Chapter 3: Advanced Wastewater Treatment for Nitrogen Removal

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Faculty of Engineering & Applied Science
3.1 Nitrogen in wastewaters

1. Common forms of nitrogen

- organic-N
- ammonia-N $\rightarrow$ decomposition of nitrogenous organic matter releases ammonia to solution

Organic nitrogen compounds $\xrightarrow{\text{bacteria}}$ decompostion $\rightarrow$ NH$_3$ (ammonia)

- nitrite-N and nitrate-N $\rightarrow$ under aerobic conditions, nitrifying bacteria oxidize ammonia to nitrite and subsequently to nitrate

NH$_3$ + O$_2$ $\xrightarrow{\text{aerobic bacteria}}$ NO$_2^-$ (nitrite) $\xrightarrow{\text{aerobic bacteria}}$ NO$_3^-$ (nitrate)
- gaseous-N ➔ bacterial denitrification occurs under anaerobic or anoxic conditions when organic matter (AH₂) is oxidized and nitrate is used as a hydrogen acceptor releasing nitrogen gas:

\[
\text{NO}_3^- + AH_2 \xrightarrow{\text{anaerobic bacteria}} \text{denitrification} A + H_2O + N_2↑
\]

- Total Kejeldahl Nitrogen (TKN)

\[
\text{TKN} = \text{NH}_3 + \text{org-N}
\]

- Total-Nitrogen (total-N)

\[
\text{Total-N} = \text{TKN} + \text{NO}_3 + \text{NO}_2
\]
2. Sources of nitrogen in wastewaters

- organic-N ➔ human excreta, ground garage and industrial waste, particularly from food processing ➔ contains proteins, amines, nucleic acids, peptides, amino acids and other organic constituents excreted in human fecal matter

- ammonia ➔ While traveling through sewer pipes, the majority of the nitrogen contained in raw sewage (urea and fecal material) is converted from organic-nitrogen to ammonia through a process called hydrolysis ➔ Ammonification
nitrite and nitrate → typically not found in raw wastewater because of the lack of free oxygen for nitrification → nitrates may be contributed from industrial discharge or from drinking water high in nitrate concentrations (negligible)

Nitrogen in wastewater influent ≈ 60% in ammonia + 40% in nitrogen bound to organic matter + negligible nitrate
http://www.youtube.com/watch?v=BosHU4ARR9w ➔ a very interesting video
3. Nitrogen removal in conventional treatment

<table>
<thead>
<tr>
<th></th>
<th>Before Sedimentation</th>
<th>After Sedimentation</th>
<th>Biologically Treated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total solids</td>
<td>800</td>
<td>680</td>
<td>530</td>
</tr>
<tr>
<td>Total volatile solids</td>
<td>440</td>
<td>340</td>
<td>220</td>
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<tr>
<td>Suspended solids</td>
<td>240</td>
<td>120</td>
<td>30</td>
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<tr>
<td>Volatile suspended solids</td>
<td>180</td>
<td>100</td>
<td>20</td>
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<tr>
<td>BOD</td>
<td>200</td>
<td>130</td>
<td>30</td>
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<tr>
<td>Ammonia nitrogen as N</td>
<td>22</td>
<td>22</td>
<td>24</td>
</tr>
<tr>
<td>Total nitrogen as N</td>
<td>35</td>
<td>30</td>
<td>26</td>
</tr>
<tr>
<td>Soluble phosphorus as P</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Total phosphorus as P</td>
<td>7</td>
<td>6</td>
<td>5</td>
</tr>
</tbody>
</table>

(Viessman et al., Water Supply and Pollution Control, 2009)
most of the organic nitrogen in sanitary wastewater influent in soluble and colloidal organic forms

N removed by primary sedimentation is limited to 15\% N content of dry sludge solids in primary sludge is in the range of 2\%-4\% (organic-N removed)

N removal by subsequent biological treatment is another 10\% N content of dry sludge solids in waste-activated sludge is 2\%-6\% (organic-N removed)

During biological metabolism in the activated-sludge process, org-N released to solution in the form of ammonia (ammonia con. Increased)

