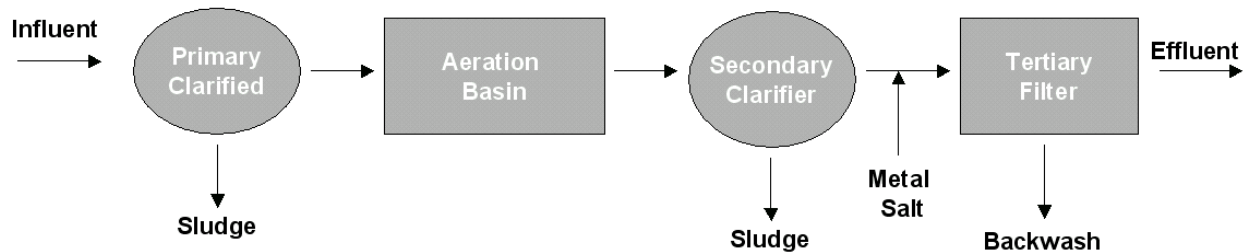


PHOSPHORUS REMOVAL MECHANISMS

- ◆ Metal salts can also be added directly to the aeration basin or the influent to the secondary clarifier.
 - Optimal phosphate precipitation using alum or ferric chloride occurs within a pH range of about 5 to 7, which is compatible with the biological processes occurring within the aeration tank.
 - Phosphorus is removed from the liquid phase by precipitation and adsorption and removed from the entire system with the wasted sludge.



- ◆ Polymers in conjunction with metal salts can be added to the wastewater in or immediately following the secondary clarifier.
 - Polymers are typically added to the mixing zone of the secondary clarifier, prior to a static or dynamic mixer or in an aerated channel. In all cases, the polymer is added after the addition of metal salt.
 - Onsite testing, either full-scale or bench-scale, must be conducted to determine the need for polymer addition.





Key Points for Unit 2 – Biological Phosphorus Removal

- Phosphorus is an essential nutrient for plant and algae growth, but excessive phosphorus can lead to algal blooms which may create taste and odor problems in drinking water supplies.
- The A/O process involves both anaerobic and oxic (aerobic) stages.
- The A/O process is called a “mainstream” process because the phosphorus removal occurs along the main plant flow stream as opposed to a “sidestream” removal process.
- In the A/O process, the introduction of dissolved oxygen, or molecularly bound oxygen such as nitrate, into the anaerobic environment will inhibit the release, and subsequent uptake, of phosphorus.
- The PhoStrip biological phosphorus removal process uses lime addition to remove phosphorus in a sidestream flow through a reactor-clarifier.
- When using lime to remove phosphorus, the pH must be raised to about 11.
- Metal salts such as aluminum phosphate (alum) and ferric chloride can be used to precipitate and remove phosphorous within the wastewater treatment process.



Exercise for Unit 2 – Biological Phosphorus Removal

1. List the three forms of phosphorus considered important for wastewater.
 - a. _____
 - b. _____
 - c. _____

2. List four metal salts that can be used in treating water for phosphorus removal.
 - a. _____
 - b. _____
 - c. _____
 - d. _____

3. Using lime to remove phosphorus requires that the wastewater be raised to a pH of about 11. After phosphorous removal, _____ can be injected into the water to lower the pH.

4. How do the three phosphorus removal mechanisms differ?

¹George Tchobanoglous and Frank Burton, *Wastewater Engineering: Treatment, Disposal, Reuse*, 3rd Edition, (New York, NY: Irwin/McGraw-Hill, 1991), p. 728.

²Tchobanoglous, p. 729.

³Tchobanoglous , p.728.

⁴Tchobanoglous, p. 729.

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Unit 3 – Combined Nitrogen and Phosphorus Removal or Biological Nutrient Removal (BNR)

Learning Objectives

- Explain how the A²O process works.
- Explain how the Bardenpho process works.
- Explain how the processes are controlled.

The combined removal of carbon, nitrogen and phosphorus can be achieved by several biological treatment processes. Two common biological treatment processes are the A²O and Bardenpho processes.

The A²O process is a modification of the A/O phosphorus removal process to include an anoxic stage for denitrification. A flow schematic of the A²O process is shown in the following figure.

