Lecture 20 - Nutrient removal

Nitrogen and phosphorus are essential nutrients for aquatic plant growth

When available in excess in a water body, the water body can become "eutrophic" - literally "well fed"

Algae can be represented as $C_{106}H_{263}O_{110}N_{16}P_1$

Algal growth requires $C : N : P$
$106 : 16 : 1$ in moles

$\sim$ $40 : 7 : 1$ in weight

Liebig's Law of the Minimum states that growth will be limited by the nutrient that is least available relative to the organisms' needs

P is usually limiting in fresh water
N is usually limiting in estuaries and coastal waters

In water bodies where eutrophication is a problem, the nutrient load from wastewater must be controlled

Typical concentrations in wastewater (USEPA, 1997)

	Total N (mg/L)	Total P (mg/L)
Raw wastewater	50 (15-100)	10 (4-15)
Primary treatment	~40	~7
Secondary treatment	25-30	~6
Biological N removal	5-8	
Biological P removal		<1

Nitrogen removal

Nitrification - conversion of ammonia to nitrate

Two-step process: (see M&E Fig 7-21, pg 3)

1. oxidation of ammonium, NH_4^+, to nitrite, NO_2

$$2\,NH_4^+ + 3O_2 \xrightarrow{\text{nitroso-bacteria}} 2NO_2^- + 4H^+ + 2H_2O$$

2. oxidation of nitrite NO_2 to nitrate NO_3

$$2\,NO_2^- + O_2 \xrightarrow{\text{nitro-bacteria}} 2NO_3^-$$

Nitrification is slightly less thermodynamically favorable than oxidation with oxygen, but both can proceed in biological treatment such as AST

Nitrifying bacteria grow more slowly than heterotrophic bacteria and have lower cell yield — longer detention times needed to achieve nitrification in AST

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

1 gram N uses 4.57 grams O_2 based on stoichiometry

In actuality, less O_2 is needed since O is generated by fixing CO_2 and N into cell mass. This uses [Alk]:

$$NH_4^+ + 2HCO_3^- + 2O_2 \rightarrow NO_3^- + 2CO_2 + 3H_2O$$

1 gram N uses 7.14 g Alk as $CaCO_3$

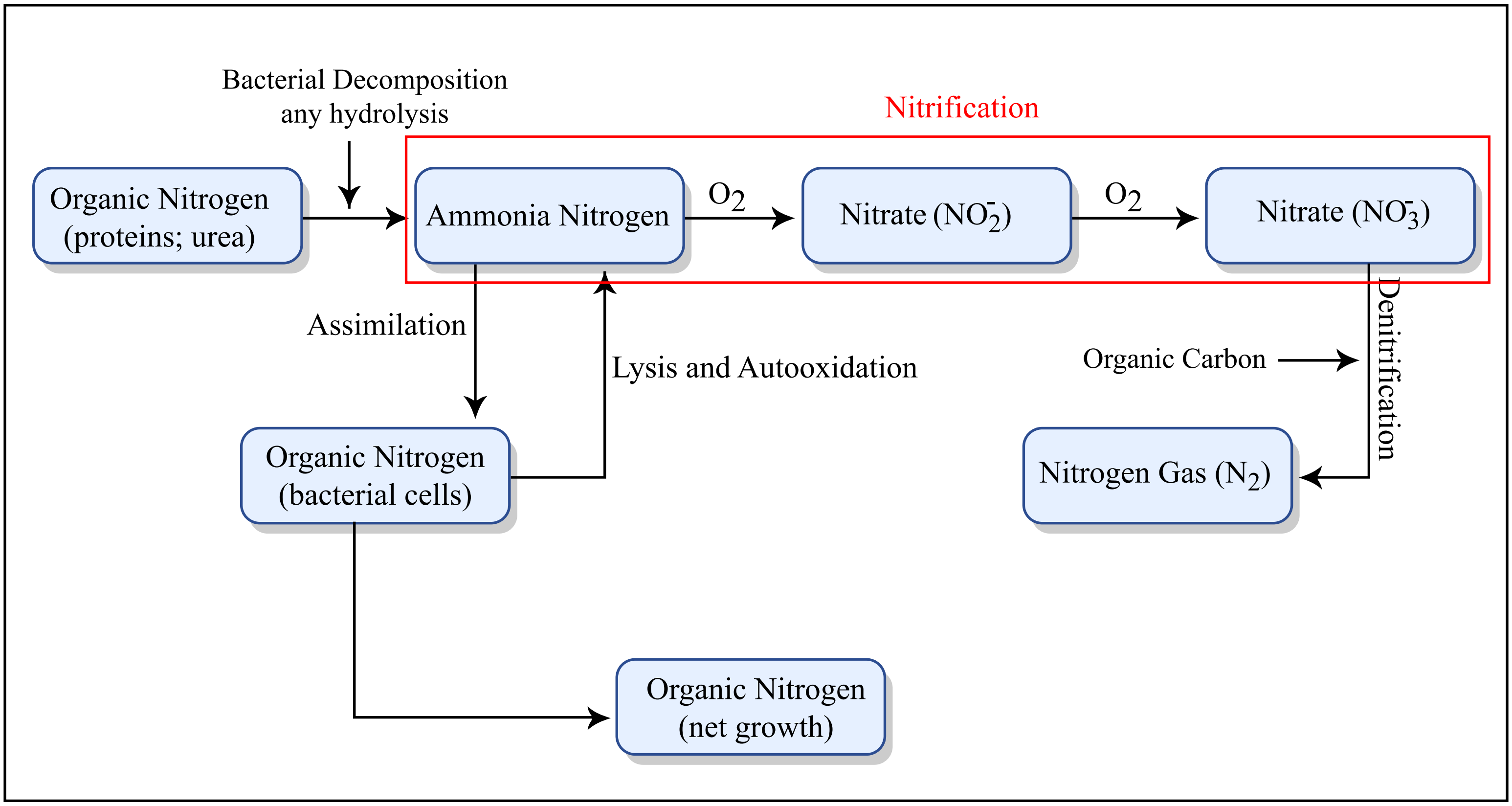


Figure by MIT OCW.

Adapted from: G. Tchobanoglous, F. L. Burton, and H. D. Stensel. *Wastewater Engineering: Treatment and Reuse*. 4th ed. Metcalf & Eddy Inc., New York, NY: McGraw-Hill, 2003, p. 617.