Total N removal by conventional treatment about 25\%
(Viessman et al., Water Supply and Pollution Control, 2009)
4. Nitrogen removal in advanced treatment

- Membrane treatment ➔ Electrodialysis
- Membrane treatment ➔ Reverse osmosis
- Ion exchange ➔ using strong base anion resins regenerated with NaCl
- Biological nitrification and denitrification ➔ using methanol or ethanol addition
3.2 Nitrogen removal by physical and chemical processes

1. Physical processes

- 75% of N left for advanced wastewater treatment
- N in the forms of organic-N, ammonia and nitrate
- some physical processes can help the N removal ➔ membrane processes, such as reverse osmosis technology
- Main membrane processes
  - Dialysis
  - Electro-dialysis
  - Reverse osmosis
Membrane separation

- separates an influent stream into two effluent streams known as the permeate and the concentrate
- the permeate ➔ the portion of the fluid that has passed through the semi-permeable membrane
- the concentrate stream ➔ contains the constituents that have been rejected by the membrane
Driving forces that cause mass transfer of solutes during membrane separation

- Difference in concentration (dialysis)
- Difference in electric potential (electro-dialysis)
- Difference in pressure (reverse osmosis)

Dialysis

- depends on separating solutes of different ionic or molecular size in a solution by means of a selectively permeable membrane divided by the difference in the solute concentration across the membrane
- Applications of dialysis with very limited application in environmental engineering. In industrial applications, dialysis can be used to recover Sodium Hydroxide from textile wastewater
Dialysis treatment

(Al-Malack, Water Supply and Wastewater Engineering, 2007)
Electrodialysis

- depends on the presence of an electrical filed across the selectively permeable membrane
- the driving force is an electromotive force (electrical potential)
- when electromotive force is applied across the permeable membrane → an increased rate of ion transfer will occur + results in decrease in the salt concentration of the treated solution
- the process can demineralize (removes dissolved solids) brackish water and seawater to produce fresh water + tertiary effluents
When direct current is applied to electrodes ➔

- All cations (+ charged) migrate towards cathode
- All anions (- charged) migrate towards anode
- Cations can pass through the cation-transfer permeable membrane (C) but cannot pass through anion-transfer permeable membrane (A)
- Anions can pass through (A) but cannot pass through (C)

(Al-Malack, Water Supply and Wastewater Engineering, 2007)
Reverse osmosis

(1) Definition

- It is the process of forcing a solvent (like water) from a region of high solute concentration through a membrane to a region of low solute concentration by applying a pressure in excess of the osmotic pressure.
- It is the reverse of the normal osmosis process, which is the natural movement of solvent from an area of low solute concentration, through a membrane, to an area of high solute concentration when no external pressure is applied.
- The membrane here is semi-permeable → it allows the passage of solvent but not of solute.
(2) Mechanism

(Al-Malack, Water Supply and Wastewater Engineering, 2007)
(3) Types of reverse osmosis membranes

- The most common membrane materials are polyamide thin film composites (TFC) or cellulose-type membranes (CTA)
- CTA membranes
  - use CTA when the source water is chlorinated, such as a municipal or city water source
  - It's advantages over a TFC are being chlorine resistant + less costly
- TFC membranes
  - use TFC when the source water has a high TDS (total dissolved solids) and/or the source water is non-chlorinated
  - A TFC membrane is bacteria resistant + has superior rejection and flow rates
  - The TFC was developed by NASA and will need a carbon filter before the membrane when used with chlorinated water
Reverse osmosis membranes ➔ Spiral wound (like a rolled up newspaper)
Reverse osmosis membranes ➔ hollow fibres ➔ can be bundled together. This provides a very large surface area for water treatment within a compact tube element

(Al-Malack, Water Supply and Wastewater Engineering, 2007)
(4) Application of reverse osmosis membranes

- Producing potable water from sea or brackish water
- Ultrapure water for food processing and electronic industries
- Pharmaceutical grade water and water for chemical, pulp & paper industry
- Waste (e.g., N) removal and treatment