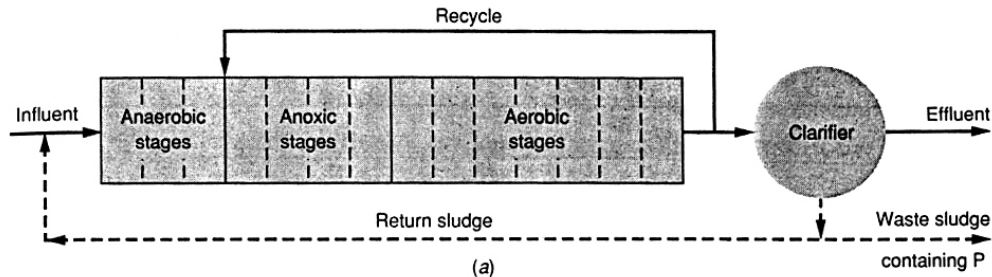


Figure 3.1 Combined Biological Nitrogen and Phosphorus Removal Processes¹

◆ Typical operating parameters for the A²O process are shown in the following table.

Table 3.1 Typical Design Information for Combined Removal of Nitrogen and Phosphorus by Biological Processes²

Design parameter	Units	Process			
		A ² O	Bardenpho (5-stage)	UCT	VIP
Food-to-microorganism ratio (F/M)	lb BOD/ lb MLVSS · d	0.15–0.25	0.1–0.2	0.1–0.2	0.1–0.2
Solids retention time, θ_c	d	4–27	10–40	10–30	5–10
MLSS	mg/L	3,000–5,000	2,000–4,000	2,000–4,000	1,500–3,000
Hydraulic retention time, θ	h				
Anaerobic zone		0.5–1.5	1–2	1–2	1–2
Anoxic zone – 1		0.5–1.0	2–4	2–4	1–2
Aerobic zone – 1		3.5–6.0	4–12	4–12	2.5–4
Anoxic zone – 2			2–4	2–4	
Aerobic zone – 2			0.5–1		
Return activated sludge	% of influent	20–50	50–100	50–100	50–100
Internal recycle	% of influent	100–300	400	100–600	200–400

^a Adapted from Refs. 11, 27, and 41.

◆ The A²O process is capable of producing an effluent phosphorus concentration of 2 mg/L without tertiary filtration and less than 1.5 mg/L with tertiary filtration.

Phase 1: Anaerobic

- ◆ In this stage, phosphorus release occurs.
- ◆ The influent first enters an anaerobic stage where the polyphosphates stored in bacterial cells are converted to phosphates and released to the wastewater. The hydraulic retention time (HRT) in the anaerobic stage ranges from 0.5 to 1.5 hours.

Phase 2: Anoxic

- ◆ In this stage, the wastewater then enters an anoxic stage, where denitrification occurs. Wastewater from the end of the aerobic stage is recycled to the beginning of the anoxic stage and provides bound-oxygen in the form of nitrate to the denitrifying bacteria. The HRT in the anoxic stage is about 0.5 to 1.0 hours.

Phase 3: Aerobic

- ◆ This final stage is an aerobic stage. Nitrogen gas formed in the anoxic stage is liberated to the atmosphere, carbonaceous material is oxidized, luxury phosphorus uptake occurs and ammonia is oxidized to nitrate. The HRT of the final stage is about 3.5 to 6.0 hours.

The four-stage proprietary Bardenpho process described earlier for achieving carbon and nitrogen removal can be modified for combined carbon, nitrogen and phosphorus removal by adding an anaerobic stage prior to the first anoxic stage. This process modification results in the proprietary five-stage Bardenpho process, shown schematically in the following figure.

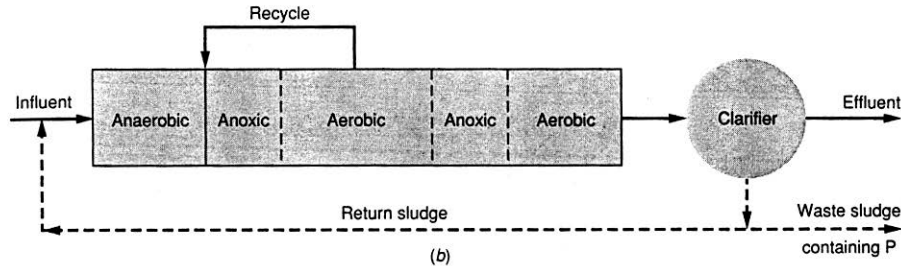


Figure 3.2 Schematic of Bardenpho Process³

Phase 1: Anaerobic

- ◆ Influent first enters an anaerobic stage where phosphorus-accumulating bacteria release stored phosphorus to the wastewater. Ammonia passes through the anaerobic stage untreated.
- ◆ The hydraulic retention time (HRT) for this stage is about 1 to 2 hours.

