### **Hydrolysis of Particulate BOD**

Hydrolysis is the biochemical process by which complex particulate organic matter is enzymatically broken down into simpler soluble compounds. It is typically the first and often rate-limiting step in the overall degradation of particulate biodegradable material in wastewater treatment systems (Batstone et al., 2002).

The products of hydrolysis (e.g., soluble BOD) serve as substrates for subsequent processes like fermentation and oxidation, and therefore the efficiency of hydrolysis strongly affects downstream biological conversions.

This reaction occurs through extracellular enzymes excreted by primarily heterotrophic bacteria. For example, cellulases degrade insoluble cellulose polymers into soluble glucose monomers, lipases convert triglycerides into free fatty acids and glycerol, and proteases hydrolyze proteins into peptides and amino acids.

The kinetics of these reactions are frequently modeled as first-order processes with respect to particulate substrate concentration, although more mechanistic approaches using enzymatic kinetics (e.g., Contois or saturation models) have also been applied to capture process variability under different operational conditions (Tchobanoglous et al., 2003).The reaction has the general chemical formula:

$$BODₚ → BODₛ$$

Rate Expression

$$r\_{hyd} = k\_{hyd} \cdot BOD\_p$$

While the underlying biochemical mechanism of hydrolysis is similar across unit operations, the rates and extents differ substantially depending on environmental and operational factors specific to each reactor. Hydrolysis kinetics and their contributions to overall treatment performance must be calibrated specifically for each unit operation.

For example, in units that favor conditions associated with extended retention times for particulate matter (lower temperatures, limited microbial attachment surfaces, and less turbulent mixing), hydrolysis often proceeds slowly (Batstone et al., 2002).

In units where the sedimentation of solids concentrates particulate substrates in the sludge layer, resulting in enhanced biomass density and localized anoxic or aerobic conditions, hydrolytic rates are higher (Tchobanoglous et al., 2003).

**Anoxic tanks** maintain an active biomass capable of producing extracellular enzymes, although denitrification and low dissolved oxygen can moderate hydrolytic rates.

In **aerobic tanks**, vigorous aeration and bioflocculation enhance enzymatic breakdown and improve contact between particulates and microbes, often resulting in faster hydrolysis compared to anoxic or anaerobic reactors (Tchobanoglous et al., 2003).

**Membrane bioreactors** can achieve higher hydrolysis efficiencies because solids retention times (SRT) are decoupled from hydraulic retention times (HRT), promoting the accumulation of slow-growing hydrolytic populations (Judd, 2006).

In units such as **clear water tanks**, the concentration of particulate substrates is much lower, making hydrolysis negligible relative to upstream units.

**Examples of hydrolysis include:**

A) Hydrolysis of Cellulose (Vavilin et al.,1996).

This is the enzymatic cleavage of insoluble cellulose polymers (C₆H₁₀O₅)\_n into soluble glucose (C₆H₁₂O₆). This is mediated by cellulase enzymes. The reaction liberates fermentable sugars essential for downstream biological processes.

**Chemical Reaction:**

$$\text{(C}*6\text{H}*{10}\text{O}\_5\text{)}\_n + n \cdot \text{H}\_2\text{O} \rightarrow n \cdot \text{C}*6\text {H}*{12}\text{O}\_6$$



Example Species::

* **Reactant:** Cellulose polymer (C₆H₁₀O₅)ₙ
* **Product:** Glucose (C₆H₁₂O₆)

**Rate Expression:**

r\_{\text{hydrolysis, cellulose}} = k\_{\text{hydrolysis, cellulose}} \cdot c\_{\text{cellulose}}



**Units:**

* **r\_{hydrolysis,cellulose}:** mol·m⁻³·s⁻¹ glucose produced
* **k\_{hydrolysis,cellulose}:** s⁻¹
* **c\_{cellulose}:** mol·m⁻³ cellulose

**The rate refers to:** This rate denotes the moles of glucose produced per m³ reactor volume per second.

Typical Rate Constant (20–35 °C):

* **r\_{hydrolysis,cellulose}:**≈ 1.0×10⁻⁶ – 5×10⁻⁶ s⁻¹ (depending on temperature and inoculum)
* θ \_{cellulose}(temperature coefficient) = 1.07–1.09 (dimensionless)
  + *θ means: k\_T = k\_20 × θ^(T-20)*
  + Higher θ indicates stronger temp sensitivity

B) Hydrolysis of Proteins (Angelidaki and Ahring, 1994)

This is the protease-catalyzed hydrolysis of protein macromolecules (C₄H₇O₂N)\_n to soluble amino acids such as alanine (C₄H₉O₃N). This provides nitrogen and carbon for microbes

**Chemical Reaction:**

\text{(C}\_4\text{H}\_7\text{O}\_2\text{N})\_n + n \cdot \text{H}\_2\text{O} \rightarrow n \cdot \text{C}\_4\text{H}\_9\text{O}\_3\text{N}



**Example Species:**

* **Reactant:** Protein polymer ((C₄H₇O₂N)\_n)
* **Product:** Soluble Amino acids (e.g., C₄H₉O₃N)

**Rate Expression:**

r\_{\text{hydrolysis, protein}} = k\_{\text{hydrolysis, protein}} \cdot c\_{\text{protein}}



**Units:**

* **r\_{hydrolysis,protein}: mol·m⁻³·s⁻¹ amino acids produced**
* **k\_{hydrolysis,protein}: s⁻¹**
* **c\_{protein}: mol·m⁻³ protein**

**The rate refers to moles** of amino acids produced per cubic meter per second.

**Typical Rate Constant:**

* k\_{hydrolysis, protein} ≈ 1.5×10⁻⁶ – 4×10⁻⁶ s⁻¹
* θ\_{protein} = 1.08–1.09

C) Hydrolysis of Lipids (Palatsi et al. ,2010)

This is the lipase-driven hydrolysis of triglycerides (e.g., triolein, C₅₇H₁₀₄O₆) yields glycerol (C₃H₈O₃) and fatty acids (C₁₈H₃₄O₂). This is a slower process, especially in low-temperature conditions.