(Al-Malack, Water Supply and Wastewater Engineering, 2007)
### Table 4: Design Data from Milan Area Reverse Osmosis Nitrate Removal Plants

<table>
<thead>
<tr>
<th>Location</th>
<th>Aicurzio</th>
<th>Bellusco</th>
<th>Ornago</th>
<th>Sulbiate</th>
<th>Bernareggio Mezzago</th>
<th>Barlassina</th>
<th>Cesano Maderno</th>
<th>Varedo</th>
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<tbody>
<tr>
<td></td>
<td>Via Remembranze</td>
<td>Via Dolomiti</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Well water in m3/h</td>
<td>30.1</td>
<td>127.0</td>
<td>43.1</td>
<td>144.9</td>
<td>137.5</td>
<td>58.0</td>
<td>97.0</td>
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<td>By-pass m3/h</td>
<td>17.8</td>
<td>83.0</td>
<td>27.7</td>
<td>71.2</td>
<td>79.2</td>
<td>38.5</td>
<td>60.0</td>
<td>36.8</td>
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<tr>
<td>RO feed m3/h</td>
<td>12.3</td>
<td>44.0</td>
<td>15.4</td>
<td>73.6</td>
<td>58.3</td>
<td>19.5</td>
<td>37.0</td>
<td>19.6</td>
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<tr>
<td>RO permeate m3/h</td>
<td>7.2</td>
<td>27.0</td>
<td>9.3</td>
<td>39.8</td>
<td>33.8</td>
<td>11.5</td>
<td>22.0</td>
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<td>RO brine m3/h</td>
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<td>17.0</td>
<td>6.1</td>
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<td>8.0</td>
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<td>Delivered drinking water m3/h</td>
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<td>110.0</td>
<td>37.0</td>
<td>111.0</td>
<td>113.0</td>
<td>50.0</td>
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<td>RO recovery %</td>
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<td>61</td>
<td>60</td>
<td>54</td>
<td>58</td>
<td>59</td>
<td>59</td>
<td>60</td>
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<tr>
<td>Overall recovery %</td>
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<td>87</td>
<td>86</td>
<td>77</td>
<td>82</td>
<td>86</td>
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<tr>
<td>Well water NO3 ppm</td>
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<td>52.4</td>
<td>53.0</td>
<td>61.5</td>
<td>56.4</td>
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<td>Water conductivity@20°C mS/cm</td>
<td>620</td>
<td>610</td>
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<td>690</td>
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<td>520</td>
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<td>Assumed permeate NO3 ppm</td>
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<td>1.5</td>
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<tr>
<td>Brine NO3 ppm</td>
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<td>Pressure Vessels</td>
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<tr>
<td>RO feed pressure bar</td>
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<td>13.3</td>
<td>11</td>
<td>12</td>
<td>13.3</td>
<td>12.3</td>
<td>12.1</td>
<td>9.7</td>
</tr>
</tbody>
</table>

(Elyanow, Advances in Nitrate Removal, 2005)
2. Chemical processes

- Ammonia can be removed chemically by air stripping ➔ stripping ammonia gas after raising the wastewater pH above 10
- Ammonium ions can be exchanged by another cation + nitrate exchanged by another anion ➔ through using ion-exchange resins
- Ammonia may also be removed using breakpoint chlorination to chemically convert ammonia to nitrogen gas ➔ the process is costly to operate, only installed as a backup to biological nitrification
Air stripping

- Air stripping ➔ the process of transferring a contaminant from the liquid phase to the gas phase ➔ primarily used for removing volatile organic chemicals (VOCs)
- In the air stripping process ➔ air and water are contacted in a packed column (air stripping tower) designed to maximize the contact surface area between the water and air
- Air stripping towers ➔ serve to breakup the water into droplets and allow contact between the water and air with subsequent transfer of VOC to air phase
- In its most efficient form, the packed tower is operated in a counter-current manner ➔ water/wastewater is loaded to the top of the tower, while fresh air is blown in from the bottom
L = liquid flow rate (m³/min);
G = air flow rate (m³/min);
C = concentration of volatile solute in the liquid (mol/m³);
P = partial pressure of the volatile solute in the gas phase (atm);
Zₜ = total height of packing (m);

