CHAPTER 13 – Advanced Wastewater Treatment
• Advanced wastewater treatment refers to methods and processes that remove more contaminants than are taken out by conventional biological treatment.
  – Than are taken out by conventional biological treatment.

• The term tertiary treatment is an often-used synonym.
  – The two terms do not have precisely the same meaning.
• Advanced wastewater treatment processes...
  – Remove phosphorus from solution
  – Oxidize ammonia to nitrate—**nitrification**
  – Convert nitrate to nitrogen gas—**denitrification**
  – Remove or inactivate pathogenic bacteria and viruses—**disinfection**
• Conventional wastewater treatment remove organic matter by combining physical & biological processes

• Conventional treatment typically results in:
  – Negligible reduction in ammonia and phosphorus
  – Incomplete disinfection
  – Removal of toxins present in raw wastewater to varying degrees
  – No removal of soluble nonbiodegradable chemicals

• As NPDES permits are renewed, total maximum daily loads (TMDL) are established for each pollutant
• The primary effect of phosphorus in surface waters is eutrophication

• Un-ionized ammonia is toxic to fish and other aquatic animals

• Protection of public health is the primary concern regarding pathogens in wastewaters discharged to surface waters

• Soluble organic/inorganic chemicals are difficult to remove by biological treatment
  – Best removed at their point of origin
• Inability of gravity sedimentation to remove small particles is a major limitation of conventional treatment for removal of suspended solids (Fig. 13–1)

• Membrane filtration removes particles by straining
  – Depending on media porosity, it has the ability to remove bacteria, viruses, and dissolved solids

• Reverse osmosis can be used to remove viruses and reduce dissolved solids
• Design of gravity filtration systems must account for higher suspended solids content and fluctuating rates
  – Not common in water treatment

• Preferred filters are coal-sand dual media or mixed media containing anthracite coal, garnet, and sand

• Efficient backwashing requires an auxiliary scour
  – Hydraulic suspension of media by upward flow of water through the bed does not provide adequate cleaning
• Direct filtration, chemical coagulation, flocculation and sedimentation is most common (Fig. 13–2)

• A coarse-media upflow filter instead of flocculation & sedimentation reduces area & cost of treatment units
  – Pressure, traveling-bridge & upflow filters

• Hydraulic loading and time of filtration before a bed requires backwashing are interrelated
  – Proper design depends on sufficient bed area

• Design and media size are coordinated as part of an overall system with subsequent disinfection
• Membrane filters provide an increased degree of treatment for industrial applications, wastewater reuse, and reclamation (Fig. 13–4)
  – Replacing the flocculation tank, settling tank, and filters

• Membranes are categorized by pore size, ranging from microfiltration to ultrafiltration, nanofiltration, and reverse osmosis (Fig. 13–5)

• Membranes filter from either outside-to-inside or inside-to-outside
  – Periodically pulsed with treated water under pressure to dislodge solids from the surface
• Processing may be a cross-flow with recirculation, or a direct-flow (dead-end) filtration (Fig. 13–7)
  – Many manufacturers use a combination

• Plugging/fouling results from solids, high-molecular-weight organics, bacterial slimes, metal oxides, and precipitates (Fig. 13–8)
  – If backwashing loses effectiveness, cleaning is required

• Reverse-osmosis equipment & processing for wastewater is similar to potable water treatment (Fig. 13–9)
  – Pretreatment to reduce solids is critical
• Type & concentration of pathogens in domestic wastewater varies with the health of a community population

• In the reuse of wastewater effluents containing enteric viruses, human contact is of major concern

• Disinfection of biologically treated wastewater requires coagulation and granular-media filtration (Fig. 13–10)
  – Followed by chlorination with an extended contact time
A chlorination chamber must be properly designed for effective disinfection.

Rapid mixing is critical to blend a chlorine solution with wastewater, followed by plug flow through a long, narrow, serpentine contact tank.
• Currently, over 100 substances are listed as priority toxic water pollutants

• To qualify, a substance must be hazardous to aquatic life or human health and known to be present
  – Environmental persistence and treatability are also factors

• Gross toxicity of a raw wastewater is evidenced by upset to biological processes in wastewater treatment
The general goal of municipal wastewater treatment with pretreatment of industrial wastewaters is to reduce discharge of toxic pollutants to an insignificant level.
• The conventional way to evaluate toxicity is to test raw & treated wastewater samples for specific substances.

• The second approach is biomonitoring of effluent.
  – Often referred to as whole-effluent toxicity.