**Chemical Reaction:**

\text{C}*{57}\text{H}*{104}\text{O}\_6 + 3 \cdot \text{H}\_2\text{O} \rightarrow \text{C}\_3\text{H}*8\text{O}3 + 3 \cdot \text{C}{18}\text{H}*{34}\text{O}\_2



**Example Species:**

* **Reactant:** Triglycerides (C₅₇H₁₀₄O₆)
* **Products:** Glycerol (C₃H₈O₃), Oleic acid (C₁₈H₃₄O₂)

**Rate Expression:**

r\_{\text{hydrolysis, lipid}} = k\_{\text{hydrolysis, lipid}} \cdot c\_{\text{lipid}}



**Units:**

* **r\_{hydrolysis,lipid}:** mol·m⁻³·s⁻¹ glycerol produced
* **k\_{hydrolysis,lipid}:** s⁻¹
* **c\_{lipid}:** mol·m⁻³ triglycerides

**The rate refers to:** Moles of glycerol formed per m³·s.

**Typical Rate Constant:**

* k\_{hydrolysis,lipid} = 5×10⁻⁷ – 1×10⁻⁶ s⁻¹
* θ\_{lipid} = 1.06–1.09

D) Hydrolysis of Biomass (Batstone et al.,2002).

This is the autolytic lysis of decaying biomass (heterotrophic bacteria, C₅H₇O₂N), releasing soluble intermediates and gases (CO₂, NH₃, CH₄).

**Chemical Reaction:**

\text{C}\_5\text{H}\_7\text{O}\_2\text{N} + 3 \cdot \text{H}\_2\text{O} \rightarrow 5 \cdot \text{CO}\_2 + \text{NH}\_3 + \text{CH}\_4



**Example Species:**

* **Reactant:** Active biomass (C₅H₇O₂N) (heterotrophs)
* **Products:** CO₂, ammonia (NH₃), methane (CH₄)

**Rate Expression:**

r\_{\text{hydrolysis, biomass}} = k\_{\text{hydrolysis, biomass}} \cdot c\_{\text{biomass}}



**Units:**

* **r\_{hydrolysis,biomass}:** mol·m⁻³·s⁻¹ CO₂ produced
* **k\_{hydrolysis,biomass}:** s⁻¹
* **c\_{biomass}:** mol·m⁻³ biomass

**The rate refers to:** The rate is moles of CO₂ released per m³·s.

**Typical Rate Constant:**

* k\_{hydrolysis,biomass} = 1×10⁻⁷ – 1×10⁻⁶ s⁻¹
* θ\_{biomass} = 1.07–1.09

**Carbon Oxidation (Aerobic): Consolidated Reactions, Rates, and References**

Carbon oxidation is the microbial process in which heterotrophic bacteria consume biodegradable organic matter in the presence of oxygen to produce carbon dioxide, water, and new biomass. Carbon oxidation reactions in wastewater treatment vary significantly across unit operations in both kinetics and the factors limiting their rates.

The kinetics are generally modeled using **Monod kinetics**, which account for:

* substrate limitation (half-saturation for substrate)
* oxygen limitation (half-saturation for oxygen)

**Monod kinetics** means:

* As substrate concentration increases, the rate approaches a maximum asymptotically.
* As oxygen increases, the rate also approaches a maximum.
* The combined limitation is represented by the product of both limiting terms.

The general **Monod form** is:

r\_{\text{carbon oxidation}} = \mu\_{\text{H}} \cdot \frac{c\_{\text{S}}}{K\_{\text{S}} + c\_{\text{S}}} \cdot \frac{c\_{\text{O}*2}}{K{\text{O}} + c*{\text{O}*2}} \cdot c*{\text{X,H}}

Insert eplanation for rate equations



* This expression is based on **Monod kinetics** extended for **dual-substrate limitation**, commonly applied to **carbon oxidation** in aerobic biological wastewater treatment. It is an extension of classic Monod kinetics that includes oxygen as a second limiting substrate. The equation models the **rate of substrate consumption or biomass growth** under dual limitation by both substrate and oxygen. Each specific reaction uses a different substrate C\_S.
* **μ\_H**: Maximum specific growth rate of heterotrophic bacteria
* **c\_S**: Concentration of **soluble substrate** (e.g. BODₛ, glucose)
* **K\_S**: Half-saturation constant for the substrate – indicates the substrate concentration at which the specific growth rate is half of μ\_H
* **c\_O₂**: Dissolved oxygen concentration
* **K\_O**: Half-saturation constant for oxygen
* **c\_X,H**: Concentration of **heterotrophic biomass**

### **Units:**

* r typically refers to **substrate** consumed) and is expressed in **mol substrate degraded per m³·s (mol·m⁻³·s⁻)**.
* μ\_H: **s⁻¹**
* c\_S, K\_S, c\_O₂, K\_O: **mol·m⁻³**
* c\_X,H: **mol·m⁻³**

### **Typical Values :**

* μ\_H: 3.0 × 10⁻⁵ s⁻¹ (equivalent to ≈ 2.6 d⁻¹)
* K\_S: 2 × 10⁻³ mol·m⁻³
* K\_O: 1 × 10⁻³ mol·m⁻³
* θ\_H (Temperature coefficient): typically ranges from **1.03–1.07**

### **References:**

* Henze et al. (2000). *Activated Sludge Models ASM1, ASM2, ASM2d and ASM3*. IWA Publishing.
* Tchobanoglous, G., Burton, F. L., & Stensel, H. D. (2003). *Wastewater Engineering: Treatment and Reuse*. McGraw-Hill.
* Rittmann, B. E., & McCarty, P. L. (2001). *Environmental Biotechnology: Principles and Applications*.