An air stripping tower
(Bisogni, Physical/Chemical Process, 2010)
Pᵢ( = 0 for clean air)
Structure of an air stripping tower

- The packing generally consists of plastic pieces, approximately 1 to 2 inches in nominal size which are randomly dumped into the column structure.
- Common varieties of the plastic pieces include "rings" and "saddles".
- Whatever its type, the packing is supported by a retention structure.
- Liquid is distributed over the packing using either nozzles or trays.
Air stripping tower packings

(LANTEC, Tower Packings for Air Strippers, 2010)
Benefits

- proven and experienced technology
- able to be a low profile addition to a treatment process
- high percentage of removal (99% and above)

Limitations

- proper air flow is necessary to prevent flooding or excess air flow
- scaling and biological fouling may impact the performance of the air stripper
(2) Ion-exchange

- Ion exchange ➔ an adsorption phenomenon where the mechanism of adsorption is electrostatic
  - Electrostatic forces hold ions to charged functional groups on the surface of the ion exchange resin
  - The adsorbed ions replace ions that are on the resin surface on a 1:1 charge basis

- Applications of ion exchange in water & wastewater
  - Removal of NO$_3$, NH$_4$, PO$_4$ (nutrient removal) ➔ through using strong base anion resins regenerated with NaCl
  - Ca, Mg (hardness removal) exchange with Na or H
  - Fe, Mn removal from groundwater
  - Recovery of valuable waste products (e.g., Ag, Au)
Cation exchanger → has a negative charge to attract cations

Anion exchanger → has a positive charge to attract anions

(Bisogni, Physical/Chemical Process, 2010)
Ion-exchangers

- Natural ones ➔ Proteins, Soils, Lignin, Coal, Metal oxides, Aluminosilicates (zeolites) (NaOAl₂O₃.4SiO₂)
- Synthetic ones ➔ zeolite gels and polymeric resins (macroreticular, large pores)

Polymeric resins ➔ most commonly used ion-exchanger ➔ made in 3-D networks by cross-linking hydrocarbon chains with the resulting resin insoluble, inert and relatively rigid

Cationic ion exchange resin with fixed anionic sites and exchangeable mobile cations

(Viessman et al., Water Supply and Pollution Control, 2009)
Resins are classified based on the type of functional group they contain and their % of cross-linkages

- Cationic exchangers
  - Strongly acidic ➔ functional groups derived from strong acids, e.g., R-SO$_3$H (sulfonic)
  - Weakly acidic ➔ functional groups derived from weak acids, e.g., R-COOH (carboxylic)

- Anionic exchangers
  - Strongly basic ➔ functional groups derived from quaternary ammonia compounds, R-N-OH
  - Weakly basic ➔ functional groups derived from primary and secondary amines, R-NH$_3$OH or R-R’-NH$_2$OH.
Strong Exchangers stay ionized as pH varies between 2 and 12. Weak exchangers can lose ionization as a function of pH.

(Bisogni, Physical/Chemical Process, 2010)
The isotherms of ion-exchange have the same format as those for carbon adsorption i.e., Langmuir, Freundlich, etc. (Bisogni, Physical/Chemical Process, 2010)
3.3 Nitrogen removal by biological nitrification and denitrification

1. Nitrification

(1) Definition

- Bacteria remove nitrogen from wastewater by a two step biological processes: nitrification followed by denitrification
- Nitrification ➔ the biological conversion of ammonium to nitrate nitrogen
- It is a two-step process: Bacteria known as Nitrosomonas convert ammonia/ammonium to nitrite ➔ Next, bacteria called Nitrobacter finish the conversion of nitrite to nitrate
- The reactions are generally coupled and proceed rapidly to the nitrate form ➔ nitrite levels at any given time are usually low
(2) Nitrification reactions

[Chemical equations and reactions]

From the above equations, it can be calculated that for every pound of ammonia oxidized to nitrate, the following occurs:

- 4.18 pounds of oxygen are consumed
- 7.14 pounds of alkalinity (as CaCO₃) is consumed
(3) Factors affecting nitrification