Phase 2: Anoxic

- ◆ Wastewater from the anaerobic stage flows into an anoxic stage where the first stage of denitrification occurs.
- ◆ This stage is anoxic because it has no free oxygen and the only form of oxygen supplied is from the nitrate in the recycle stream from the next stage. Denitrifying bacteria metabolize the nitrate and convert it to nitrogen gas as they consume the organic matter in the wastewater. Ammonia passes through this stage untreated.
- ◆ The phosphorus released during the previous stage also passes through this stage.
- ◆ The hydraulic retention time (HRT) for this stage is about 2 to 4 hours.

Phase 3: Aerobic

- ◆ In this stage, heterotrophic bacteria metabolize free oxygen supplied by the aerators as they consume the remaining organic matter originating from the raw wastewater.
- ◆ Autotrophic nitrifying bacteria convert ammonia to nitrate while deriving their carbon source from the alkalinity in the wastewater. Nitrate produced in this stage is recycled to the second stage to supply the oxygen required for the denitrifying bacteria.
- ◆ Phosphorus-accumulating bacteria uptake the phosphorus released in first stage and the residual phosphorus from the influent in a process called "luxury uptake."
- ◆ Aeration of the wastewater in this stage liberates the nitrogen gas originating from stage two.
- ◆ The hydraulic retention time (HRT) for this stage is about 4 to 12 hours.

Phase 4: Anoxic

- ◆ The second stage of denitrification occurs in this stage. Nitrate from stage three that is not recycled to stage two enters this stage for denitrification.
- ◆ At this point, most of the organic matter originating from the influent wastewater has been consumed. Therefore, the carbon source required by the denitrifying bacteria in this stage is supplied by dead and decaying bacterial cells. The consumption of dead and decaying bacterial cells by activated sludge bacteria is called endogenous respiration.
- ◆ The phosphorus-accumulating bacteria hold onto their phosphorus stores in this stage because it is not anaerobic; however, some phosphorus will be released due to endogenous respiration.
- ◆ The hydraulic retention time (HRT) for this stage is about 2 to 4 hours.

Phase 5: Aerobic

- ◆ The final stage is aerated to liberate the nitrogen gas originating from the prior denitrification stage.
- ◆ Phosphorus-accumulating bacteria will uptake residual phosphorus released from the previous stage. From this point on, it is important to maintain aerobic conditions so that the phosphorus release does not occur.

- ◆ The hydraulic retention time (HRT) for this stage is about 0.5 to 1 hours.
- ◆ The sludge from the mixed liquor from the last stage is separated in a clarifier. A portion of the sludge from the clarifier underflow is wasted and the remainder is returned to the influent.



Explain the difference between the A²O process and the Bardenpho process.

Biological nutrient removal processes are controlled by maintaining process control parameters, such as mean cell residence time (MCRT), return activated sludge (RAS) recycle rate, mixed-liquor suspended solids (MLSS) concentration and recycle rate, and the food-to-microorganism (F/M) ratio. Typical values for these control parameters for the A²O and five-stage Bardenpho processes are shown in the following table.

Design parameter	Units	Process	
		A ² O	Bardenpho (5-stage)
Food-to-microorganism ratio (F/M)	lb BOD / lb MLVSS · d	0.15 – 0.25	0.1 – 0.2
Solids retention time, θ_c	d	4 – 27	10 - 40
MLSS	mg/l	3000 – 5000	2000 – 4000
Hydraulic retention time, θ	h		
Anaerobic zone		0.5 – 1.5	1 – 2
Anoxic zone – 1		0.5 – 1.0	2 – 4
Aerobic zone – 1		3.5 – 6.0	4 – 12
Anoxic zone – 2			2 – 4
Aerobic zone – 2			0.5 – 1
Return activated sludge	% of influent	20 – 50	50 – 100
Internal recycle	% of influent	100 – 300	400

Table 3.2 Typical Design Information for Combined Removal of Nitrogen and Phosphorus by Biological Processes

Mean Cell Residence Time (MCRT)

- ◆ Typical MCRTs for the A²O and Bardenpho processes are 4-27 days and 10-40 days, respectively.