In units which primarily function as an equalization and sedimentation basins, the process can be partially aerobic but is frequently dominated by hydrolysis and fermentation. This is because oxygen is often severely limited, and only occasional mixing or surface aeration provides dissolved oxygen. Therefore, if carbon oxidation does occur in micro-aerobic pockets, it is strongly limited by oxygen transfer.

The typical maximum heterotrophic growth rate (mu\_H) in this zone ranges from 0.5 to 2 per day, with a half-saturation constant for soluble substrate (Ks) of 5 to 30 milligrams BOD per liter, and the process is sensitive to temperature fluctuations between 10 and 20 degrees Celsius (Henze et al., 2000). Under these conditions, Monod kinetics still govern the reaction, but oxygen becomes the rate-limiting reactant instead of the organic substrate itself.

In the units designed mainly for solid-liquid separation, the conditions are even less favorable for aerobic oxidation. Most of the settled sludge is anoxic or anaerobic, and only the overflow and near-surface regions have enough oxygen to support carbon oxidation. Here, diffusion through biofilm layers becomes the main constraint, and substrate must slowly migrate from the bulk liquid to thin aerobic layers on floc surfaces. As a result, the mu\_H typically ranges from 0.3 to 1.0 per day, and the Ks is usually higher than in fully aerated systems—commonly between 10 and 40 milligrams BOD per liter. The rate-limiting step in clarifiers is often a combination of mass transfer resistance and the low oxygen gradient (Metcalf & Eddy, 2013).

In the **anoxic tank where o**xygen is effectively absent and carbon oxidation still depends on hydrolysis and fermentation to generate soluble organics that heterotrophic bacteria can use as electron donors. The maximum specific growth rate under anoxic conditions is lower, commonly between 0.1 and 0.5 per day, and Ks ranges from 5 to 20 milligrams BOD per liter (Grady et al., 2011). Since oxygen is not the limiting factor, nitrate concentration becomes critical for determining whether denitrification or other anaerobic processes dominate.

Completely mixed activated sludge reactors are optimized for efficient carbon oxidation. Aeration systems maintain dissolved oxygen concentrations well above 2 milligrams per liter, so substrate concentration rather than oxygen limits the reaction rate. The mu\_H in aerobic reactors is typically between 3 and 6 per day, and Ks is in the range of 10 to 20 milligrams BOD per liter. Temperature control is important: as temperature increases from 15 to 30 degrees Celsius, the rate accelerates, governed by the temperature coefficient theta\_H, which commonly ranges from 1.03 to 1.07 per degree Celsius (Henze et al., 2000; Rittmann and McCarty, 2001). In these systems, Monod kinetics adequately describe the process, and yield coefficients are well-characterized, which allows for robust process modeling.

The **membrane bioreactor** represents a further intensification of aerobic treatment, with biomass concentrations significantly higher than in conventional activated sludge. High mixed liquor suspended solids (MLSS) concentrations—often above 10 kilograms per cubic meter—enhance degradation capacity but also introduce diffusion limitations inside flocs. The mu\_H in these reactors can be higher, around 4 to 8 per day, with Ks as low as 5 to 15 milligrams BOD per liter due to the high biomass density (Metcalf & Eddy, 2013). Membrane fouling can indirectly affect oxygen transfer, therefore becoming a secondary rate-limiting factor. Temperature effects are similar to aerobic tanks but more pronounced at higher operating temperatures (20–35 degrees Celsius), where microbial decay can also increase (Judd, 2006).

In the **clear water tank, t**he dissolved organic concentration here is extremely low, and consequently, the kinetics shift from Monod-type dependence on substrate to near first-order decay kinetics. In these polishing tanks, the process is slow and mainly designed for fine-tuning effluent quality. The mu\_H is typically between 0.2 and 0.5 per day, Ks falls below 5 milligrams BOD per liter, and oxygen levels are moderate due to passive aeration or limited mechanical mixing (Henze et al., 2000).

Carbon Oxidation of Soluble Glucose Henze et al., 2000 – ASM1 Henze, M. et al. (1987). *Activated Sludge Model No. 1..* Batstone, D. et al. (2002). *Anaerobic Digestion Model No.1.*

Heterotrophic bacteria oxidize soluble glucose into CO₂ and water, deriving energy for growth and biomass synthesis. Aerobic oxidation of glucose by heterotrophic bacteria. The glucose is used both as an energy source and carbon skeleton for cell synthesis. Oxygen acts as the terminal electron acceptor. This reaction is fast under sufficient dissolved oxygen and is critical in activated sludge systems.

* Glucose is oxidized by heterotrophs to yield CO₂.
* This reaction supplies energy for microbial growth.
* Monod kinetics describe dependence on glucose and oxygen.

