BIOLOGICAL PROCESSES WITH MULTIPLE ZONES

PROCESS CONSIDERATIONS FOR NITROGEN REMOVAL VIA NITRIFICATION AND DENITRIFICATION IN CELL RECYCLE SYSTEM

DENITRIFICATION
- ASSIMILATORY (NO_3 used for cell synthesis) NO_3^- → organic N
- DISSIMILATORY (NO3 is e^- acceptor in respiration) NO_3^- → N_2 typically. Dissimilatory process carried out by facultative heterotrophs (genera: *Pseudomonas, Paracoccus, Hyphomicrobium, Alcaligenes*, and others) is used in wastewater treatment. May also produce NO_2^-, N_2O, even NH_4^+ PROCESS DESIGN BASED ON DISSIMILATORY DENITRIFICATION, OR NITRATE RESPIRATION.
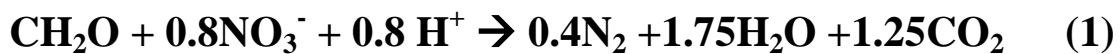
ENERGETICS OF RESPIRATION.

ORDER OF ENERGY PROVIDED BY e^- ACCEPTORS:
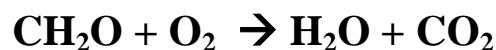
$$O_2 > NO_3^- > NO_2^- > Fe^{3+} > SO_4^{2-}$$
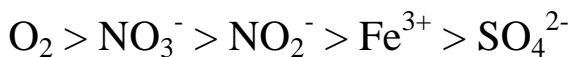
So anoxia is a condition for denitrification by facultative bacteria, which would use oxygen preferentially for energy production if available.

DENITRIFICATION PROCESS STOICHIOMETRY (MOLAR)

$$CH_2O + 0.8NO_3^- + 0.8 H^+ → 0.4N_2 + 1.75H_2O + 1.25CO_2 \quad (1)$$

COMPARE WITH AEROBIC RESPIRATION

$$CH_2O + O_2 → H_2O + CO_2$$

Compare e- acceptor consumption/gram carbohydrate:

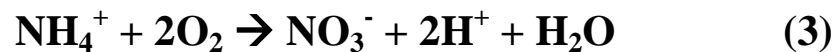1mole(32g/mole) O_2/0.8mole(14g/mole)-NO_3-N = **2.86 g- O_2/g- NO_3-N**

each gram on nitrate consumed in respiration saves 2.86 gram oxygen

COD-BASED WITH GROWTH (CELLS AS REFERENCE):

$$(-1/Y_H)S_S - ((1-Y_H)/2.86Y_H)S_{NO} + X_{BH} = 0 \qquad (2)$$

ALKALINITY EFFECTS

NITRIFICATION (MOLAR STOICHIOMETRY, NEGLECT GROWTH):

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O \qquad (3)$$

(2eq alkalinity consumed/mole NH_4^+-N oxidized)*50 g-$CaCO_3$/14 g-N/mole =..
…= **7.1 g-CaCO₃ consumed/g-NH₄⁺-N oxidized**

and **4.57 g-O2/g-NH₄⁺-N oxidized**

DENITRIFICATION

From (1):

1eq alkalinity produced/mole NO_3^--N reduced)*50 g-$CaCO_3$/14 g-N/mole = …
…= **3.6 g-CaCO₃ consumed/g-NO₃⁻-N reduced**

Denitrification Recovers Alkalinity and Oxygen:

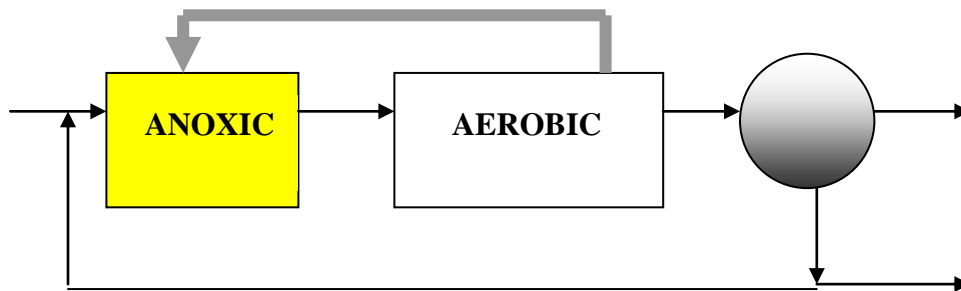**Net alkalinity consumption = 7.1 – 3.6 =…**
…= 3.5 g-CaCO₃ consumed/g-NH₄⁺-N oxidized and reduced)