Both reactions actually contribute. Overall reaction is estimated as:

$$NH_4^+ + 1.863\,O_2 + 0.098\,CO_2 \rightarrow$$

$$0.0196\,\underset{\text{(new cells)}}{C_5H_7NO_2} + 0.98\,NO_3^- +$$

$$0.0941\,H_2O + 1.98\,H^+$$

For each gram of N, 4.25 g O_2 used, 0.16 g new cells formed, 7.07 g Alk as $CaCO_3$ used

Denitrification

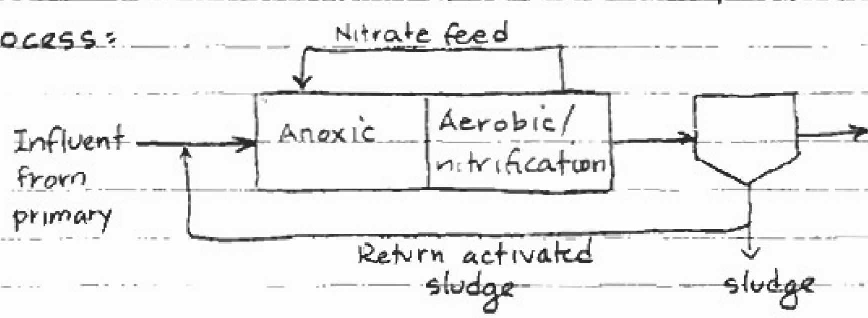
Bacteria oxidize organic substrate using nitrate/nitrite as electron acceptor

Nitrate goes as: $NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$

Organic substrate may be wastewater:

$$C_{10}H_{19}O_3N + 10\,NO_3^- \rightarrow 5\,N_2 + 10\,CO_2 + 3H_2O + NH_3 + 10\,OH^-$$

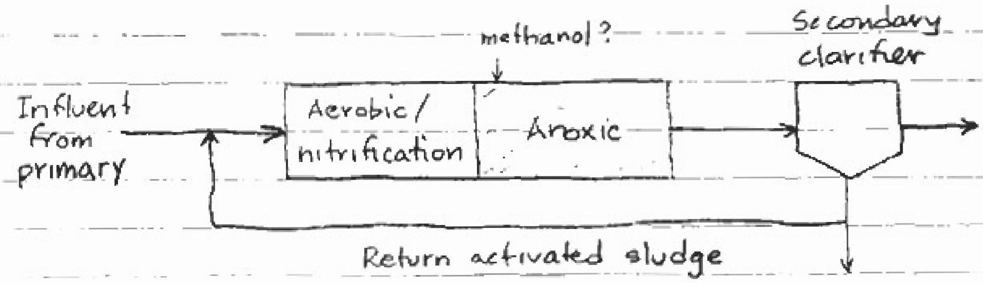
Occurs under anoxic conditions in preanoxic process:



Sometimes called "substrate-driven" denitrification

Wastewater is electron donor

Postanoxic denitrification:



Called "endogenous driven"

Endogenous decay of cells supplies electron donors → slower rate of reaction, requires longer retention times

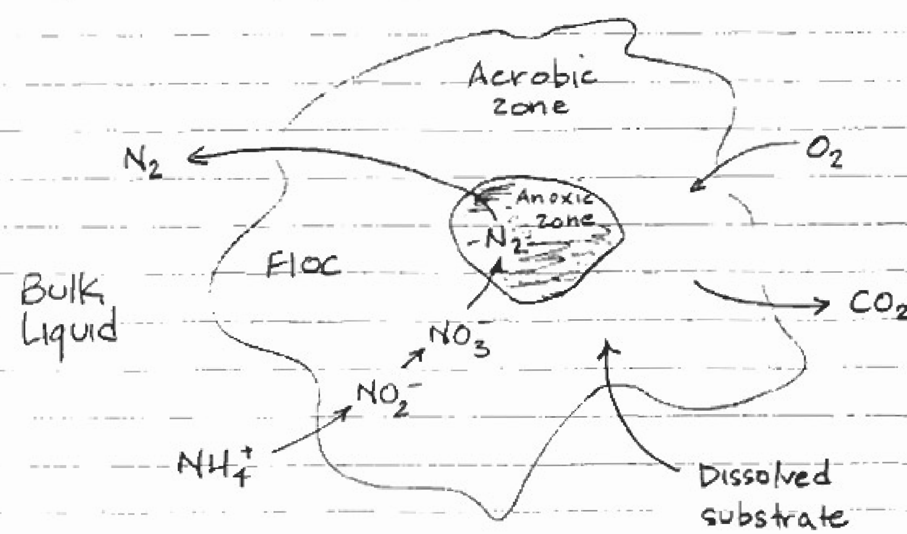
Sometimes supplementary source of carbon (electron donor) added: methanol or acetate

Methanol $5CH_3OH + 6NO_3^- \rightarrow 3N_2 + 5CO_2 + 7H_2O + 6OH^-$

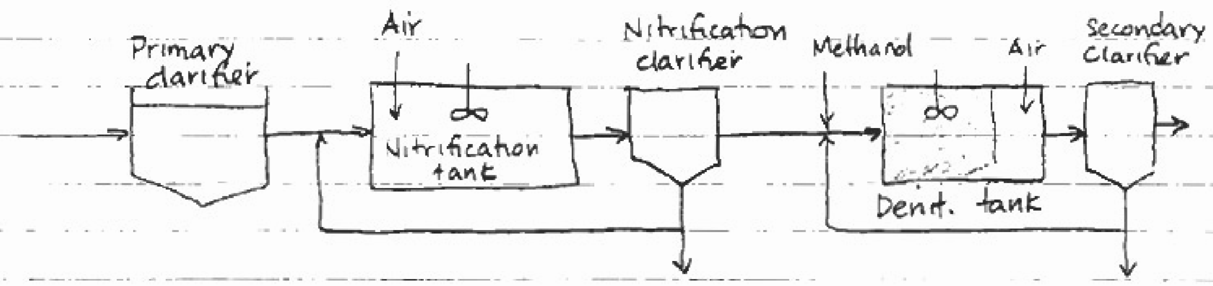
Acetate $5CH_3COOH + 8NO_3^- \rightarrow 4N_2 + 10CO_2 + 6H_2O + 8OH^-$

Conditions: DO < 0.2 mg/L in bulk liquid

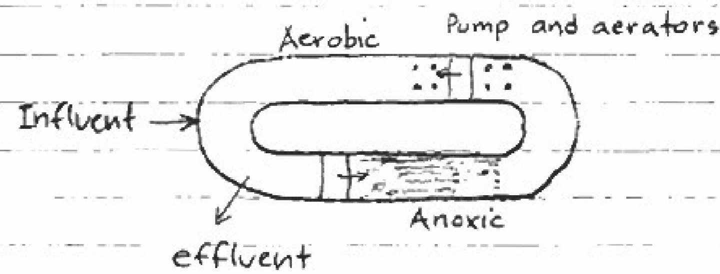
Actual DO in floc can be less than bulk liquid and nitrification and denitrification may proceed simultaneously:



Other options include a "two-sludge" system:



Race-track oxidation ditch



Same in principle as preanoxic system

Rate processes

Reactions are represented in same general form:

$$\mu_g = \mu_{max} \frac{S}{S + K_s}$$

Coefficient values differ:

	μ_{max} $\left(\frac{g\ VSS}{g\ VSS\text{-}d}\right)$	K_s $\left(\frac{g\ subst.}{m^3}\right)$	Y $\left(\frac{g\ VSS}{g\ subst.}\right)$	Substrate
Heterotrophs	3 – 13	5 – 40	0.3 – 0.5	bCOD
Nitrification	0.2 – 0.9	0.5 – 1.0	0.1 – 0.15	NH_4-N
Denitrification	3.2	9	0.4	COD
w/ methanol	0.5 – 2	9 – 13	0.17	COD (methanol)

Phosphorus removal

Phosphorus in wastewater treatment plant effluents is a concern because P is usually the limiting nutrient in fresh water bodies

P in effluent can therefore cause eutrophication of lakes and rivers

Typical P concentrations:

		Total P	Soluble P
Untreated domestic wastewater	—	10 mg/L	7 mg/L
After primary treatment	—	8	7
After secondary treatment	—	7	7

Typical removal in secondary biological treatment is 10 to 30 % of total P

In water-quality limited streams, effluent limits for P are set at 0.1 to 2 mg/L
(0.5 was once used as a generic limit but no longer)

Phosphorus chemistry:

Phosphorus analytical chemistry is tricky because there are not analytical methods to quantify the forms of P important for biota

Ironically, P cycling through organisms is well understood because there are radioactive isotopes of P that can be used as tracers

Analytically determined P forms:

- Total P (TP)
  - Particulate P – trapped by 0.45-μm filter
  - Soluble P – passes thru' filter
    - Soluble reactive P – measured by molybdate blue method (without acid digestion) = ortho-P
    - Soluble unreactive P – remainder

Forms of phosphorus available to microorganisms:

Soluble reactive P
= orthophosphate PO_4^{3-}

Polyphosphates from detergents are also a concern:
e.g. sodium tripolyphosphate $Na_5P_3O_{10}$

Boil in H_2SO_4 for 90 min.