Return Activated Sludge (RAS) Recycle Rate

- ◆ The return activated sludge (RAS) recycle rates for the A²O and Bardenpho processes range from 20-50 and 50-100 percent of the plant influent flow rate, respectively.

MLSS Concentration and Recycle Rate

- ◆ The MLSS concentrations for the A²O and Bardenpho processes range from 3,000-5,000 mg/L and 2,000-4,000 mg/L, respectively.
- ◆ The MLSS recycle, or internal recycle, for the A²O and Bardenpho processes range from 100-300 percent and 400 percent of the plant influent flow, respectively.

F/M Ratio

- ◆ The F/M ratios for the A²O and Bardenpho processes range from 0.15-0.25 lb BOD/lb MLVSS-day and 0.1-0.2 lb BOD/lb MLVSS-day, respectively.

Other Parameters

Other parameters that are important in the control of biological nutrient removal processes are dissolved oxygen (DO), alkalinity and pH.

- ◆ There should be no DO in the anaerobic or anoxic stages. Biological nitrification requires 4.6 milligrams of oxygen per milligram of ammonia-nitrogen oxidized to nitrate and a residual DO in the aeration tank of 2 to 4 mg/L.
- ◆ 7.2 milligrams of alkalinity expressed as CaCO₃ are consumed per milligram of ammonia-nitrogen oxidized to nitrate. Insufficient alkalinity in the aeration tank may result in a pH below 7.2, which is inhibitory to nitrification. Maintaining a residual alkalinity concentration of 25 to 50 mg/L as CaCO₃ will usually result in a pH range that is suitable for nitrification. The optimum pH ranges for various chemical and biological processes is shown in the following figure.