Net oxygen consumption = 4.57 – 2.86 = …
… = 1.8 g-O2/g-NH₄⁺-N oxidized and reduced)

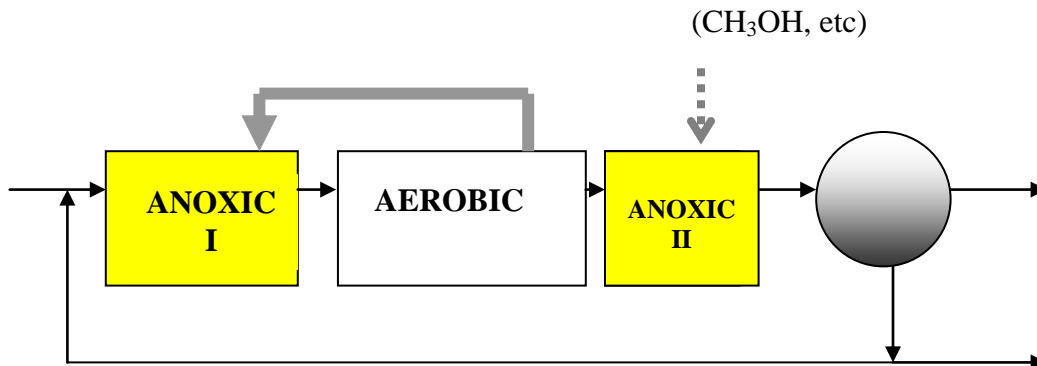# SUSPENDED GROWTH REACTORS WITH MULTIPLE ZONES
NITRIFICATION FOLLOWED BY DENITRIFICATION (ALSO "AIR ON-OFF" OPERATION)

(CH$_3$OH, etc)

AEROBIC | ANOXIC
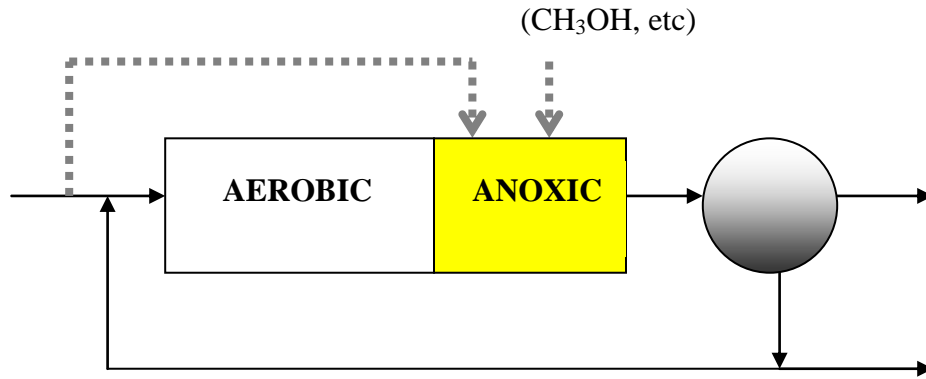
MODIFIED LUDZACK-ETTINGER PROCESS (MLE)

ANOXIC | AEROBIC

THREE-STAGE BARDENPHO PROCESS

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(CH$_3$OH, etc)

ANOXIC I | AEROBIC | ANOXIC II

CONSTRAINED DESIGN PROEDURE FOR DENITRIFICATION PROCESSES THAT USE NITRATE RECIRCULATION (MLE AND BARDENPHO). NOT MASS BALANCE APPROACH AS WAS USED FOR COD AND AMMONIA OXIDATION (NITRIFICATION)