Acid digestion of sample causes polyphosphates to break down to orthophosphates - then measure with molybdate blue method to get
Total inorganic P = ortho-P + polyphosphate

In environment, polyphosphates hydrolyze to form ortho-P over time

Strong acid digestion (nitric or perchloric acid) of unfiltered sample breaks down organic particulates to ortho-P - then measure with molybdate blue to get Total P =
Total inorganic P + organic P

Summary:

No digestion - ortho-P
H_2SO_4 acid digestion - Inorganic P = ortho-P + poly-P
Strong acid digestion - Total P = inorganic P + organic P

Above can be done on filtrate of 0.45-µm filter to get soluble fraction or on unfiltered sample to get totals

Biological P removal systems are designed to create conditions favorable to Phosphorus Accumulating Organisms (PAOs) – see pg 10 and 11

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Certain bacteria (e.g. Acinetobacter) synthesize polyphosphates and store it in their cellular material – process is sometimes called "luxury uptake"

PAOs are favored by alternating aerobic/anaerobic conditions

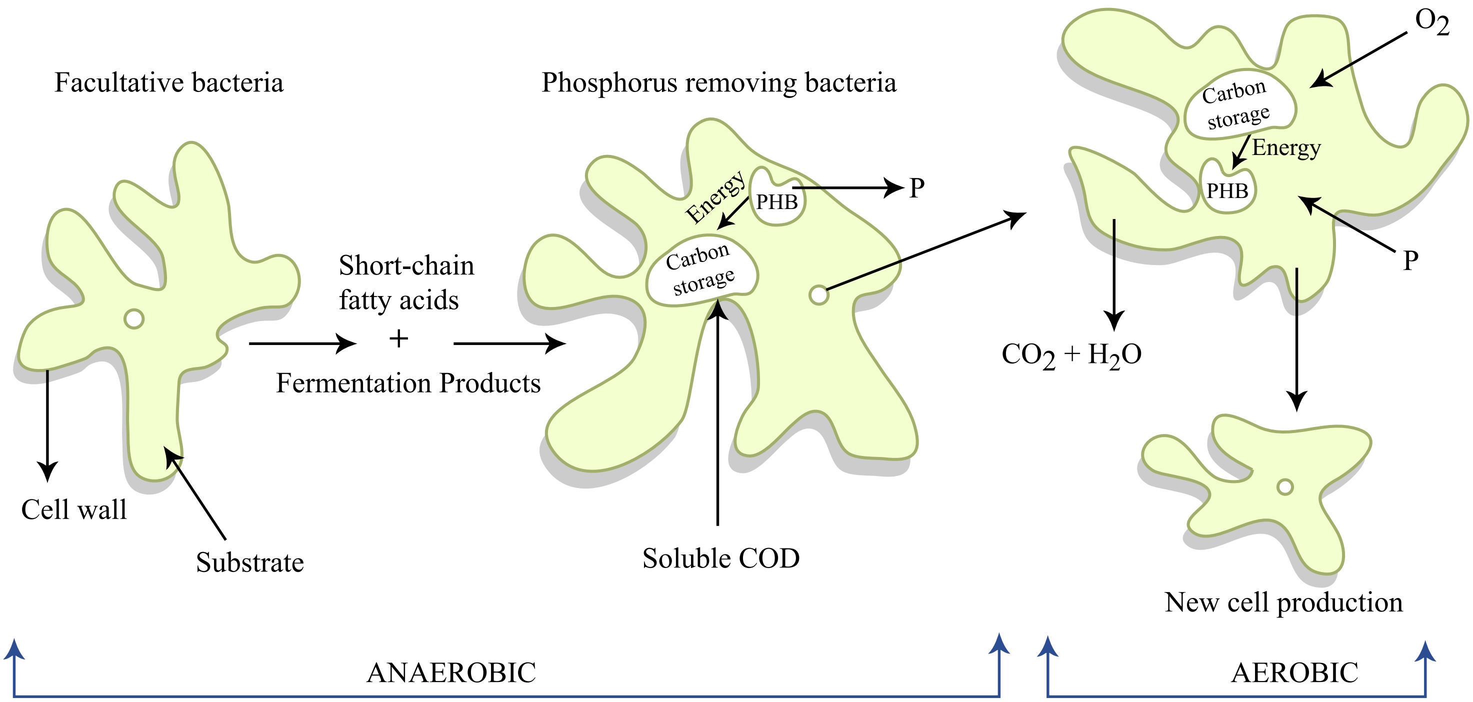
First step is anaerobic:
Available carbon and electrons are stored in polyhydroxybutyrate (PHB) and other volatile fatty acids. This storage is not done if electron acceptors like O_2 or NO_3 are present, hence the need for anaerobic conditions. Simultaneously, polyphosphate is broken down and ortho-P is released to mixed liquor (see Figure 7-23 from M+E, pg 12)

Next step is aerobic or anoxic (denitrifying):
Bacteria metabolize stored PHB, uptake ortho-P, stored as poly-P within cell material. Cells become enriched in polyphosphates

Last step is removal of P-enriched cells in wasted sludge – P is removed along with cells.

Key to success of P removal is encouraging the growth of the particular types of bacteria that accumulate P.

