ENVE 302

Environmental Engineering Unit Processes

CHAPTER: 6

Nitrification

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NITRIFICATION

$$NH_3 \xrightarrow[\text{Nitrosomonas}]{} NO_2^- \xrightarrow[\text{Nitrobacter}]{} NO_3^-$$

Autotrophs Carbon Source → inorganic carbon(CO_2)

energy source (electron donor) : Oxidation of NO_2^- (for nitrobacter)

Oxidation of NH_3 (for nitrosomonas)

Electron acceptor →O_2

ENERGY & SYNTHESIS REACTIONS

Energy Yielding Reactions

$$NH_4^+ + 1.5\ O_2 \xrightarrow{\text{Nitrosomonas}} 2\ H^+ + H_2O + NO_2^-$$

$$NO_2^- + 0.5\ O_2 \xrightarrow{\text{Nitrobacter}} NO_3^-$$

$$\boxed{NH_4^+ + 2\ O_2 \longrightarrow NO_3^- + 2H^+ + H_2O \quad \text{Overall energy reaction}}$$

Based on above total oxidation reactions,

$$\text{the oxygen required for complete oxidation of ammonia} = 4.57\ \frac{g\ O_2}{g\ NH_4.N\ oxidized}$$

Biomass (cell) Synthesis Reactions

$$15CO_2 + 13NH_4^+ \xrightarrow{\text{Nitrosomonas}} 10NO_2^- + \underbrace{3C_5H_7NO_2}_{\text{Synthesised nitrosomonas cells}} + 23H^+ + 4H_2$$

$$5CO_2 + NH_4^+ + 10NO_2^- + 2H_2O \xrightarrow{\text{Nitrobacter}} 10NO_3^- + \underbrace{C_5H_7NO_2}_{\text{Synthesised nitrobacter cells}} + H^+$$

The CO_2 in the air is adequate because of their low cell yield

Synthesis and Energy Reaction for Nitrosomonas

$$55NH_4^+ + 76O_2 + 109HC0_3^- \rightarrow C_5H_7NO_2 + 54\ NO_2^- + 57H_20 + 104H_2C0_3$$

Nitrosomonas

Synthesis and Energy Reaction for Nitrobacter

$$40NO_2^- + NH_4^+ + 4H_2CO_3 + HCO_3^- + 195O_2 \rightarrow C_5H_7NO_2 + 3H_20 + 400NO_3^-$$

Nitrobacter

Overall Synthesis and Energy Reaction for Nitrifiers

$$\boxed{NH_4^+ + 1.83O_2 + 1.98HCO_3^- \rightarrow 0.021C_5H_7NO_2 + 1.041H_20 + 0.98\ NO_3^- + 1.88H_2CO_3}$$

$$\frac{0.021(113)\ \text{g cell mass}}{14\ \text{g NH}_4-\text{N oxidized}} = 0.16\frac{\text{g cells produced}}{\text{g NH}_4-\text{N oxidized}}$$

cell yield of nitrifiers < cell yield of heterotrophs

$$\frac{1.83(16x2)\ \text{g O}_2}{14\text{g NH}_4-\text{N oxidized}} = 4.18\frac{\text{g O}_2\ \text{consumption}}{\text{g NH}_4-\text{N oxidized}}$$

$\rightarrow$ It is less than theorotical oxygen demand calculated from energy equations.