FACTORS
1. TIME BIOMASS SPENDS IN APPROPRIATE PROCESS ZONE
2. COD SUBSTRATE AVAILABLE FOR DENITRIFICATION
3. NITRATE RECIRCULATION RATE

1. Define a solids retention time for each zone based on fraction of total solids retention time cells are aerated and anoxic to zone volumes:

$$f_{XM,aer} = \Theta_{aer}/\Theta = \Sigma_i(V_iX_{Bi})_{aer}/(VX_B)_{system}$$

$$f_{XM,anox} = \Theta_{anox}/\Theta = \Sigma_i(V_iX_{Bi})_{anox}/(VX_B)_{system}$$

where $f_{XM,i}$ = fraction that biomass of concentration X_{Bi} spends in a zone, i, characterized as aerated (aer) or unaerated (anox), with volume, V_i, where $\Theta_i = \Sigma_i(V_iX_{Bi})/Q_wX_w$, $\Theta = (VX_B)_{system}/Q_wX_w$, and $\Sigma_i\Theta_i = \Theta$.
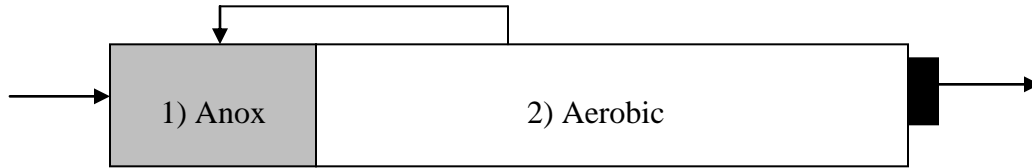
Assume that biomass concentration is uniform throughout system (cell recirculation is more significant in determining X_{Bi} than growth. Then:

$$\Theta_{aer}/\Theta = \Sigma_i(V_i)_{aer}/(V)_{system} \qquad \textbf{(4)}$$

and

$$\Theta_{anox}/\Theta = \Sigma_i(V_i)_{anox}/(V)_{system} \qquad \textbf{(5)}$$

For example, for an MLE process:

Given: $V_1 = 3{,}000 \text{ m}^3$, $V_2 = 7{,}000 \text{ m}^3$, and $\Theta_{system} = 7$ d, then

$$\Theta_{anox} = 2.1 \text{ d and } \Theta_{aer} = 4.9 \text{ d}$$

For an MLE PROCESS with one aerobic and one anoxic zone:

$$\mathbf{V_{system} = V_{aer} + V_{anox}}$$

Substituting (6) into (4) and (5) for the following relation:

$$\mathbf{V_{anox}/V_{aer} = \Theta_{anox}/(\Theta - \Theta_{anox}) = (\Theta - \Theta_{aer})/\Theta_{aer}}$$

And

$$\mathbf{\Theta = \Theta_{anox} + \Theta_{aer}} \qquad \mathbf{(6)}$$

2. COD REQUIREMENT FOR DENITRIFICATION

O_2 consumption rate, RO, for aerobic respiration,

$$\mathbf{RO \text{ (g-}O_2/day) = Q(S_{SO} - S_S)(1 - Y_{Hobs})} \qquad \mathbf{(g\text{-}O_2/d)}$$

For denitrification, equivalent nitrate consumption rate, RO_N, expressed as oxygen equivalents:

$$\mathbf{RO_N = 2.86 RNO \text{ (g-}O_2/day) = 2.86 Q(S_{NNO} - S_{NO})}$$

Where
RO_N = rate of nitrate consumption expressed as oxygen equivalents
RNO = mass rate of nitrate consumption (kg/d)
S_{NNO} = soluble nitrate nitrogen influent to anoxic tank or zone (mg/L N)
S_{NO} = anoxic tank concentration of soluble nitrate nitrogen (mg/L N)
Q = flow rate (m^3/d)

Since nitrate is expressed as oxygen equivalents, now can write

$$RO_N = 2.86Q(S_{NNO}\text{-}S_{NO}) = Q(S_{SO} - S_S)_N(1 - Y_{Hobs}) \text{ (g-}O_2\text{/d)} \qquad (6)$$

Since the mass of substrate COD oxidized during denitrification in the anoxic zone, $(S_{SO} - S_S)_N(1 - Y_{Hobs})$, accounts for the mass of nitrate reduced, expressed as oxygen.