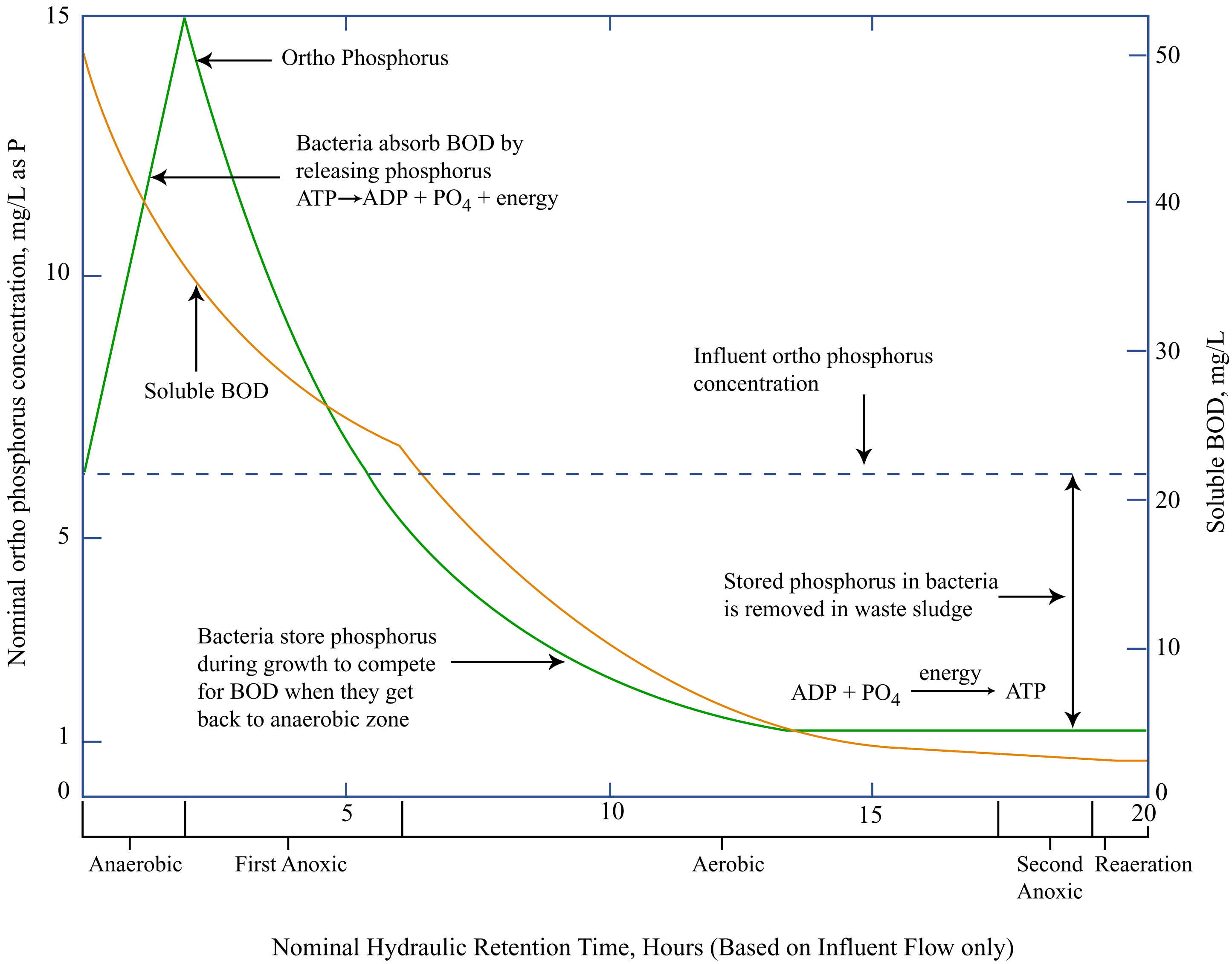
The anaerobic reactor causes fermentation that breaks down COD to acetate, a substrate preferred by PAOs. This step is sometimes called the "selector" since it favors (selects for) PAOs.



Removal mechanisms for excess biological phosphorus (COD = chemical oxygen demand, PHB = poly-β-hydroxybutyrate).

Figure by MIT OCW.

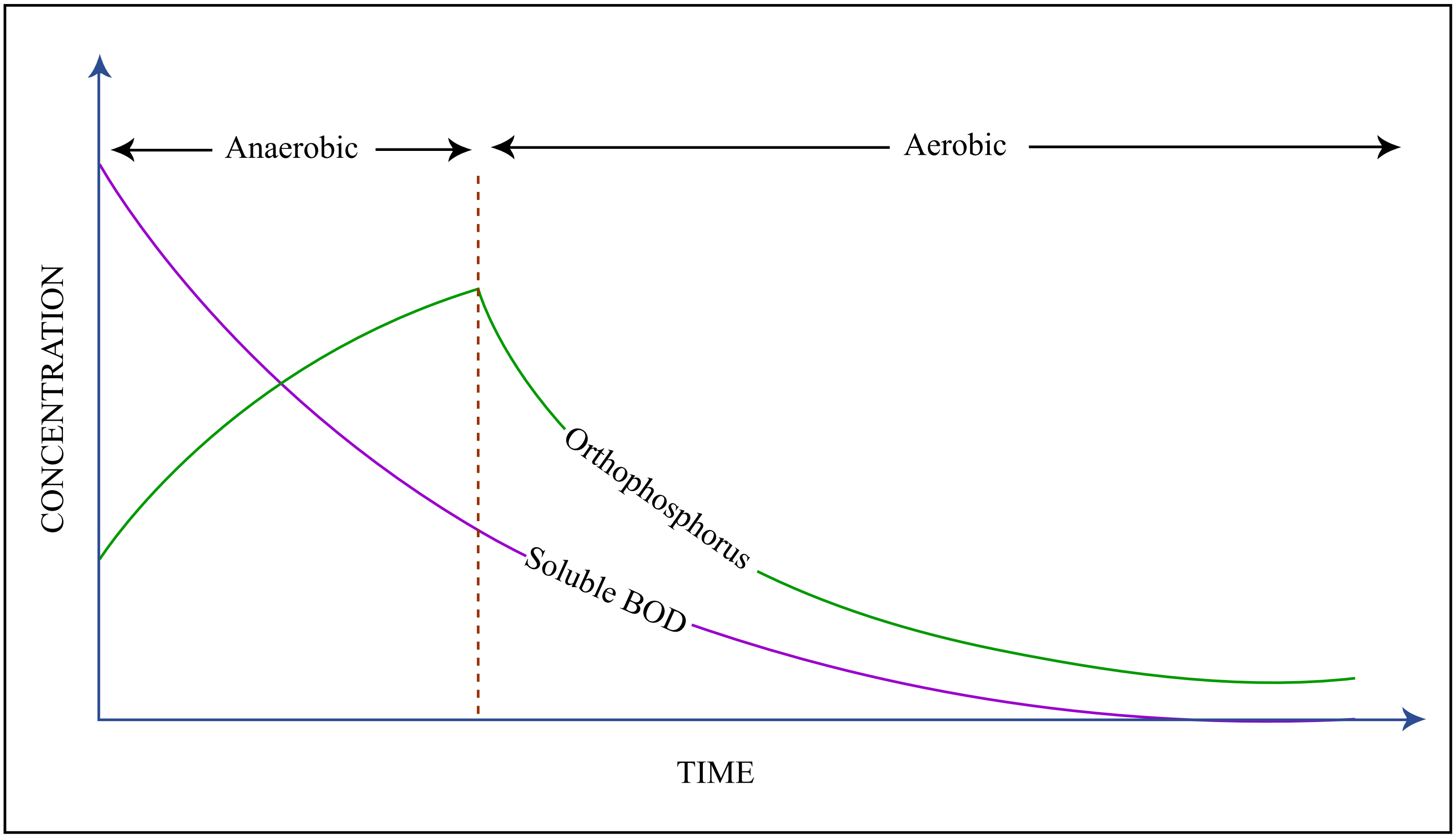
Adapted from: Rittman, Bruce E., and Perry L. McCarty. *Environmental Biotechnology: Principals and Applications*. New York, NY: McGraw-Hill, 2001.



Typical profile of soluble phosphorus concentrations in a biological nutrient removal process (ATP = adenosine triphosphate, ADP = adenosine diphosphate).

Figure by MIT OCW.

Adapted from: Rittman, Bruce E., and Perry L. McCarty. *Environmental Biotechnology: Principals and Applications*. New York, NY: McGraw-Hill, 2001.