• Bioassays to determine toxicity expose aquatic organisms to effluent in a controlled environment.
  – An enhanced bioassay method is a flow-through test, with fresh effluent continuously supplied to the lab.
  – Definitive bioassays are conducted for longer test periods at effluent dilutions in a geometric series.
• Many hazardous substances are biocides & reducing their concentration in raw wastewater is essential to effective biological processing
  – Pretreatment of industrial wastewaters is critical

• A typical list of toxic pollutants includes:
  – 13 metals; cyanide; pesticides
  – 15 poly-nuclear aromatic hydrocarbons
  – 13 aromatics; 10 phenols; 21 aliphatics; 6 phthalates
  – 2 nitrogen and 2 oxygenated compounds
• Common forms of phosphorus in wastewater:
  – Orthophosphates ($PO_4^{3-}$)
  – Polyphosphates (polymers of phosphoric acid)
  – Organically bound phosphates

• Conventional treatment removes only 20% – 40% of the influent phosphorus

• Remedial action for phosphorus pollution is treatment of wastewaters that discharge directly into lakes
  – And rivers or streams that flow into lakes
• Phosphorus enters the sewer in the form of soluble and organically bound phosphates
  – Biological activity in the sewer releases organically bound phosphates into solution

• The amount of organically bound phosphates released to soluble form varies
  – With sewer length, wastewater temperature, and biological conditions

• Phosphorus in the excess biological floc produced in activated-sludge treatment of a wastewater is about 1% of applied BOD applied (Fig. 13–11)
• Additional phosphorus can be removed along with the organic material by filtration and coagulant addition (Fig.13–12)

• Filter design, media size, and chemical addition allow operators to meet almost any target value
  – Between 0.2 and 1.3 mg/l
Chemical precipitation using aluminum or iron coagulants is effective in phosphate removal. Aluminum ions combine with phosphate ions:

$$\text{Al}_2(\text{SO}_4)_3 \cdot 14.3\text{H}_2\text{O} + 2\text{PO}_4^-$$

$$= 2\text{AlPO}_4↓ + 3\text{SO}_4^- + 14.3\text{H}_2\text{O}$$

A competing reaction—which accounts in part for an excess alum requirement—is with natural alkalinity:

$$\text{Al}_2(\text{SO}_4)_3 \cdot 14.3\text{H}_2\text{O} + 6\text{HCO}_3^-$$

$$= 2\text{Al(OH)}_3↓ + 3\text{SO}_4^- + 6\text{CO}_2 + 14.3\text{H}_2\text{O}_3$$
Chemical precipitation using aluminum or iron coagulants is effective in phosphate removal.

Iron coagulants precipitate orthophosphate by combining with the ferric ion:

\[
\text{FeCl}_3 \cdot 6\text{H}_2\text{O} + \text{PO}_4^{3-} \rightarrow \text{FePO}_4 \downarrow + 3\text{Cl}^- + 6\text{H}_2\text{O}
\]

A competing reaction—which accounts in part for an excess iron requirement—is with natural alkalinity:

\[
\text{FeCl}_3 \cdot 6\text{H}_2\text{O} + 3\text{HCO}_3^- \\
= \text{Fe(OH)}_3 \downarrow + 3\text{CO}_2 + 3\text{Cl}^- + 6\text{H}_2\text{O}
\]
As the reaction of ferric chloride with natural alkalinity is relatively slow, lime or another alkali may be applied to raise pH and supply the hydroxyl ion for coagulation:

\[
2\text{FeCl}_3 \cdot 6\text{H}_2\text{O} + 3\text{Ca (OH)}_2 = 2\text{Fe (OH)}_3 \downarrow + 3\text{CaCl}_2 + 6\text{H}_2\text{O}
\]
• Commercially available iron salts are:
  – Ferric chloride, ferric or ferrous sulfate
  – Waste pickle liquor from the steel industry

• Chemical-biological treatment combines chemical precipitation of phosphorus with biological removal of organic matter
  – Alum & ferric sulfate add sulfate molecules to waste-water

• High concentrations increase corrosion/odor problems
  – Associated with hydrogen sulfide created under anaerobic conditions in thickeners and digesters
Common forms of nitrogen are organic, ammonia, nitrate, nitrite, and gaseous.

Decomposition of nitrogenous organic matter releases ammonia to solution:

\[ \text{Organic nitrogen compounds} \xrightarrow{\text{bacterical decomposition}} \text{NH}_3 \text{(ammonia)} \]

Under aerobic conditions, nitrifying bacteria oxidize ammonia to nitrite, and subsequently to nitrate:

\[ \text{NH}_3 + \text{O}_2 \xrightarrow{\text{aerobic nitrification}} \text{NO}_3^- \text{(nitrate)} \]
Bacterial denitrification occurs under anaerobic or anoxic conditions

Organic matter (AH₂) is oxidized and nitrate is used as a hydrogen acceptor, releasing nitrogen gas:

\[
\text{NO}_3^- + \text{AH}_2 \xrightarrow{\text{anaerobic denitrification}} \text{A} + \text{H}_2\text{O} + \text{N}_2\uparrow
\]
• The greatest source of nitrogen in wastewater is from human fecal matter

• Approximately 40% of influent nitrogen is ammonia
  – 60% is bound in organic matter with negligible nitrate

• Ammonia is created by decomposition of organic matter and can be removed by biological or chemical processes
  – Also by breakpoint chlorination to chemically convert ammonia to nitrogen gas
• With most nitrogen in soluble and colloidal organic forms, the amount removed by primary sedimentation is limited to about 15% (Fig. 13–13)