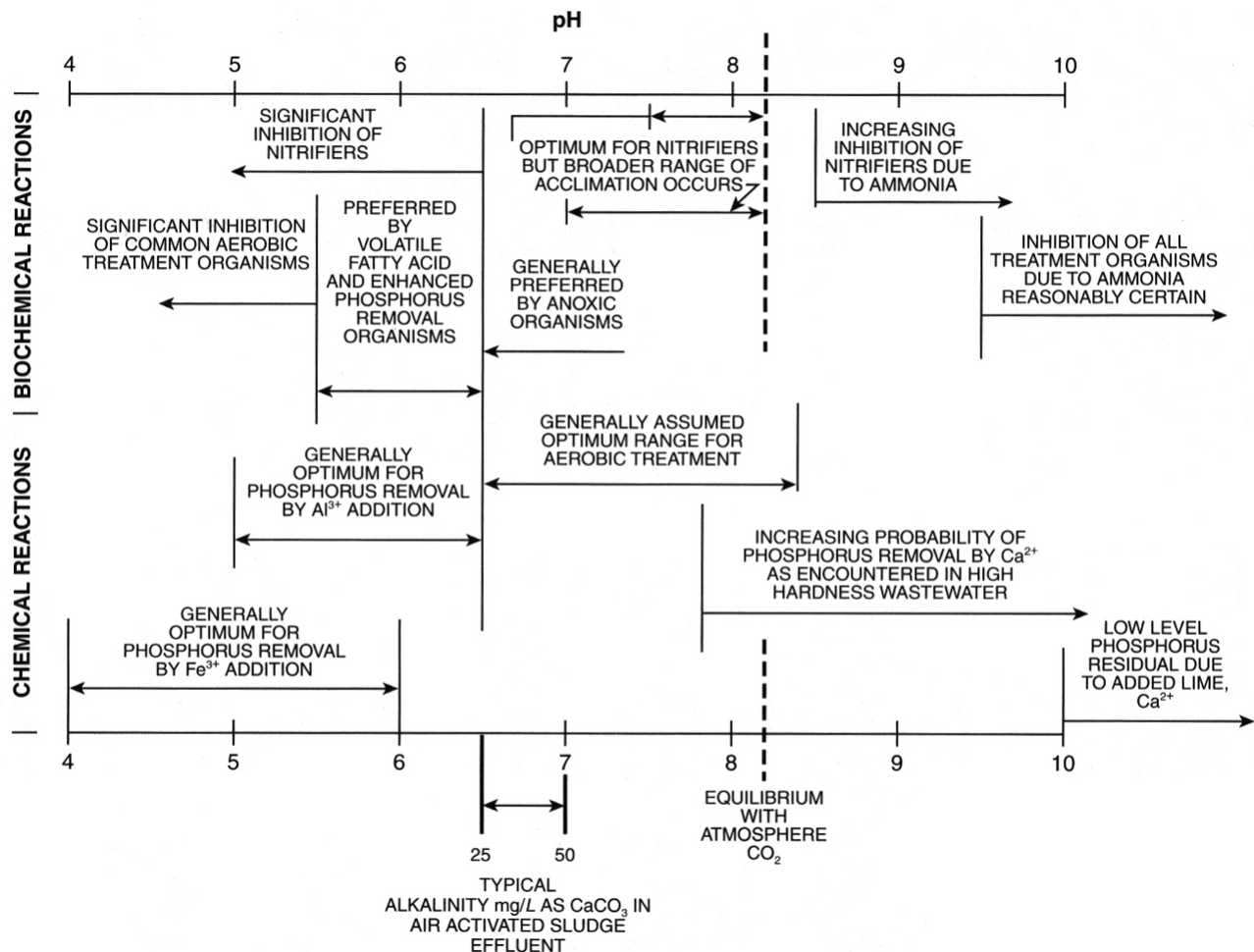


Figure 3.3 Optimum pH Ranges⁵



Key Points for Unit 3 – Combined Nitrogen and Phosphorus Removal or Biological Nutrient Removal (BNR)

- The A²O and Bardenpho processes are commonly used to remove carbon, nitrogen and phosphorus from wastewater.
- The A²O process is modified from the A/O phosphorus removal process by adding an anoxic stage for denitrification.
- The A²O process consists of three main stages:
 - anaerobic
 - anoxic
 - aerobic
- Adding an anaerobic stage to the front end of a Bardenpho process allows phosphorus to be removed in addition to carbon and nitrogen.
- Process control for biological nutrient removal is accomplished by varying parameters such as MCRT, RAS rate, MLSS concentration, recycle rates and F/M ratio.
- The pH and DO levels may need adjustment so that individual processes will proceed efficiently.

**Exercise for Unit 3 - Combined Nitrogen and Phosphorus Removal or Biological Nutrient Removal (BNR)**

1. In the spaces below, write in the typical range of values for the indicated process control parameters:
 - a. MCRT A²O _____ Bardenpho _____
 - b. RAS recycle rate A²O _____ Bardenpho _____
 - c. MLSS concentration A²O _____ Bardenpho _____
 - d. F/M ration A²O _____ Bardenpho _____

2. From the chart in Figure 3.3, determine the optimum pH range for the following processes:
 - a. Aerobic treatment _____
 - b. optimum for nitrifiers _____
 - c. phosphorus removal by Al³⁺ addition _____
 - d. phosphorus removal by Fe³⁺ addition _____

¹ George Tchobanoglous and Frank Burton, *Wastewater Engineering: Treatment, Disposal, Reuse*, 3rd Edition, (New York, NY: Irwin/McGraw-Hill, 1991), p. 733.

² Tchobanoglous, p. 732.

³ Tchobanoglous, p. 733.

⁴ Tchobanoglous, p. 734.

⁵ Ross Cudgel, "Enhanced Biological (Nutrient) Control," in *Advanced Waste Treatment*, (Sacramento, CA: California State University, Sacramento Foundation, 1998), p. 532.

Unit 4 – Treatment of Combined Municipal and Industrial Wastewater

Learning Objectives

- List some common industrial wastes and explain their effects on treatment plant performance.
- Describe the appropriate operational responses to a shock load.
- Explain the importance of recordkeeping and describe what types of records should be kept.

Industrial Wastes

Contributions from industrial wastes to the overall characteristics (flow, BOD or COD, pH, etc.) of the influent wastewater range from insignificant to several times the domestic contribution. Typically, wastewater treatment plants in smaller service areas are more vulnerable to shock loads from commercial or industrial sources than plants servicing metropolitan areas.



High strength waste is typically defined as waste having a BOD₅ in excess of 400 mg/L and a COD in excess of 1,000 mg/L.



A **shock load** is a slug of high strength waste.