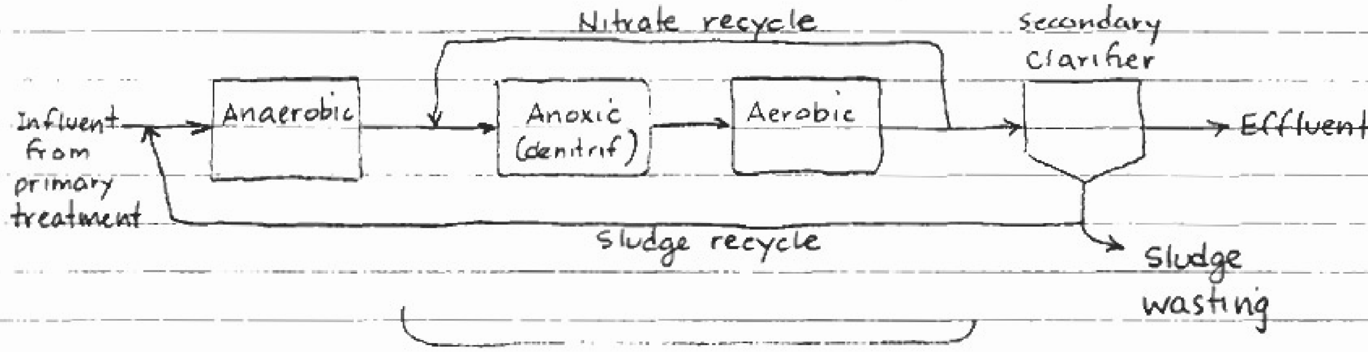


Fate of soluble BOD and phosphorus in nutrient removal reactor.

Figure by MIT OCW.
Adapted from: G. Tchobanoglous, F. L. Burton, and H. D. Stensel. *Wastewater Engineering: Treatment and Reuse*. 4th ed. Metcalf & Eddy Inc., New York, NY: McGraw-Hill, 2003, p. 626.

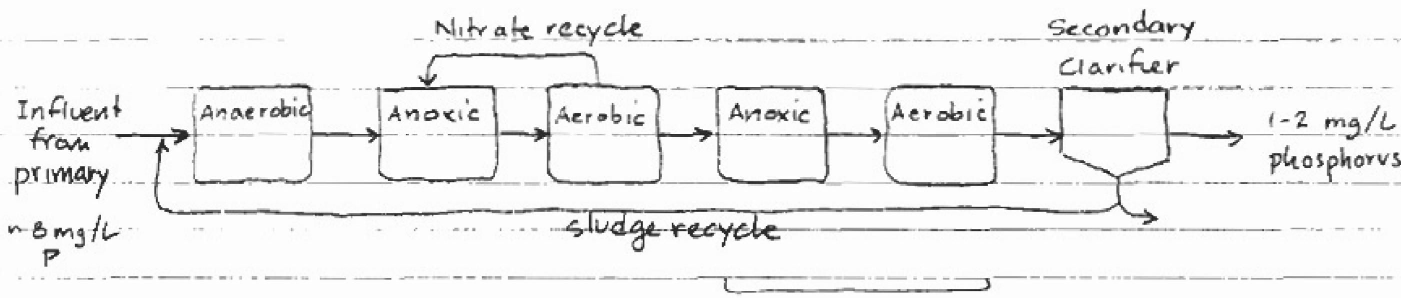
Configurations for biological P removal

Predenitrification: (also called A^2O process)



Preanoxic nitrogen removal process

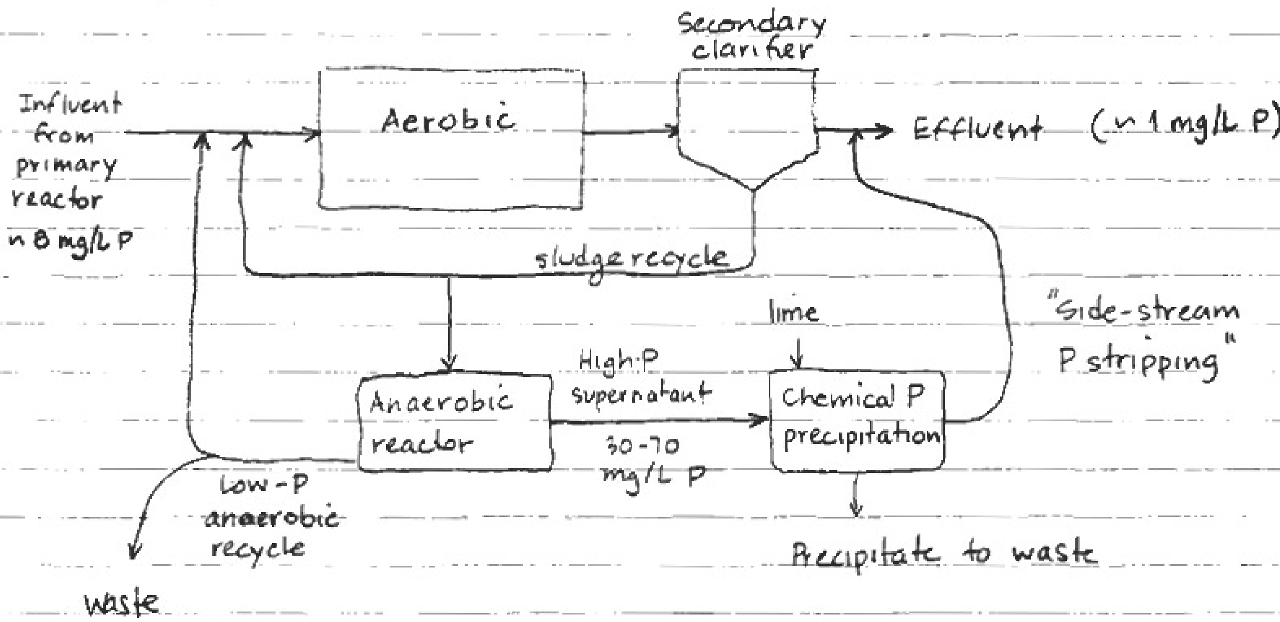
Bardenpho process:



Achieves added N removal

Removes 93% total N, 65% total P

PhoStrip process:



Hydrolysis in anaerobic reactor releases poly-P to water (supernatant) — 30-70 mg P/L

Addition of lime to precipitator tank raises pH to ~11, causes $Ca_3(PO_4)_2$ (s) to precipitate

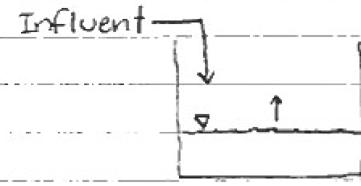
Requires more sophisticated operation than alternatives above

Sequencing batch reactor (SBR)

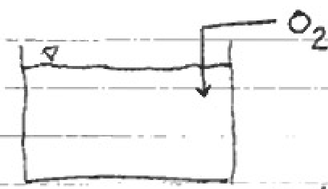
Rather than continuous flow through sequence of tanks for different treatment steps, all steps are done sequentially in a single tank

For conventional AST:

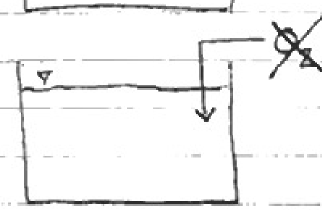
Step 1 - Fill
(add substrate)