**Chemical Reaction:**

\text{C}*6\text{H}*{12}\text{O}\_6 + 6 \cdot \text{O}\_2 \rightarrow 6 \cdot \text{CO}\_2 + 6 \cdot \text{H}\_2\text{O}



**Example species:**

* **Reactant substrate:** Glucose (C₆H₁₂O₆)
* **Oxidant:** Oxygen (O₂)
* **Products:** Carbon dioxide (CO₂), Water (H₂O)

**Kinetic Rate Expression (Monod)**

r\_{\text{oxidation,glucose}} = \mu\_{\text{H}} \cdot \frac{c\_{\text{glucose}}}{K\_{\text{S,glucose}} + c\_{\text{glucose}}} \cdot \frac{C\_{\text{O}\_2}}{K{\text{O}} + C{\text{O}*2}} \cdot c*{\text{X,H}}



r\_{\text{glucose}} = \mu\_H \cdot \frac{S\_{\text{glucose}}}{K\_{S,\text{glucose}} + S\_{\text{glucose}}} \cdot \frac{S\_{O\_2}}{K\_O + S\_{O\_2}} \cdot X\_H



**Units:**

* R\_glucose : mol glucose oxidized per m³ per s
* K
* C

**Monod Kinetics Description:**

* Expresses **substrate and oxygen limitation**. Numerator mols refer to glucose (reactant).
* The first fraction models glucose availability.
* The second fraction models oxygen availability.
* X\_H is active biomass concentration (heterotrophs).
* When glucose ≫ K\_S , the substrate term ≈1.
* When O₂ ≫ KO , oxygen term ≈1.
* Both must be sufficient to achieve maximum rate.
* This is **double-substrate Monod kinetics**, i.e., both glucose and oxygen limit

**Typical Constants** Henze, M. et al. (1987).**:**

* r\_{ox,glucose} : Moles of **glucose degraded per cubic meter per second**
* \mu\_{\text{H}} = 3.5 \times 10^{-5} \ s^{-1}
  + Max growth rate of heterotrophs consuming glucose) (Maximum specific growth rate on glucose.) 2e-5–5e-5 s^{-1}.
* K\_{\text{S,glucose}} = 2 \times 10^{-3} \ mol \cdot m^{-3}
  + (Half-saturation constant for glucose substrate). Mols refer to glucose. 1e-3–5e-3 mol/m³
* K\_{\text{O}} = 1 \times 10^{-3} \ mol \cdot m^{-3}
  + *(Half-saturation constant for dissolved oxygen) Mols refer to dissolved oxygen.* 1e-4–1e-3 mol/m³
* \theta\_{\text{H}} = 1.07
  + Temperature correction factor applying only to \mu\_{\text{H}}. Adjusts max growth rate. Applies to all carbonaceous substrate oxidations by heterotrophs.
* \mu\_{T} = \mu\_{20} \cdot \theta\_{\text{H}}^{(T - 20)}
  + T in °C.
  + Recommended range: 10–35 °C.

Carbon Oxidation of Soluble Acetate

This is the aerobic oxidation of acetate, a fermentation product and occurs rapidly when oxygen is not limiting, providing a preferred carbon source for many heterotrophs.

Acetate oxidation yields CO₂ and water. This substrate is **r**apidly biodegradable, used as a model for readily available organics.

**Chemical Reaction:**

\text{C}\_2\text{H}\_4\text{O}\_2 + 2 \cdot \text{O}\_2 \rightarrow 2 \cdot \text{CO}\_2 + 2 \cdot \text{H}\_2\text{O}



### **Example Species**

* **Substrate:** Acetic acid (C2 H4 O2 )
* **Oxidant:** Oxygen (O2 )
* **Products:** Carbon dioxide (CO2 ), water (H2 O)

**Rate Expression (Monod):**

r\_{\text{oxidation,acetate}} = \mu\_{\text{H}} \cdot \frac{C\_{\text{acetate}}}{K\_{\text{S,acetate}} + C\_{\text{acetate}}} \cdot \frac{C\_{\text{O}*2}}{K{\text{O}} + C*{\text{O}*2}} \cdot C*{\text{X,H}}



r\_{\text{oxidation,acetate}} = \mu\_H \cdot \frac{S\_{\text{acetate}}}{K\_{S,\text{acetate}} + S\_{\text{acetate}}} \cdot \frac{S\_{O\_2}}{K\_O + S\_{O\_2}} \cdot X\_H



**Monod Kinetics Description:**

* Substrate limitation captured by KS,acetate .
* Oxygen limitation captured by KO .
* Same Monod principle as glucose.
* Substrate limitation (acetate) and oxygen limitation.

**Typical Constants** Reference: Henze et al. (1987)**:**

* r\_oxidation,acetate = Moles acetate degraded per m³·s.**mol acetate oxidized per m³ per s**
* \mu\_{\text{H}} = 3.5 \times 10^{-5} \ s^{-1}
  + Max growth rate on acetate. 2×10−5 to 4×10−5 s−1
* K\_{\text{S,acetate}} = 1 \times 10^{-3} \ mol \cdot m^{-3}
  + Moles refer to acetate 5×10−4 to 2×10−3 mol·m−3
* K\_{\text{O}} = 1 \times 10^{-3} \ mol \cdot m^{-3}
  + Mols refer to oxygen 1 x 10 –4 to 1 x 10-3 mol.m-3
* \theta\_{\text{H}} = 1.07
  + Temperature coefficient for heterotrophs.

**Typical Ranges:**

* Same as glucose oxidation.

Reaction 3: Oxidation of Soluble Amino Acids (Alanine Example) Henze et al. (1987) Palatsi et al. (2010)

Aerobic oxidation of amino acids to CO2 and ammonia. Releases nitrogen for nitrification downstream.