High Strength

- ◆ Vegetables and fruit packing, dairy processing, meat packing, tanning, poultry processing, oil processing and pulp and paper manufacturing are examples of industries that have the potential to generate high strength wastewater. (The average BOD range for typical dairy wastewater is 940 to 4790 mg/L.)
- ◆ Generally, anything over 400 mg/L BOD or 1,000 mg/L COD is considered high strength, which is stronger than typical domestic wastewater.

Metals and Solvents

- ◆ Metal finishing operations often generate wastewaters with elevated metal and solvent concentrations.

Oils, Greases and Fuels

- ◆ Metal finishing operations, floor cleaning and food processing are examples of industrial processes that have the potential for elevated concentrations of oil and grease in discharged wastewater.
- ◆ Oils and greases can be of animal or vegetable origin or of mineral origin.
- ◆ Common flammable oils are crude gasoline, benzene, naphtha, fuel oil and mineral oil. Elevated levels of oil and grease are typically greater than 50 to 100 mg/L.

MONITORING PROGRAM AND PRETREATMENT REQUIREMENTS

Fuels

- ◆ Fuels released by underground storage tanks can enter the sanitary sewer system through leaking sewer joints or from surface spills that enter combined storm and sanitary sewers.
- ◆ Fuel oil and gasoline are lighter than water and therefore will typically float on the surface and accumulate in wet wells. The accumulation of fuels presents an explosion hazard in the collection system as well as in the treatment plant if the concentration of hydrocarbons in the air space above the water is between the lower explosive limit (LEL) and the upper explosive limit (UEL) as determined by a combustible gas monitor.
- ◆ Skimming devices are commonly used to remove floating hydrocarbons from wet wells and tanks.

High/Low pH

- ◆ Industrial processes using caustic and/or acidic cleaners have the potential for generating wastewater with high or low pH.
- ◆ In general, any process utilizing a strong acid or base has the potential for generating a highly corrosive or caustic wastewater.

Other Toxic Materials

Toxic Gases

- ◆ Toxic gases generated in wastewater collection systems present health and safety concerns for maintenance personnel and plant operators.
- ◆ Hydrogen sulfide (H₂S), generated by decomposing organic matter under anaerobic conditions is the most common toxic gas encountered in collection systems. Industrial discharges containing sulfate can exacerbate H₂S problems. Hydrogen sulfide can be toxic, flammable, explosive and malodorous.
- ◆ Other toxic gasses include hydrogen cyanide (HCN) phosgene (mustard gas) and tear-gas type substances.

MONITORING PROGRAM AND PRETREATMENT REQUIREMENTS

Amines

- ◆ Amines, compounds formed from reactions with ammonia, may react with compounds in wastewater to form nitrosoamines, which are considered carcinogens.

Surface-Active Agents

- ◆ Surface-active agents, or surfactants, are common components of industrial cleaning chemicals and can cause excessive foaming in aeration tanks and inhibit the flocculation process.
- ◆ Anti-foam agents are often used to control the accumulation of foam in aeration tanks.

Biocides

- ◆ Biocides can be toxic to both humans and activated sludge bacteria and can completely disrupt the operation of a biological treatment system. These compounds are difficult to detect before a severe die-off occurs in the biological treatment system and create biosolids disposal problems.

High Strength Waste

Low DO

- ◆ A sudden increase in BOD load to the activated sludge system may result in a drop in the DO concentration in the aeration tank if the capacity of the blowers is exceeded.
- ◆ Low DO levels in the aeration tank may result in odor problems and create conditions favorable to filamentous organisms.
- ◆ As long as you have adequate aeration capacity, you should be able to maintain DO concentrations in the 2 to 4 mg/L range.

High Effluent BOD

- ◆ A shock load of oxygen-demanding material (high BOD) may exceed the plant's organic loading capacity. If this happens, the DO in the aeration tank will drop and the BOD removal efficiency will drop, resulting in elevated effluent BOD concentrations.

Poor Settling Sludge

- ◆ High strength waste has the potential to cause problems associated with elevated food-to-microorganism ratios, which can lead to sludge bulking.
- ◆ Microorganisms in a high F/M ratio environment tend to grow rapidly in a dispersed state rather than in clumps, or flocs. When this occurs, activated sludge settling characteristics are poor and it is difficult to retain the sludge in the secondary clarifier without the addition of a chemical flocculant or incorporating some other method to improve sludge settleability.
- ◆ It is important to note that poor settling sludge can also be caused by the growth of filamentous bacteria due to rapidly varying F/M ratios.