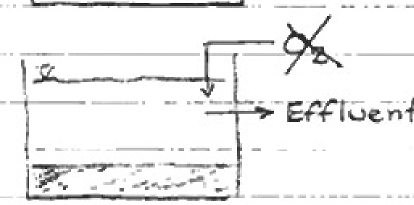
Step 2 - React



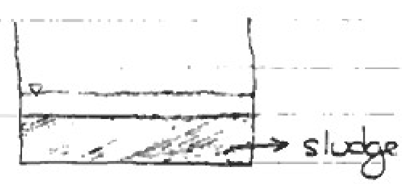
Step 3 - Settle



Step 4 - Draw
(decant effluent)



Step 5 - Idle
(waste sludge)



SBRs are very flexible as to steps, making it possible to add anoxic and anaerobic steps to the sequence for N or P removal

SBR for P removal

Step 1 - Fill

Step 2 - Anaerobic react
(tank is mixed but without aeration)

Step 3 - Aerobic react

Step 4 - Anoxic react (denitrification)

(Note: steps 3 and 4 may be repeated)

Step 5 - Settle

Step 6 - Decant

Step 7 - Idle (waste sludge)

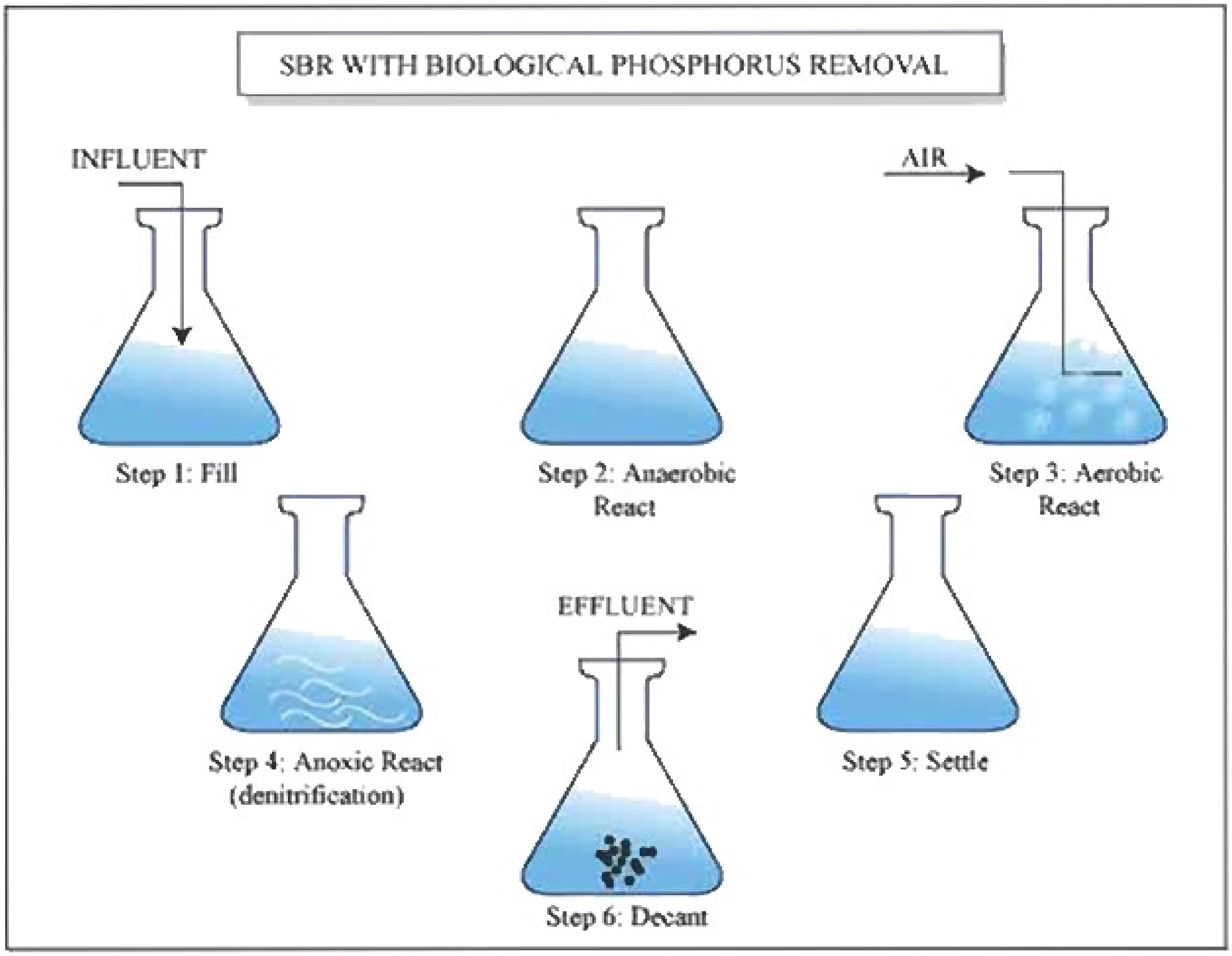


Figure by MIT OCW.

Adapted from: G. Tchobanoglous, F. L. Burton, and H. D. Stensel. *Wastewater Engineering: Treatment and Reuse*. 4th ed. Metcalf & Eddy Inc., New York, NY: McGraw-Hill, 2003, p. 813.

Chemically - enhanced primary treatment (CEPT)

Also called Advanced primary treatment
Chemically assisted primary treatment
Chemically assisted settling

Improves removal rates in primary treatment by enhancing settling

Also very effective for P removal, odor control

Chemicals used:

Metal salt (usually ferric chloride, $FeCl_3$
sometimes alum, $Al_2(SO_4)_3$
others - see pg 19.

Anionic polymer

Typical concentrations: $FeCl_3$ - 20-30 mg/L
polymer - 0.25 mg/L

Phosphorus removed by chemical precip.:

$$FeCl_3 + H_2PO_4^- + 2HCO_3^- \longrightarrow$$

$$FePO_4 \downarrow + 3Cl^- + 2CO_2 + 2H_2O$$

Coagulant action of ferric salts and polymer increases settling of solids - see pg 20

Very effective as technique to upgrade existing treatment plants - see page 21

Allows increased wastewater flow rate to be treated - see page 22

Inorganic Chemicals Used Most Commonly for Coagulation and Precipitation Processes in Wastewater Treatment

Chemical	Formula	Molecular Weight	Equivalent Weight	AVAILABILITY	
				Form	Percent
Alum	$Al_2(SO_4)_3 \cdot 18H_2O$#	666.5		Liquid	8.5 (Al_2O_3)
				Lump	17 (Al_2O_3)
	$Al_2(SO_4)_3 \cdot 14H_2O$#	594.4	114	Liquid	8.5 (Al_2O_3)
				Lump	17 (Al_2O_3)
Aluminum Chloride	$AlCl_3$	133.3	44	Liquid	
Calcium Hydroxide (lime)	$Ca(OH)_2$	56.1 as CaO	40	Lump	63-73 as CaO
				Powder	85-99
				Slurry	15-20
Ferric Chloride	$FeCl_3$	162.2	91	Liquid	20 (Fe)
				Lump	20 (Fe)
Ferric Sulfate	$Fe_2(SO_4)_3$	400	51.5	Granular	18.5 (Fe)
Ferrous Sulfate (copperas)	$FeSO_4 \cdot 7H_2O$	278.1	139	Granular	20 (Fe)
Sodium Aluminate	$Na_2Al_2O_4$	163.9	100	Flake	46 (Al_2O_3)

Number of bound water molecules will typically vary from 14 to 18

Figure by MIT OCW.