- **Bacteria**
  - These bacteria known as “nitrifiers” are strict “aerobes” → must have free dissolved oxygen
  - Nitrification occurs only under aerobic conditions at dissolved oxygen levels of 1.0 mg/L or more
  - At dissolved oxygen (DO) concentrations less than 0.5 mg/L, the growth rate is minimal

- **Design parameters → Nitrification requires**
  - a long retention time
  - a low food to microorganism ratio (F:M)
  - a high mean cell residence time (measured as Sludge Age)
  - adequate buffering (alkalinity)
  → An extended aeration tank is ideal
The nitrification process produces acid, which lowers the pH of the biological population in the aeration tank and can cause a reduction of the growth rate of nitrifying bacteria.

- The optimum pH for Nitrosomonas and Nitrobacter is between 7.5 and 8.5.
- Nitrification stops at a pH below 6.0.

Alkalinity

- The nitrification reaction (that is, the conversion of ammonia to nitrate) consumes 7.1 mg/L of alkalinity as CaCO₃ for each mg/L of ammonia nitrogen oxidized.
- An alkalinity of no less than 50-100 mg/L is required to insure adequate buffering.
Water temperature

- Nitrification reaches a maximum rate at temperatures between 30 and 35 °C
- At 40 °C and higher → nitrification rates fall to near zero
- At temperatures below 20 °C → nitrification proceeds at a slower rate, but will continue at temperatures of 10 °C and less
- However, if nitrification is lost → it will not resume until the temperature increases to well over 10 °C

Toxic compounds

- Compounds toxic to nitrifiers → include cyanide, thiourea, phenol and heavy metals
- Nitrifying bacteria can also be inhibited by nitrous acid and free ammonia.
(4) Nitrification by second-stage suspended-growth aeration

(Viessman et al., Water Supply and Pollution Control, 2009)
2. Denitrification

(1) Definition

- The biological reduction of nitrate (NO$_3^-$) to nitrogen gas (N$_2$) by facultative heterotrophic bacteria
- “Heterotrophic” bacteria need a carbon source as food to live
- “Facultative” bacteria get their oxygen by taking dissolved oxygen out of the water or by taking it off of nitrate molecules

(2) The formula describing the nitrification reaction

\[ 6\text{NO}_3^- + 5\text{CH}_3\text{OH} \rightarrow 3\text{N}_2 + 5\text{CO}_2 + 7\text{H}_2\text{O} + 6\text{OH}^- \]
(3) Factors affecting denitrification

- Carbon source
  - A carbon source (shown in the above equation as CH$_3$OH) is required for denitrification to occur
  - The presence of sufficient organic matter → driving force of the denitrification reaction
  - Organic matter may be in the form of raw wastewater, or supplemental carbon

- pH
  - Optimum pH values for denitrification → 7.0 - 8.5
  - Denitrification is an alkalinity producing process → approximately 3.0 to 3.6 pounds of alkalinity (as CaCO$_3$) produced per pound of nitrate → partially mitigating the lowering of pH caused by nitrification in the mixed liquor
Denitrifying bacteria are facultative organisms—they can use either dissolved oxygen or nitrate as an oxygen source for metabolism and oxidation of organic matter.

If dissolved oxygen and nitrate are present, bacteria will use the dissolved oxygen first. Bacteria will not lower the nitrate concentration.

Denitrification occurs only under anaerobic or anoxic conditions.

Toxic compounds

Denitrifying organisms are generally less sensitive to toxic chemicals than nitrifiers. They recover from toxic shock loads quicker than nitrifiers.
Temperature

- Denitrification can occur 5 - 30º
- Greater growth rate of denitrifying organisms at higher temperatures and the rate varies with type of organic source present
- The highest growth rate can be found when using methanol or acetic acid
- A slightly lower rate using raw wastewater will occur
- The lowest growth rates are found when relying on endogenous carbon sources at low water temperatures

- Wastewater cannot be denitrified unless it is first nitrified
(4) Denitrification by suspended-growth system

(Viessman et al., Water Supply and Pollution Control, 2009)