Where $(S_{SO} - S_S)_N$ represents the COD consumed during denitrification

$$\text{COD required per amount of denitrification in terms of N} = \Delta S_{S,N}/\Delta N$$
$$= \cancel{Q}(S_{SO} - S_S)_N/\cancel{Q}(S_{NNO} - S_{NO})$$

Rearranging and substituting $\Delta S_{S,N}/\Delta N$ into (6):

$$\Delta S_{S,N}/\Delta N = 2.86/(1 - Y_{Hobs}) = 2.86(1+b\Theta_{anox})/(1+b\Theta_{anox} - Y_H(1+f_Db\Theta_{anox}))$$
$$(7)$$

note different effects of Θ on oxygen consumption and on denitrification:

for aerobic processes principal concern is the increase in oxygen required because as Θ_{aer} increases, decay becomes more important in the biological process, since soluble COD and ammonia are recycled: as $\Theta\uparrow$, $RO\uparrow$ (more decay, more soluble COD produced, more oxygen consumption, HIGHER COST)

For denitrification the principal concern is the simultaneous utilization of nitrate and COD. As Θ_{anox} ↑, the consumption of influent substrate per unit mass nitrate reduced, $\Delta COD/\Delta N$, ↓ since decay creates more soluble substrate. Two effects: 1) <u>If influent COD is relatively low</u> for the amount of nitrate to be reduced in denitrification, long values of Θ_{anox} can be advantageous since the amount of nitrate to be reduced is higher than influent COD. 2) <u>However, if influent COD is high</u>, then the extra COD supplied by biomass decay will consume nitrate in the anoxic zone, leading to higher consumption of oxygen later in the aerobic zone, if all soluble COD is to be oxidized, and HIGHER COST.

Selected Θ_{anox} should result in maximum consumption of <u>influent</u> COD <u>and</u> generated nitrate in anoxic zone and minimum oxygen required in aerobic zone. Graph below shows second (high influent COD) effect: long Θ_{anox} → less influent COD consumed per mass nitrate reduced → greater oxygen requirement. Typically $5 < \Delta S_{S,N}/\Delta N < 9$ g-COD/g-NO₃-N

Effect of Θ_{anox} on influent COD consumed in denitrification
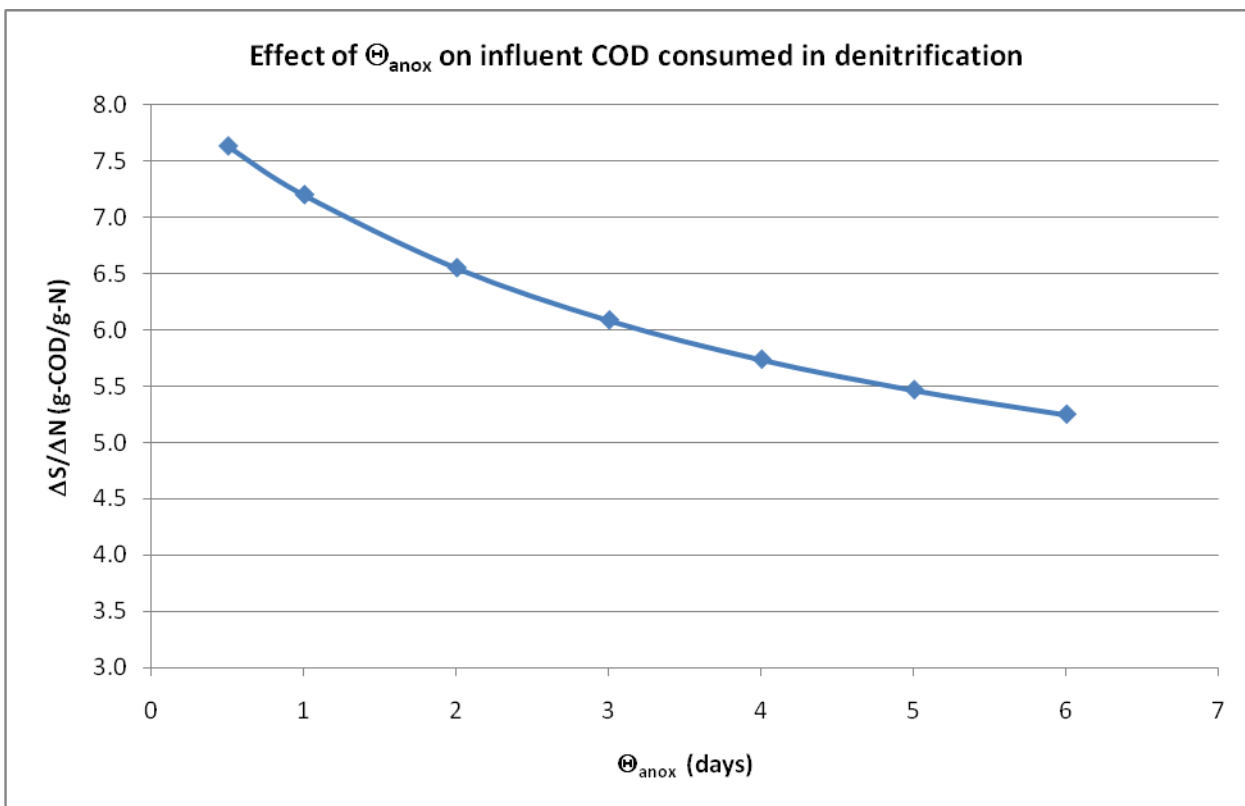
3. NITRATE RECIRCULATION, or MIXED LIQUOR RECIRCULATION (MLR)