(4.57 g O_2/g NH_4.N oxidized)

Because in energy equation, it is assumed that all NH_4.N is oxidized. However, some amount of NH_4-N is used for cell synthesis.

$$HCO_3^- = 61\frac{\text{g}}{\text{mol}}\ \text{x}\ \frac{1\text{mol}}{1\text{g}} = 61\frac{\text{g}}{\text{eq}}$$

$$\frac{1.98(61\text{g HCO}_3\text{x}\dfrac{1\text{eq}}{61\text{g HCO}_3}\text{x}\dfrac{50\text{g CaCO}_3}{1\text{eq}}}{14\text{g NH}_4-\text{N oxidized}}$$

$$\frac{7.07\ \text{g alkalinity as CaCO}_3\ \text{consumed}}{\text{g NH}_4-\text{N oxidized}}$$

SUMMARY OF NITRIFICATION OVERALL SYNTHESIS &ENERGY REACTIONS

→significant O_2 consumption

→low cell production

→alkalinity consumption

ENVIRONMENTAL FACTORS

1)TEMPERATURE → 4-45 °C (optimum: 35 °C)

Overall nitrification rate decreases with decreasing temperature

2)DISSOLVED OXYGEN CONCENTRATION

Minimum 2 mg/L is recommended in practice

In contrast to aerobic heterotrophic bacteria nitrification rates increases up to DO concentration 3-4 mg/L.

3) pH & ALKALINITY

Nitrification is pH sensitive and rates decline significantly at pH values below 6.8.

@pH 5.8 – 6 →rate of nitrification = 10 – 20 % of nitrification rate @ pH=7

Optimum pH nitrification occurs → pH values 7.5 – 8

Since the nitrification reduces HCO_3^- and increases H_2CO_3

the pH of the system decreases

For locations with low-alkalinity waters → Alkalinity is added at the wastewater treatment plant to maintain acceptable pH values.

The amount of alkalinity to be added depends on ;

→initial alkalinity concentration

→ amount of NH_4-N to be oxidized

Alkalinity may be added in the form of *lime, soda ash, sodiumbicarbonate*

4)TOXICITY

Nitrifiers are sensitive to a wide range of organic and inorganic compounds.

(inhibitory concentration of these compounds are well below those concentrations that would affect aerobic heterotrophic organisms.)

Nitrification rate is inhibited even though bacteria continue to grow and oxidize ammonia and nitrite at significantly reduced rates.

In some cases → Toxicity may be sufficient to kill the nitrifying bacteria

Examples for industrial organic compounds inhibiting nitrifiers ⟶ Acetone, Chloroform, Ethanol, Phenol, Aniline, Benzene, Tannins, etc.

Examples for metals and inorganic compounds inhibiting nitrifiers ⟶ Zn, Cu, Cr,Hg,Potassium dichromate

Nitrifying organisms are also sensitive to certain forms of nitrogen

* free ammonia (FA) → unionized ammonia
* free nitrous acid(FNA) → unionized nitrous ammonia

The inhibiton effects are dependent on;

→ total nitrogen species
→ concentration
→ pH
→ temperature

$NH_4^+ + OH^- \leftrightarrow NH_3 + H_2O$

If pH ↑, reaction shifts right, NH_3 (FA) concentration ↑, inhibiton of both,nitrosomonas &nitrobacter

$$FA = \frac{[NH_4 - N].10^{pH}}{\frac{k_b}{k_w} + 10^{pH}}$$

$$\frac{6.344}{e^{273+T(^\circ C)}}$$

$NH_4^+ + 1.5\ O_2 \longrightarrow \underbrace{2H^+ + H_2O + NO_2^-}$

$H^+ + NO_2 \leftrightarrow HNO_2$

As pH↓, reaction shifts to right.