• Nitrogen in excess biological floc produced in activated-sludge treatment of a wastewater is about 4% of BOD applied
Nitrification of wastewater is practiced where effluent ammonia content causes pollution of the receiving watercourse. The process does not remove the nitrogen but converts it to the nitrate form:

\[
\text{NH}_3 + \text{O}_2 \xrightarrow{\text{aerobic nitrification}} \text{NO}_3^- \text{ (nitrate)}
\]

Nitrification–denitrification includes conversion of the nitrate to gaseous nitrogen:

\[
\text{NO}_3^- + \text{AH}_2 \xrightarrow{\text{anaerobic denitrification}} \text{A} + \text{H}_2\text{O} + \text{N}_2 \uparrow
\]
• Nitrification is usually separate, following conventional biological treatment (Figs. 13–14 & 13–15)

• Synthetic-media filtration in biological towers can perform nitrification
  – The most reliable system is suspended-growth aeration

• Biological nitrification can result in lower pH when processing wastewaters of moderate hardness
  – Or where alum precipitation has been used for phosphorus reduction in preceding processes
Theoretically, 7.2 lb of alkalinity is destroyed per pound of ammonia nitrogen oxidized to nitrate:

\[
2\text{NH}_4\text{HCO}_3 + 4\text{O}_2 + \text{Ca(HCO}_3)_2 \\
= \text{Ca(NO}_3)_2 + 4\text{CO}_2 + 6\text{H}_2\text{O}
\]

Destroying alkalinity causes wastewater to become aggressive, attacking the cement at the concrete surface and corroding ferrous metals, such as clarifier mechanisms.
• Nitrification reduces effluent ammonia toxicity
  – But releases higher concentrations of nitrate—a groundwater pollutant

• Denitrification reduces nitrate to nitrogen gas using facultative heterotrophic bacteria (Fig. 13–7)
  – Removing nitrate from the plant effluent
An organic carbon source, in $\text{AH}_2$ is needed to act as a hydrogen donor and to supply carbon for biological synthesis.

$\text{NO}_3^- + \text{AH}_2 \xrightarrow{\text{anaerobic denitrification}} \text{A} + \text{H}_2\text{O} + \text{N}_2 \uparrow$

Methanol is common due to its availability, ease of application and because it doesn’t leave a residual BOD in the process effluent.
The denitrification reaction between methanol and nitrate:

\[
5\text{CH}_3\text{OH} + 6\text{NO}_3^- \rightarrow 3\text{N}_2 \uparrow + 5\text{CO}_2 \uparrow + 7\text{H}_2\text{O} + 6\text{OH}^- 
\]
Based on approximately 30% excess methanol needed for synthesis, total methanol demand is calculated:

\[
\begin{align*}
\text{CH}_3\text{OH} &= 0.7 \text{DO} + 1.1\text{NO}_2\text{--N} + 2.0\text{NO}_3\text{--N} \\
\text{CH}_3\text{OH} &= 0.9 \text{DO} + 1.5\text{NO}_2\text{--N} + 2.5\text{NO}_3\text{--N}
\end{align*}
\]

where \(\text{CH}_3\text{OH}\) = methanol, milligrams per liter  
\(\text{DO}\) = dissolved oxygen, milligrams per liter  
\(\text{NO}_2\text{--N}\) = nitrite nitrogen, milligrams per liter  
\(\text{NO}_3\text{--N}\) = nitrate nitrogen, milligrams per liter
Detention time required for denitrification of a domestic wastewater is usually 2 to 4 hr, depending on nitrate loading and temperature.
Unoxidized organic matter can be an oxygen acceptor (hydrogen donor) to convert nitrate to nitrogen gas.

The reaction satisfies a portion of BOD in a wastewater:

\[
\begin{array}{c}
\text{Unoxidized organic matter} + \text{NO}_3^- \\
2\text{BOD}
\end{array}
\quad \text{to} \quad
\begin{array}{c}
\text{Oxidized organic matter} + \text{N}_2 \uparrow \\
2\text{reduced BOD}
\end{array}
\]
• The plug-flow activated-sludge system blends nitrified recirculation flow with raw settled wastewater (primary effluent) in an anoxic zone (Fig. 13–18).

• The amount of return nitrate that can be reduced depends on the maximum rate of denitrification possible in the anoxic zone.
• Denitrification ahead of the nitrification zone is advantageous:
  – BOD in the raw wastewater is used as a carbon source
  – Oxygen demand of the nitrification zone is reduced
  – Denitrification recovers alkalinity lost during nitrification

• Additional nitrogen removal requires microfiltration followed by reverse osmosis to remove the remaining nitrate from solution (Fig. 13–19)
• Biological nitrification–denitrification begins treatment with an anoxic zone followed by an aerobic zone to remove nitrogen
  – Called enhanced biological phosphorus removal (EBPR)

• Continuous monitoring of dissolved oxygen, oxidation reduction potential (ORP), ammonia, nitrate, and phosphorus aids in process control
• Denitrification control is possible by adjusting the return-activated-sludge flow, recycle flow, and feed points into the aeration basin

• Phosphorus removal of 70 – 80% and nitrogen removal in the range of 50 – 70% are possible
  – With a combination of anaerobic, anoxic & aerobic zones
CHAPTER END