**Chemical Reaction:**

\text{C}\_3\text{H}\_7\text{NO}\_2 + 3 \cdot \text{O}\_2 \rightarrow 3 \cdot \text{CO}\_2 + 3 \cdot \text{H}\_2\text{O} + \text{NH}\_3



**Example Species:**

* **Reactant:** Alanine (C₃H₇NO₂)
* **Products:** CO₂, H₂O, NH₃

**Rate Expression**

r\_{\text{oxidation,amino acid}} = \mu\_H \cdot \frac{S\_{\text{amino}}}{K\_{S,\text{amino}} + S\_{\text{amino}}} \cdot \frac{S\_{O\_2}}{K\_O + S\_{O\_2}} \cdot X\_H



**Explanation:**

* Double substrate Monod kinetics.
* Moles in rate refer to amino acid oxidized.

**Typical Constants: (Henze et al)**

* R =mol amino acids per m3 per second. r**ate of consumption of soluble amino acids** in mol\cdotpm−3⋅s−1.
* \mu\_H = 3.2 \times 10^{-5} s^{-1} 2×10−5 to *3.5×10−5* s*−1*
* K\_{S,\text{amino}} = 2 \times 10^{-3} mol·m^{-3} (moles anine) 1x10-3 to 3x10-3mol/m3
* K\_O = 1 \times 10^{-3} mol·m^{-3} (moles oxygen) 1x10-4 to 1x10-3 mol/m3
* \theta\_H = 1.07

Reaction 4: Oxidation of Soluble Lipids

**Description:**

Aerobic oxidation of long-chain fatty acids. Slow due to lower solubility and need for prior emulsification.

**Chemical Reaction:**

\text{C}*{18}\text{H}*{34}\text{O}\_2 + 26 \cdot \text{O}\_2 \rightarrow 18 \cdot \text{CO}\_2 + 17 \cdot \text{H}\_2\text{O}



**Example Species:**

* **Reactant:** Oleic acid (C₁₈H₃₄O₂)
* **Products:** CO₂, H₂O

**Rate Expression:**

r\_{\text{oxidation,lipid}} = \mu\_H \cdot \frac{S\_{\text{lipid}}}{K\_{S,\text{lipid}} + S\_{\text{lipid}}} \cdot \frac{S\_{O\_2}}{K\_O + S\_{O\_2}} \cdot X\_H



**Explanation:**

* Moles refer to lipid oxidized.
* Rate limited by lipid hydrolysis and oxygen.

Constants

* R\_ox,lipid = mol amino acids per m3 per second . The *moles again refer to the reactant substrate* (soluble lipids).
* \mu\_H = 1.8 \times 10^{-5} {s^{-1}). Lower due to solubility. 1×10−5 to 2.0×10−5 s*−*−1
* K\_{S,\text{lipid}} = 1 \times 10^{-3} mol·m^{-3}. MOls lipid
  + 5×10−4 to 1.5×10−3 mol·m−3
* K\_O = 1 \times 10^{-3} mol·m^{-3}. Moles oxygen.
  + 1×10−4 to 1×10−3 mol·m−3
* \theta\_H = 1.07. temperature factor.

**References:**

* Henze, M., Gujer, W., Mino, T., van Loosdrecht, M.C.M. (2000). Activated Sludge Models ASM1, ASM2, ASM2d and ASM3. IWA Publishing.
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## **Methanogenesis (Optional)**

Methanogenesis is the final biochemical step in anaerobic digestion. In this reaction, acetate and hydrogen are converted into methane and carbon dioxide by obligate anaerobic archaea called methanogens (Zeikus, 1977). In wastewater treatment systems, methanogenesis occurs mainly in dedicated anaerobic digesters rather than mainstream biological tanks, because residual oxygen and alternative electron acceptors inhibit methanogen activity (Batstone et al., 2002).

It is a strictly anaerobic process that requires the absence of alternative electron acceptors such as oxygen, nitrate, and sulfate (Batstone et al., 2002).

Methanogenesis is often the **rate-limiting step** during anaerobic digestion, particularly under low temperatures and high ammonia concentrations (Angelidaki & Sanders, 2004). The process is highly sensitive to pH, which must be near neutral (~7.0) to maintain enzyme activity.

Methanogenesis behaves differently across treatment units. In **Collection Tanks** and **Primary Clarifiers**, hydrolysis and fermentation produce volatile fatty acids, but limited retention time and oxygen ingress inhibit methanogenesis (Angelidaki & Sanders, 2004). In **Anoxic Tanks**, nitrate and nitrite are preferential electron acceptors, suppressing methanogen growth (Batstone et al., 2002). **Aerobic Tanks** contain oxygen, which fully inhibits methanogenesis. In **Membrane Bioreactors**, localized anoxic niches inside biofilms can support small-scale methanogenesis, but most methane production is negligible. In **Clear Water Tanks**, residual dissolved oxygen and low organic load prevent methanogenesis. Substantial methane formation is therefore restricted to dedicated anaerobic digesters operating under strict anaerobic conditions.

1. **Acetoclastic Methanogenesis:**

The acetoclastic pathway converts acetate to methane and carbon dioxide, while the hydrogenotrophic pathway combines hydrogen with carbon dioxide to form methane.