Adapted from : Metcalf, and Eddy. 2003

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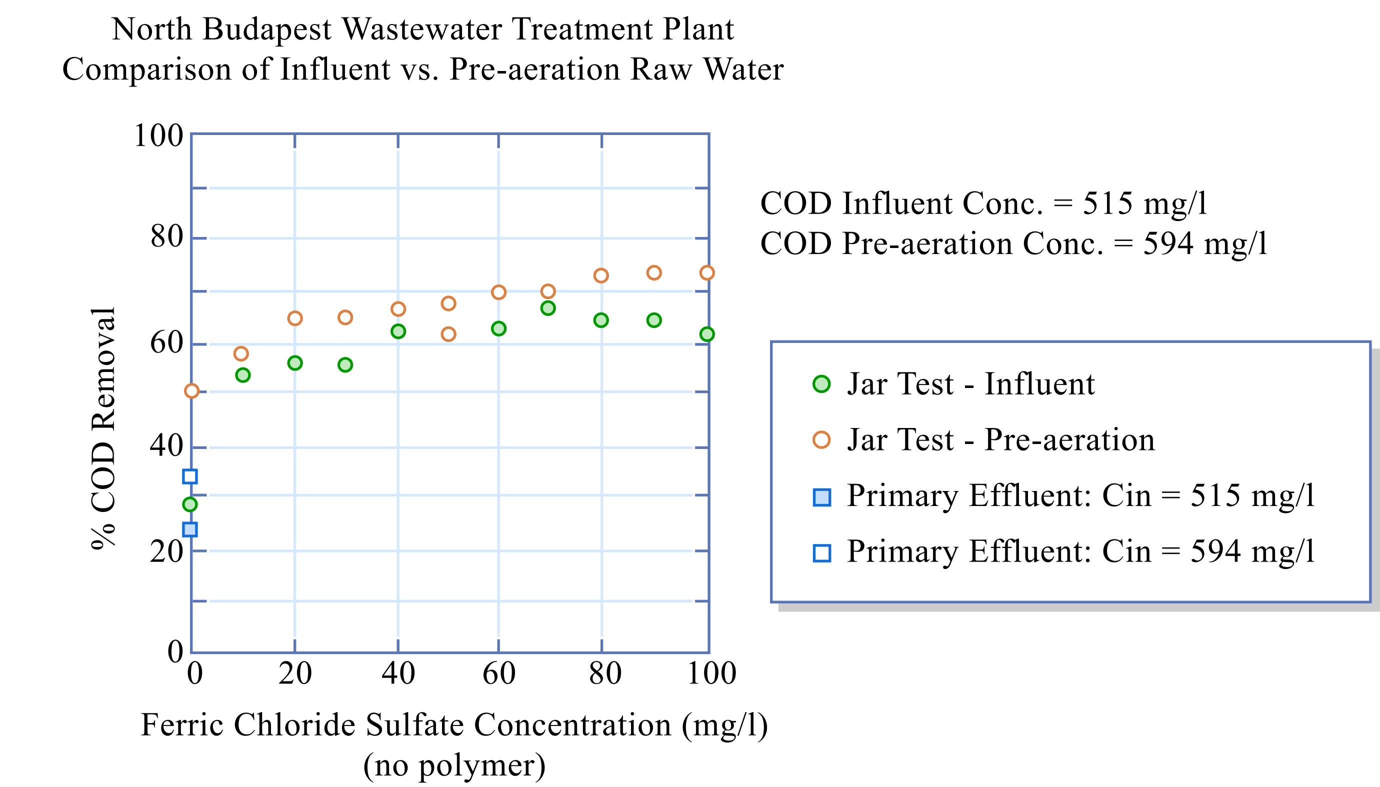


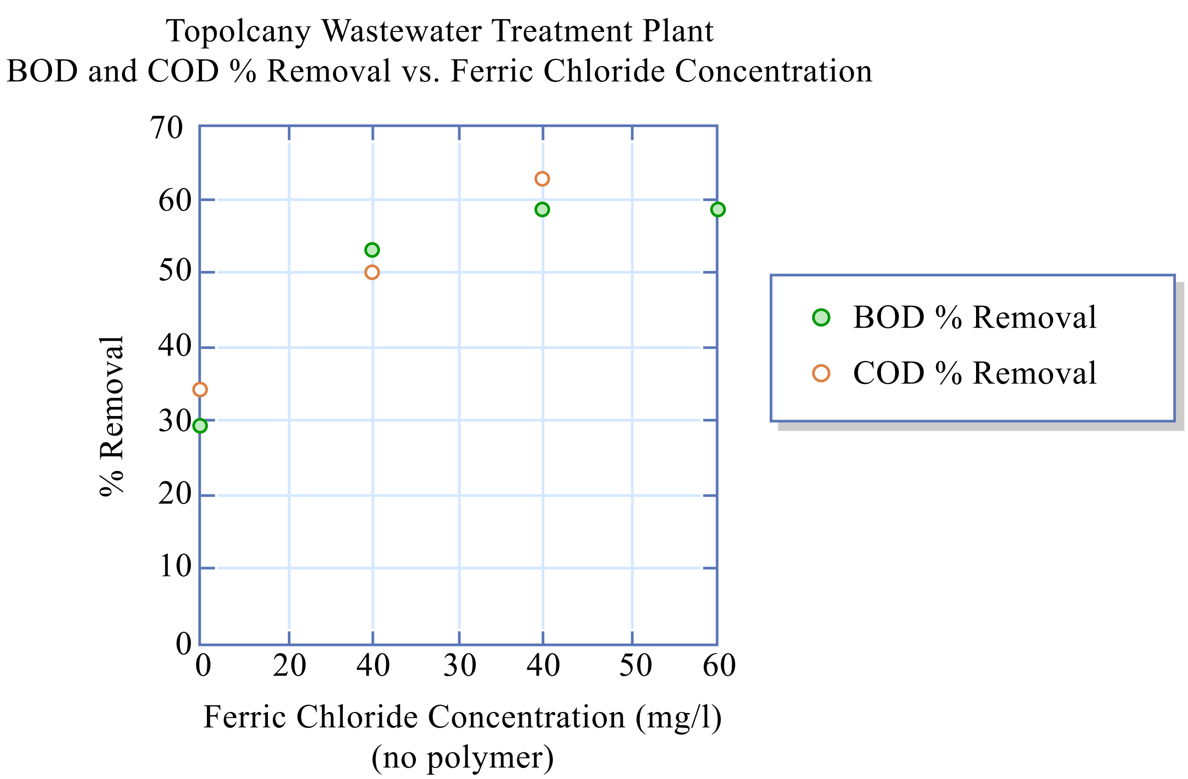
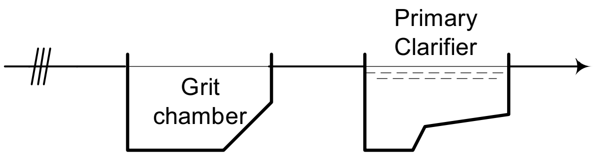
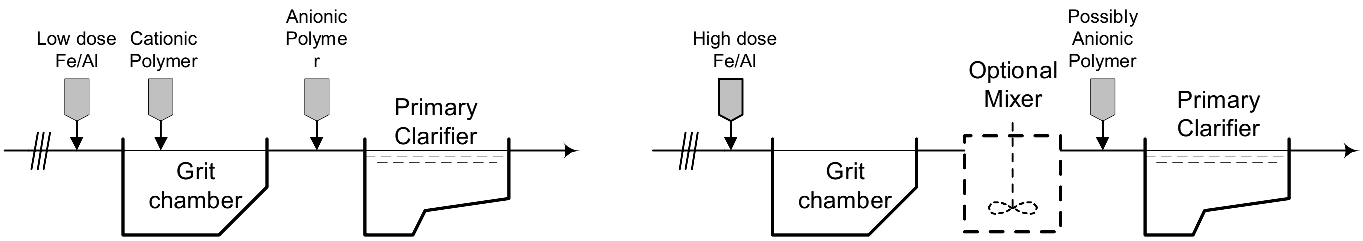