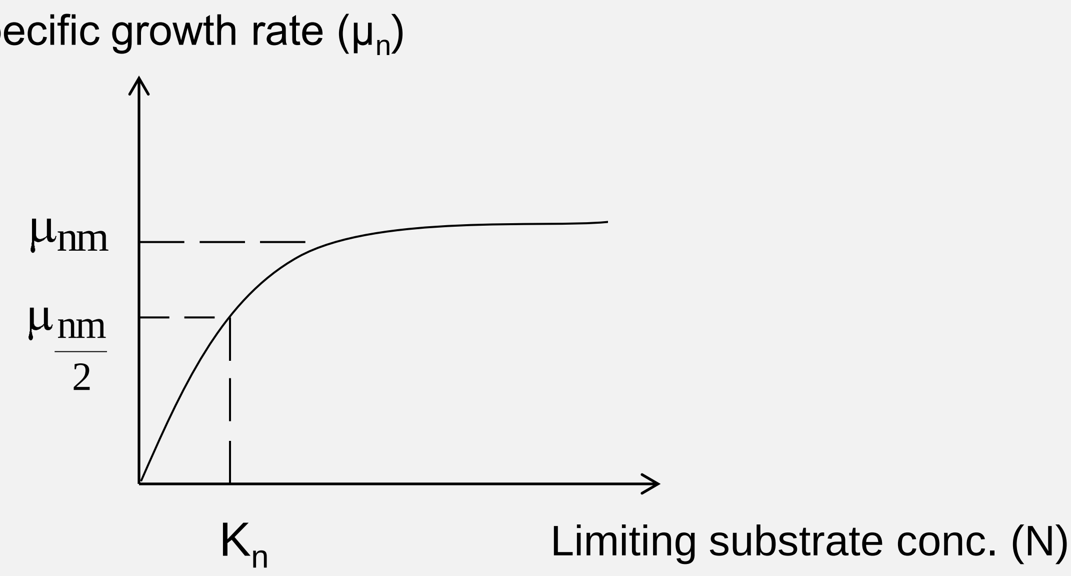
HNO_2 (FNA) is inhibiton of nitrobacter.

$$FNA = \frac{[NO_2 - N]}{[K_a.10^{pH}]}$$

Calculated Threshold Values of Ammonia plus Ammonium – Nitrogen and Nitrate plus Nitrous Acid Nitrogen where Nitrification can begin (EPA Marvel Table 3.6)

Inhibitory FA,FNA (mg/L)	Equilavent ammonia plus ammonium N @ pH = 7, 20 °C (mg/L)	Equivalent nitrite plus nitrous acid N @pH = 7, 20 °C (mg/L)
FA		
10 mg/L (nitrosomonas inhibition)	1000	-
0.1 mg/L (nitrobacter inhibition)	20	-
FNA		
0.22 (nitrification inhibition)	-	280

Growth Kinetics for Nitrifiers



$$\mu = \mu_m \frac{S}{K_S + S}$$

$$\mu' = \mu_M \frac{S}{K_s + S} - k_d$$

For Nitrification :

$$\mu_n' = \frac{\mu_{nm} N}{K_n + N} - k_{dn}$$

$\mu_{N'}$ = Net specific growth rate of nitrifying bacteria (g new cells/g cells. d)

μ_{nM} = Maximum specific growth rate of nitrifying bacteria (g new cells/g cells.d)

N = Nitrogen concentration, g/m3

K_n = Half velocity constant. (Substrate concentration at one half the maximum specific substrate utilization rate, g/m3)

K_{dn} = endogenous decay coefficient for nitrifying organisms. (g VSS / g VSS.d)

If $K_n << N$;

$\mu_n = \mu_{nM}$ (zero-order)

growth rate of nitrifiers are **independent** of ammonium concentration.

If $K_n >> N$;

$$\mu n = \frac{\mu nm}{Kn} N \quad \text{(1}^{st}\text{ order)}$$

substrate-limited condition

growth rate of nitrifiers are **dependent** on ammonium concentration.

μ_M nitrifiers < μ_M heterotrophs → slow growth rate of nitrifiers

Therefore, a sufficient SRT (θ_c) is essential in order to retain an adequate population of these organisms.

θ_c of biological systems with nitrification and carbon removal	**<**	**θ_c of biological systems with only carbon removal**.