**Chemical Reaction (**Acetoclastic Pathway:)

\text{CH}\_3\text{COO}^{-} + \text{H}^{+} \rightarrow \text{CH}\_4 + \text{CO}\_2



**Reactants:**

* Acetate (CH3COO^-)
* Hydrogen (H2)
* Carbon dioxide (CO2)

**Products:**

* Methane (CH4)
* Carbon dioxide (CO2)
* Water (H2O)

**Rate Expression:**

r\_{\text{methanogenesis,acetate}} = \mu\_{\text{methanogenesis}} \cdot \frac{S\_{\text{acetate}}}{K\_{\text{S,acetate}} + S\_{\text{acetate}}} \cdot X\_{\text{methanogenesis}}



For acetoclastic pathway, r\_meth,acetate refers to mol methane generated.

**Typical Constants:**

* Units: mol methane produced per m3 per second.
* mu\_meth ranges 1e-6 to 5e-6 per second (Zeikus, 1977).
* mu\_meth,H2 ranges 1e-6 to 4e-6 per second (Angelidaki & Sanders, 2004).
* K\_S,acetate ranges 5e-4 to 2e-3 mol per m3 (Batstone et al., 2002).
* K\_S,H2 ranges 1e-5 to 1e-4 mol per m3 (Batstone et al., 2002).
* theta\_meth typically 1.03 to 1.06 per °C between 20 and 40 °C (Batstone et al., 2002).

1. Hydrogenotrophic Pathway:

**Chemical Reaction:**

4 \cdot \text{H}\_2 + \text{CO}\_2 \rightarrow \text{CH}\_4 + 2 \cdot \text{H}\_2\text{O}



### **Example Species**

**Reactants:**

* Acetate (CH3COO^-)
* Hydrogen (H2)
* Carbon dioxide (CO2)

**Products:**

* Methane (CH4)
* Carbon dioxide (CO2)
* Water (H2O)

**Rate Expression:**

r\_{\text{meth,H2}} = \mu\_{\text{meth,H2}} \cdot \frac{S\_{\text{H2}}}{K\_{\text{S,H2}} + S\_{\text{H2}}} \cdot X\_{\text{meth}}

r\_{{methanogenesis,H\_2}} = \mu\_{{methanogenesis,H\_2}} \cdot \frac{S\_{{H\_2}}}{K\_{{S,H\_2}} + S\_{{H\_2}}} \cdot X\_{{methangogenesis}}



These equations use **Monod kinetics** (Batstone et al., 2002):

* **mu\_meth** is the maximum specific growth rate of methanogens on acetate.
* **mu\_meth,H2** is the maximum specific growth rate on hydrogen.
* **S\_acetate** is the substrate concentration of acetate in mol per m3.
* **S\_H2** is the substrate concentration of hydrogen gas in mol per m3.
* **K\_S,acetate** and **K\_S,H2** are the half-saturation constants.
* **X\_meth** is the methanogen biomass concentration in kg per m3.  
   The rate expression predicts methane production based on substrate availability and microbial density. The moles in the numerator refer to the **reactant consumed** (acetate or hydrogen), and the resulting methane produced is stoichiometrically related.

**Units**

* Units: mol methane produced per m3 per second.
* For acetoclastic pathway, r\_meth,acetate refers to mol methane generated.
* For hydrogenotrophic pathway, r\_meth,H2 refers to mol methane generated.

### **Constants and References (Plain Text, Not in Equation Format)**

* mu\_meth: Maximum specific growth rate on acetate = 3e-6 per second (Batstone et al., 2002).
* mu\_meth,H2: Maximum specific growth rate on hydrogen = 2e-6 per second (Batstone et al., 2002).
* K\_S,acetate: Half-saturation constant for acetate = 1e-3 mol per m3. This mol refers to acetate (Batstone et al., 2002).
* K\_S,H2: Half-saturation constant for hydrogen = 5e-5 mol per m3. This mol refers to hydrogen (Batstone et al., 2002).
* theta\_meth: Temperature coefficient = 1.04 per °C (applies to mu\_meth and mu\_meth,H2) (Batstone et al., 2002).

### **Typical Ranges of Constants**

* mu\_meth ranges 1e-6 to 5e-6 per second (Zeikus, 1977).
* mu\_meth,H2 ranges 1e-6 to 4e-6 per second (Angelidaki & Sanders, 2004).
* K\_S,acetate ranges 5e-4 to 2e-3 mol per m3 (Batstone et al., 2002).
* K\_S,H2 ranges 1e-5 to 1e-4 mol per m3 (Batstone et al., 2002).
* theta\_meth typically 1.03 to 1.06 per °C between 20 and 40 °C (Batstone et al., 2002).

### **Temperature Correction and Correlation**

The **temperature correction factor theta\_meth** adjusts the maximum specific growth rate to temperature above the reference (20 °C). For example, if the reactor operates at 35 °C, mu\_meth is multiplied by 1.04^(35–20) ≈ 1.80 (Batstone et al., 2002). This increases methane production rates in warmer digesters. The correction applies identically to mu\_meth and mu\_meth,H2.

### **References**

* Zeikus, J. G. (1977). The biology of methanogenic bacteria. *Bacteriological Reviews*, 41(2), 514–541.
* Batstone, D. J., Keller, J., Angelidaki, I., Kalyuzhnyi, S. V., Pavlostathis, S. G., Rozzi, A., Sanders, W. T., Siegrist, H., & Vavilin, V. A. (2002). *The IWA Anaerobic Digestion Model No.1 (ADM1)*. Water Science and Technology, 45(10), 65–73. Download link
* Angelidaki, I., & Sanders, W. (2004). Assessment of the anaerobic biodegradability of macropollutants. *Reviews in Environmental Science and Bio/Technology*, 3(2), 117–129.