Metals

Heavy metals can kill activated sludge microorganisms or inhibit their microbiological processes, resulting in a degradation of treatment plant performance. Excess metals entering an activated sludge plant can either pass through untreated to the receiving stream or become incorporated into the biosolids.

Toxicity

- ◆ Metals passing through the plant can be toxic to the organisms in the receiving stream and can pose a threat to drinking water supplies. Metals incorporated into biosolids that are land applied can result in disposal problems if the metals concentrations exceed acceptable EPA ceiling limits.
- ◆ Certain metals, such as copper, lead, silver and chromium can be toxic to microorganisms. A copper concentration of 100 mg/L, chromium and nickel concentrations of 500 mg/L, potassium concentrations of 4,000 mg/L and elevated concentrations of sodium can be toxic to bacteria in the activated sludge process and in the sludge digesters. Elevated levels of these cations have resulted in upset plant conditions.
- ◆ Metals in excess of 10 to 20 mg/L can be inhibitory to the nitrification process.

MLSS Color Change

- ◆ A sudden change in MLSS color from brownish to gray or black or a sudden decrease in the volumetric air flow rate to the aeration tank may be an indication that a toxic shock load has killed the biomass in the aeration tank.

High Effluent BOD/DO Problems

- ◆ When metals in the wastewater cause inhibition of microbiological processes, the ability of the bacteria to oxidize carbonaceous and nitrogenous compounds degrades, resulting in an increase in effluent BOD.

Poor Settling Sludge

- ◆ The ability of bacteria to assimilate and treat colloidal organic matter entering the treatment plant will decrease and dead or weakened bacteria will not flocculate and form sludge with good settling characteristics. This may result in a poorly settling sludge and increased effluent TSS concentrations.

Oils and Greases

Emulsified vegetable- and animal-based oils and greases are degradable by activated sludge bacteria, while mineral oils and greases are less biodegradable and require pretreatment or removal prior to activated sludge treatment.

DO Problems

- ◆ Excessive quantities of oil and grease can impart a large oxygen demand in aeration basins and cause a decrease in the DO concentration.

Sheen on Water Surfaces

- ◆ Oils and greases are typically lighter than water, so they float and accumulate on the surface of wet wells and tanks.

Floating Grease Balls

- ◆ Emulsified oils and greases, such as those originating from butter fat, can cause floating grease balls in aeration tanks.

Odors

- ◆ Oil and grease build-ups can clog pumps, pipes, valves, and other equipment and cause objectionable odors.

High/Low pH

Toxicity

- ◆ Wastewater high or low in pH can be corrosive to pipes and fluid handling equipment and can be toxic to activated sludge bacteria. Optimal pH ranges for biological treatment processes are discussed in Unit 3.

MLSS Color Change

- ◆ A sudden change in MLSS color from brownish to gray or black or a sudden decrease in the volumetric air flow rate to the aeration tank may be an indication that a toxic shock load has killed the biomass in the aeration tank.

High Effluent BOD/DO Problems

- ◆ When low or high pH in the wastewater causes inhibition of microbiological processes, the ability of the bacteria to oxidize carbonaceous and nitrogenous compounds degrades, resulting in an increase in effluent BOD.

Poor Settling Sludge

- ◆ The ability of bacteria to assimilate and treat colloidal organic matter entering the treatment plant will decrease and dead or weakened bacteria will not flocculate and form sludge with good settling characteristics. This may result in a poorly settling sludge and increased effluent TSS concentrations.

Monitor DO and Aeration Rates

- ◆ As a toxic shock load passes through the aeration tank, the residual DO will increase without a corresponding increase in the volumetric air flow rate from the blowers. This signifies a reduction in the respiration rate and the death of bacteria in the aeration tank. On the other hand, a decrease in the DO residual with a corresponding increase in the aeration rates signifies the presence of a shock load of high-strength waste.
- ◆ By monitoring the DO concentration and the aeration rates in the aeration tank several times per day, you may be able to identify a shock load situation before it wipes your plant out.
- ◆ If your aeration system has enough capacity, try to maintain a reasonable DO concentration of at least 1-2 mg/L without causing foaming.