Process constraint, providing sufficient nitrate for maximizing COD removal and saving oxygen.

Invert (7):

$$\Delta N/\Delta S_{S,N} = (1+b\Theta_{anox}-Y_H(1+f_Db\Theta_{anox}))/2.86(1+b\Theta_{anox}) \; (g\text{-}N/g\text{-}COD) \quad (8)$$

$$\Delta N = Q\Delta S_{S,N}(1+b\Theta_{anox}-Y_H(1+f_Db\Theta_{anox}))/2.86(1+b\Theta_{anox}) \quad (g\text{-}N/d) \quad (8a)$$

Available nitrate for denitrification (S_{NO}) is calculated assuming that influent nitrogen is either stored in heterotrophic cells (neglect autotroph cell growth), oxidized to nitrate or in effluent:

$$NO = Q(S_{NHO}+ S_{NSO} + X_{NSO} - NR(S_{SO}\text{-}S_S) - S_{NH} - S_{NS}) \; (g\text{-}N/d) \; (9)$$

Formula assumes influent ammonia, soluble and particulate organic nitrogen ($S_{NHO}+ S_{NSO} + X_{NSO}$) minus cell synthesis and effluent soluble ammonia and organic nitrogen is available nitrate

Define the fraction of available nitrate that can be denitrified, NO, in the anoxic zone, $f_{NO,D}$, which is a function of available substrate COD (from 8)