**Nitrification**

Nitrification is the aerobic, chemoautotrophic biological oxidation of ammonium to nitrate. It is a two-step process mediated by specialized bacterial guilds. In wastewater systems, nitrification is essential for removing ammonia toxicity and enabling denitrification to achieve nitrogen removal targets (Henze et al., 2000). Retention time, solids concentration, and aeration regime control nitrifier activity (Siegrist & Gujer, 1995).

This step generates protons, contributing to pH reduction in the mixed liquor. In the **second stage**, nitrite-oxidizing bacteria (NOB) such as *Nitrobacter winogradskyi* oxidize nitrite to nitrate.Both groups derive metabolic energy from electron transfer during oxidation and assimilate inorganic carbon for growth (Prosser, 1989). The process is highly sensitive to dissolved oxygen (must be above 1–2 mg per liter), temperature (optimal 25–30 °C), and pH (optimal 7.5–8).

Nitrification potential varies across wastewater treatment units. In units with low dissolved oxygen (collection tanks, primary clarifiers etc.), nitrification is negligible due to low dissolved oxygen, short retention time, and minimal nitrifier biomass (Henze et al., 2000). In Anoxic Tanks, nitrate is present as an electron acceptor but oxygen is lacking, so nitrification is fully inhibited. In Aerobic Tanks, nitrification is the primary ammonia removal mechanism and proceeds rapidly when dissolved oxygen exceeds 2 mg/L, and temperatures are above 15 °C (Prosser, 1989). In Membrane Bioreactors, nitrification rates can be higher due to higher solids retention times, supporting slow-growing nitrifiers (Siegrist & Gujer, 1995). Clear Water Tanks typically do not support nitrification because residual ammonia concentrations are too low to sustain active nitrifier populations.

1. Ammonia Oxidation (Nitrosomonas)

Ammonia oxidation is the first step in nitrification and is carried out by **ammonia-oxidizing bacteria (AOB)** such as *Nitrosomonas europaea* (Prosser, 1989). The process is essential for nitrogen removal because it initiates conversion of toxic ammonia into less toxic oxidized forms. This reaction converts ammonium ions (NH4+) into nitrite ions (NO2-). Oxygen serves as the terminal electron acceptor, and autotrophic bacteria derive energy from ammonia oxidation.

The process It is strongly influenced by pH (optimum ~7.8), temperature (optimum ~25–30 °C), and dissolved oxygen concentration (>2 mg/L) (Prosser, 1989), and it is rate-limiting in wastewater systems with low temperatures or low dissolved oxygen (Henze et al., 2000; Siegrist & Gujer, 1995).

**Chemical Reaction**

\text{NH}\_4^{+} + 1.5 \cdot \text{O}\_2 \rightarrow \text{NO}\_2^{-} + 2 \cdot \text{H}^{+} + \text{H}\_2\text{O}



**Example Species:**

* Reactant: Ammonium ion (NH4+)
* Products: Nitrite ion (NO2-), protons (H+), water (H2O)

**Rate Expression**

r\_{\text{nitrification,ammonia}} = \mu\_{\text{AOB}} \cdot \frac{S\_{\text{NH4}}}{K\_{\text{S,NH4}} + S\_{\text{NH4}}} \cdot \frac{S\_{\text{O2}}}{K\_{\text{S,O2}} + S\_{\text{O2}}} \cdot X\_{\text{AOB}}



* r\_{nit,amm} is the **rate of ammonium oxidation** during **nitrification**, expressed typically in **mol/m³/s** or **kg/m³/s** depending on unit convention.
* The subscript nit,amm means:
  + nit: This process is part of **nitrification**.
  + amm: It specifically refers to the **ammonium (NH₄⁺) oxidation step**, as opposed to the second step (nitrite oxidation).
* \mu\_{AOB}: The **maximum specific growth rate** of AOB (ammonia-oxidizing bacteria), usually in **1/s** or **1/day**.
* S\_{NH4}:
* Substrate concentration of **ammonium** (NH₄⁺), in **mol/m³** or **mg/L**.
* K\_{S,NH4}:
* The **half-saturation constant** for ammonium for AOB (i.e., substrate concentration at which rate is half of max), in **mol/m³**.
* S\_{O2}:
* Dissolved oxygen concentration (O₂), also in **mol/m³**.
* K\_{S,O2}:
* Oxygen half-saturation constant for AOB.
* X\_{AOB}:
* Active biomass concentration of ammonia-oxidizing bacteria, in **kg/m³** or **mol/m³ of cells**.
* **Explanation of Rate Expression:**  
   This is a **double Monod expression**, reflecting substrate limitation by **ammonium** and **oxygen**:
* mu\_AOB is the **maximum specific growth rate of AOB** (per second), reflecting how fast AOB can grow when both substrates are abundant.
  + Typical range: 2e-6 to 6e-6 per second.
  + *Reference*: Henze et al. (2000).
* S\_NH4 is the ammonium concentration in mol per cubic meter.
* K\_S,NH4 is the **half-saturation constant for ammonium** in mol per cubic meter.
  + It is the concentration at which the growth rate is half of mu\_AOB.
  + Typical range: 1e-4 to 4e-4 mol/m3.
  + *Reference*: Henze et al. (2000).
* S\_O2 is the dissolved oxygen concentration in mol per cubic meter.
* K\_S,O2,AOB is the **oxygen half-saturation constant** in mol per cubic meter.
  + Reflects oxygen affinity of AOB.
  + Typical range: 2e-5 to 1e-4 mol/m3.
  + *Reference*: Henze et al. (2000).
* X\_AOB is the active biomass concentration of AOB in kg/m3.
* **The moles in the rate r refer to moles of ammonium oxidized per cubic meter per second.**

**Units of Reaction Rate:**  
mol NH4+ oxidized / m3 / second

**Constants:**

* mu\_AOB: maximum growth rate = 4e-6 per second (Henze et al., 2000).
* K\_S,NH4: half-saturation ammonium = 2e-3 mol per m3 (refers to ammonium).
* K\_S,O2: oxygen half-saturation = 2e-4 mol per m3 (refers to O2).
* theta\_AOB: temperature coefficient = 1.07 per °C (Henze et al., 2000).