Check pH

Monitoring the pH of the plant influent at least daily will help you to potentially catch a toxic shock load before it kills the bacteria in the plant and at the very least, will help you to diagnose problems caused by toxicity.

Adjust pH

- ◆ If your plant has chemical metering capabilities, add acid or caustic to adjust the pH back to the optimal range.
- ◆ Sulfuric acid is commonly used to lower pH and sodium hydroxide is commonly used to increase the pH.
- ◆ pH neutralization is best accomplished in complete-mix tanks with adequate detention time (e.g., 15 to 20 minutes).

Increase RAS Rates; Decrease WAS Rates



In response to toxic or high-strength shock loads, the first priority should be to retain as much activated sludge as possible in the system. Toxic shock loads may kill a significant portion of the active biomass in the system, so anything you can do to retain biomass will help in the recovery effort.

- ◆ If your plant is operating in the conventional or complete-mix mode, you should increase the return activated sludge (RAS) rate and decrease the waste activated sludge (WAS) rate to retain as much biomass in the aeration tank as possible.
- ◆ If you are operating in the contact stabilization mode and you identify a toxic shock load early on, it is better to decrease the RAS rate and increase the WAS rate to “hold” the relatively healthy, unaffected biomass in the reaeration tank and “flush out” the dead biomass and toxic contamination from the aeration tank and secondary clarifiers.
- ◆ In response to a high-strength shock load, decrease the WAS rate and increase the RAS rate to hold as much biomass in the aeration tank as possible. You will need as much active biomass as possible to treat the increased BOD load in the aeration tank.
- ◆ High-strength shock loads may require the addition of supplement nitrogen and/or phosphorus if the ratio of BOD-to-nitrogen-to-phosphorus exceeds 100:5:1.

Investigate Possible Sources

- ◆ In some instances, there may not be much you can do to prevent a shock load from an industrial source from wiping your plant out. In these situations, the best thing to do is to try to identify the source and to address the source so that similar future shock loads do not occur. Identifying the source can be difficult, especially when the plant has many industrial customers.
- ◆ Investigating possible sources may be as simple as making phone calls and interviewing local industries, but may require conducting visual observations and/or collecting wastewater and/or sediment samples in sewer manholes throughout the collection system to trace the path of the contamination.

Recordkeeping

- ◆ It is essential that you keep daily operating logs of critical parameters such as flow, pH, temperature, BOD and COD. These daily logs can be used to develop trends and to prepare monthly reports. They also provide critical information for future updates of the treatment plant.
- ◆ The importance of recordkeeping and the types of records that need to be kept are covered in Module 16: The Activated Sludge Process Part II. Please consult that module for information on recordkeeping.

**Key Points for Unit 4 – Treatment of Combined Municipal and Industrial Wastewater.**

1. Generally, anything over 400 mg/L BOD or 1,000 mg/L COD is considered high strength, which is stronger than typical domestic wastewater and can cause a shock load when entering a treatment plant.
2. Hydrogen sulfide (H₂S), generated by decomposing organic matter under anaerobic conditions is the most common toxic gas encountered in collection systems. Industrial discharges containing sulfate can exacerbate H₂S problems. Hydrogen sulfide can be toxic, flammable, explosive and malodorous.
3. A sudden increase in BOD load to the activated sludge system may result in a drop in the DO concentration in the aeration tank if the capacity of the blowers is exceeded.
4. A sudden change in MLSS color from brownish to gray or black or a sudden decrease in the volumetric air flow rate to the aeration tank may be an indication that a toxic shock load has killed the biomass in the aeration tank.
5. Monitoring the pH of the plant influent at least daily will help you to potentially catch a toxic shock load before it kills the bacteria in the plant and at the very least, will help you to diagnose problems caused by toxicity.
6. Sulfuric acid is commonly used to lower pH and sodium hydroxide is commonly used to increase the pH.
7. It is essential that you keep daily operating logs of critical parameters such as flow, pH, temperature, BOD and COD. These daily logs can be used to develop trends and to prepare monthly reports. They also provide critical information for future updates of the treatment plant.



Exercise for Unit 4 - Treatment of Combined Municipal and Industrial Wastewater.

1. In the space below, write a short description of a plant upset that you have experienced or are familiar with. Explain what caused the upset and what steps were taken to return the plant to normal operation. Also, indicate any action taken to help insure that this kind of upset does not happen again.