Figure by MIT OCW.

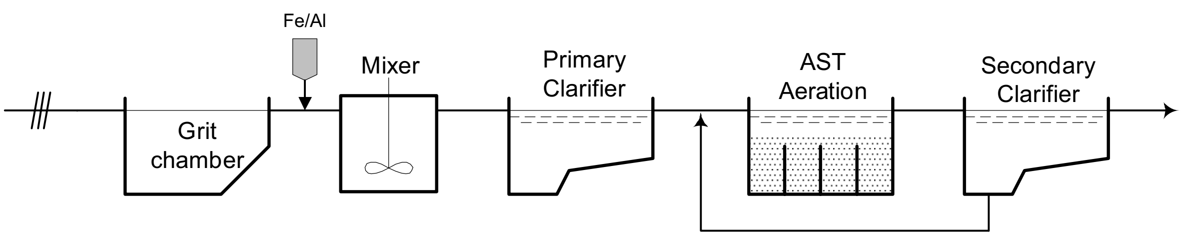
Adapted from: Murcott, and Hurleman. 1994, p. 24



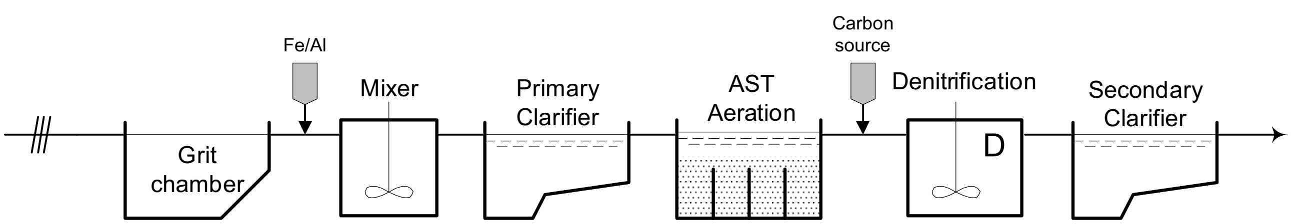
a. Existing primary treatment plant



b. CEPT (left) and primary precipitation (right)

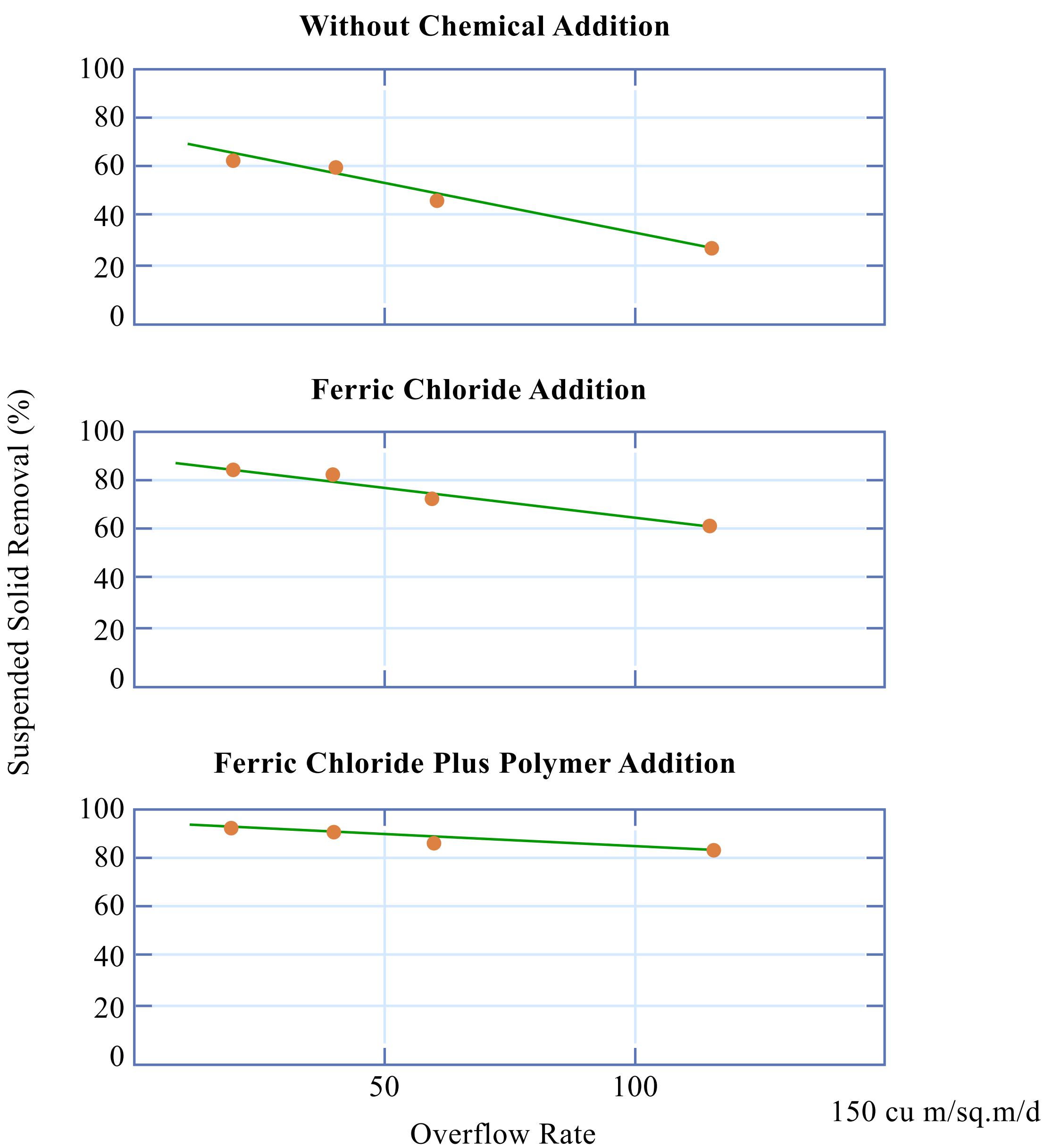


c. Preprecipitation (or CEPT) followed by ASP



d. Preprecipitation with ASP and postdenitrification

Multi-stage upgrading of an existing
primary treatment plant



Overflow Rate Verses TSS Removal for Sarnia Treatment Plant

Figure by MIT OCW.