$$f_{NO,D} = \Delta N/NO \quad (10)$$

For the MLE system shown below, introduce the term fraction of nitrate produced in the aerobic tank that is recirculated (assuming negligible nitrate in the influent to the aerobic tank):
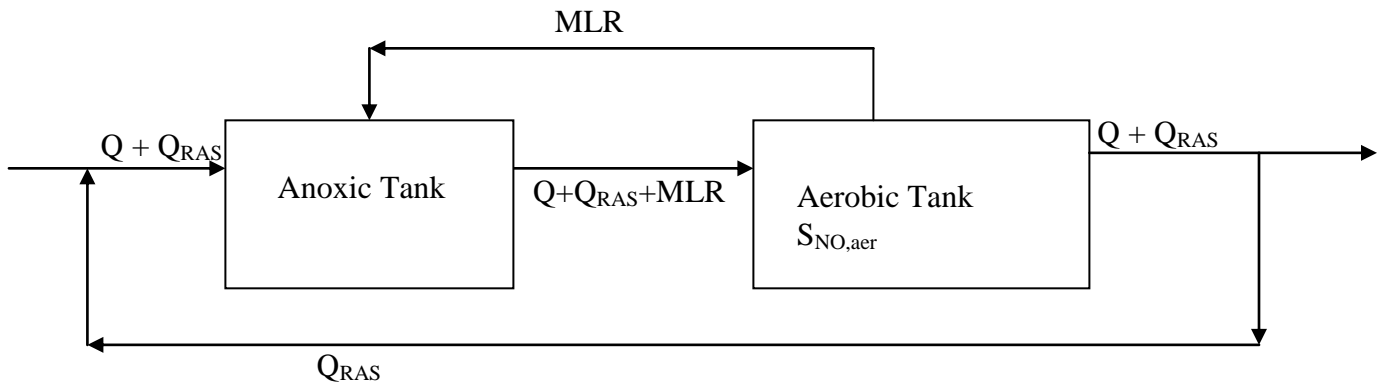
f$_{NO,R}$ = (NO$_3$-N flow into anoxic zone)/(NO$_3$-N flow out of aerobic zone)

$$f_{NO,R} = [(MLR + Q_{RAS})S_{NO,aer}]/[(Q + MLR + Q_{RAS})S_{NO,aer}]$$

where S$_{NO,aer}$ = nitrate concentration in aerobic tank and in both flows, MLR = mixed liquor recirculation flow rate from aerobic to anoxic tank, Q = system influent flow rate, Q$_{RAS}$ = recycled biomass flow rate from secondary clarifier.

divide numerator and denominator by Q and define:

$$\alpha = Q_{RAS}/Q$$

and

$$\beta = MLR/Q$$

$$f_{NO,R} = (\alpha+\beta)/(1+\alpha+\beta)$$

Rearranging to solve for the recirculation/recycle flow rate design values:

$$(\alpha+\beta) = f_{NO,R}(1+\alpha+\beta) = f_{NO,R} + f_{NO,R}(\alpha+\beta)$$

$$f_{NO,R} = (\alpha+\beta)(1- f_{NO,R})$$

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$$(\alpha+\beta) = f_{NO,R}/(1- f_{NO,R}) \qquad (11)$$

Objective: set α and β such that $f_{NO,R} = f_{NO,D}$ from (10), that is, design the recirculation/recycle flows such that the recirculated fraction equals the fraction of available nitrate that can be denitrified, given a limited supply of COD. After substituting $f_{NO,D}$ for $f_{NO,R}$ from (10)

$$\alpha+ \beta = f_{NO,D}/(1-f_{NO,D}) \qquad (12)$$

SUMMARY

Process factors control denitrification in a recirculation process:

      I.   Ratio of available COD to nitrate reduction (g-COD/g-NO$_3$-N reduced) which is a function of Θ_{anox} (Equation 8)

      II.   Recirculation of nitrified water, β, determines available nitrate nitrogen to be reduced. (Equation 11)

      III.   Recycled biomass flow rate, α is also a source of nitrate as in MLR (which has a lesser effect and is usually fixed by considerations that have nothing to do with denitrification, e.g., secondary clarifier performance and solids wasting rate)

Design procedure for MLE process:

1. **Select Θ_{anox} (typically between 1 and 3 d), determine system volume using CSTR-with-solids-recycle formula for VX_T then select $X_{T,max}$ (constrained by $r_{O,max}$ for τ_{min} or clarifier capacity). Use total volume and Θ_i ratios to determine aerated/anoxic zone volumes.**
2. **Calculate $\Delta N/\Delta S_{S,N}$ using (8)**
3. **Calculate <u>attainable</u> ΔN (g-N/day) assuming complete consumption of soluble influent COD from (8a)**
4. **Calculate NO from (9)**
5. **calculate $f_{NO,D}$ from (10)**
6. **Calculate $(\alpha + \beta)$ from (12). Select α based on secondary clarifier requirements and wasting rate, usually $0.25 < \alpha < 1$.**
7. **Effluent nitrate nitrogen = $\{(1-f_{NO,D})*NO\}/Q$**