The Effect of DO on Nitrification Rate

Nitrification rate increases up to DO concentration of 3-4 mg /L

To account for the effects of DO, the expression for the net specific growth rate (μn’) is modified as follows;

$$\mu_n' = \left(\frac{\mu_{nm} N}{K_n + N}\right)\left(\frac{DO}{K_o + DO}\right) - k_{dn}$$

DO = dissolved oxygen conc. (g/m^3)

K_o = half saturation coefficient for DO (g/m^3)

@ low DO concentrations (<0.5 mg/L)

DO inhibition effect is greater for nitrobacter than for nitrosomonas

Incomplete nitrification will occur with increased NO_2-N concentration in the effluent

@ T <25 ^{0}C

max growth rate of nitrobacter > max growth rate of nitrosomonas

→ nitrite (NO_2^-) does not accumulate in large amounts under steady-state conditions.

→ Conversion of ammonium to nitrite is a rate limiting step of nitrification.

SLUDGE PRODUCTION

(for systems including both carbon removal and nitrification)

$$P_{X,VSS} = \frac{QY(S_0 - S)}{1 + k_d\theta_c} + \frac{f_d k_d QY(S_0 - S)\theta_c}{1 + k_d\theta_c} + \frac{QY_n(NO_x)}{1 + k_{dn}\theta_c} + Q(nbVSS)$$

Heterotrophic biomass

Cell debris

Nitrifying bacteria biomass

Non-biodegr. VSS in influent

$$P_{X,TSS} = \frac{\frac{QY(S_0 - S)}{1 + k_{dn}\theta_c}}{VSS/TSS fraction} + \frac{\frac{f_d k_d QY(S_0 - S)\theta_c}{1 + k_{dn}\theta_c}}{VSS/TSS fraction} + \frac{\frac{QY_n(NO_x)}{1 + k_{dn}\theta_c}}{VSS/TSS fraction} + Q(nbVSS) + Q(TSS_0 - VSS_0)$$

Y_n = cell yield of nitrifiers(g VSS/ g NH_4-N)

NO_x = nitrogen oxidized (mg/L)

K_{dn} = endogenous decay coefficient for nitrifying organisms (g VSS/ g VSS.d)

TSS_0 = influent ww TSS concentration (mg/L)

VSS_0 = effluent ww VSS concentration (mg/L)

OXYGEN REQUIREMENT
(for systems including both carbon removal and nitrification)

Oxygen Req. (kg/d) = $Q(S_0\text{-}S) - 1.42\,P_{X,bio} + 4.33\,Q\,(NO_x)$

Nitrogen Mass Balance to determine NO_x

$$\boxed{Q(NO_x) = Q(TKN)_0 - QN_e - 0.12P_{X,bio}}$$

Nitrogen oxidized	Nitrogen influent	Nitrogen effluent	Nitrogen in cell tissue

Table 8-11

Activated-sludge nitrification kinetic coefficients at 20 C*

Ref: Metcalf & Eddy

Coefficient	Unit	Range	Typical value
μ_{mn}	*g VSS/ g VSS.d*	0,20-0,90	0,75
K_n		0,5-1,0	0,74
Y_n		0,10-0,15	0,12
k_{dn}	*g VSS / gVSS.d*	0,05-0,15	0,08
K_o		0,40-0,60	0,50
θ values			
μ_m	Unitless	1,06-1,123	1,07
K_n	Unitless	1,03-1,123	1,053
k_{dn}	Unitless	1,03-1,08	1,04

* Adapted from Henze et al. (1987a); Barker and Dold (1997); and Grady et al. (1999)

Example: Design a complete mix activated sludge process to treat 22.464 m^3/d of primary effluent for BOD removal with nitrification

Wastewater Characteristics

BOD → 140 g/m3

sBOD → 70 g/m3

COD → 300 g/m3

sCOD → 132 g/m3

rbCOD →80 g/m3

TSS → 70 g/m3

VSS → 60 g/m3

bCOD / BOD → 1.6

ww temp → 12^0C

Design MLSS (X_{TSS}) conc=3000 g/m3

TKN peak/ave factor= 1.5

SVI= 125 ml/g

VSS/TSS= 0.85

Neff= 0.5 g/m3