**Typical Ranges of Constants:**

* mu\_AOB: 2e-6 to 5e-6 per second. Henze et al. (2000)
* K\_S,NH4: 1e-3 to 3e-3 mol per m3. Henze et al. (2000)
* K\_S,O2: 1e-4 to 3e-4 mol per m3. Henze et al. (2000)
* theta\_AOB: 1.06 to 1.08 per °C over 15–35 °C. Blackburne et al. (2007)

**Temperature Correction and Correlation:**  
 theta\_AOB applies to mu\_AOB. For example, at 25 °C, mu\_AOB increases by factor of 1.07^(25–20) = approx 1.40 (Henze et al., 2000).

* Henze et al., 2000. *Activated Sludge Models ASM1, ASM2, ASM2d and ASM3*. IWA Scientific and Technical Report No. 9.
* Tchobanoglous et al., 2003. *Wastewater Engineering: Treatment and Reuse*.
* Metcalf & Eddy, 2014. *Wastewater Engineering: Treatment and Resource Recovery*.

1. **Nitrite Oxidation (Nitrobacter)**

Nitrite oxidation is the second nitrification step, converting nitrite to nitrate. This is catalyzed by Nitrobacter species and requires oxygen to provides metabolic energy to the bacteria through chemolithotrophic electron transfer. This step is slightly slower kinetics than ammonia oxidation, and is sensitive to low temperatures (Prosser, 1989). In conventional activated sludge, Nitrobacter biomass is smaller in proportion, making nitrite oxidation a potential nitrification bottleneck during high ammonia loads. Optimal temperature is 25–30 °C, and oxygen concentration above 2 mg/L is necessary (Henze et al., 2000). Nitrite accumulation can occur under low oxygen or low biomass conditions.

**Chemical Reaction**

\text{NO}\_2^{-} + 0.5 \cdot \text{O}\_2 \rightarrow \text{NO}\_3^{-}



**Example Species:**

* Reactant: Nitrite ion (NO2-)
* Product: Nitrate ion (NO3-)

**Rate Expression**

r\_{\text{nitrification,nitrite}} = \mu\_{\text{NOB}} \cdot \frac{S\_{\text{NO2}}}{K\_{\text{S,NO2}} + S\_{\text{NO2}}} \cdot \frac{S\_{\text{O2}}}{K\_{\text{S,O2,NOB}} + S\_{\text{O2}}} \cdot X\_{\text{NOB}}



**Explanation of Rate Expression:**  
 Monod-type kinetics: This is a Monod model describing substrate-limited growth:

* mu\_NOB: maximum specific growth rate of nitrite oxidizers. Maximum specific growth rate of Nitrobacter (per second). It represents the rate of biomass growth under non-limiting conditions.
* S\_NO2: nitrite concentration in mol per m3.
* K\_S,NO2: Half-saturation constant for nitrite (mol per cubic meter), referring to the nitrite concentration at which the reaction proceeds at half the maximum rate.
* S\_O2: Dissolved oxygen concentration in mol per cubic meter.
* K\_S,O2,NOB: Half-saturation constant for oxygen (mol per cubic meter), referring to the oxygen concentration for half-maximal activity.
* X\_NOB: Biomass concentration of Nitrobacter in kg per cubic meter.

**Units of Reaction Rate:**  
 mol NO2- oxidized per m3 per second. The moles in the rate (r) refer specifically to moles of nitrite oxidized per unit volume per time.

**Constants (Plain Text):**

* mu\_NOB: 3e-6 per second (Henze et al., 2000).
* K\_S,NO2: 1e-3 mol per m3 (refers to nitrite).
* K\_S,O2,NOB: 1e-4 mol per m3 (refers to O2).
* theta\_NOB: 1.06 per °C (Henze et al., 2000).

**Typical Ranges of Constants:**

* mu\_NOB: 1e-6 to 4e-6 per second. Reference: Henze et al. (2000)
* K\_S,NO2: 5e-4 to 2e-3 mol per m3. Reference: Henze et al. (2000)
* K\_S,O2,NOB: 5e-5 to 2e-4 mol per m3. Reference: Henze et al. (2000)
* theta\_NOB: 1.05–1.07 per °C. Reference: Siegrist & Gujer (1995)

This is a **Monod-based** rate expression describing the **oxidation of nitrite (NO₂⁻) to nitrate (NO₃⁻)** by **nitrite-oxidizing bacteria (NOB)**. It represents the **second stage of nitrification**.

* **r\_{nitrification,nitrite}**:
  + Rate of **nitrite oxidation**, usually in **mol/m³/s** or **kg/m³/s**.
  + Subscript breakdown:
    - nitrification: the overall process.
    - nitrite: specifically the **second step** — nitrite being converted to nitrate.
* **\mu\_{NOB}**:
  + Maximum specific growth rate of NOB (nitrite-oxidizing bacteria), in **1/s** or **1/day**.
* **S\_{NO2}**:
  + Concentration of **nitrite (NO₂⁻)** in the reactor, in **mol/m³**.
* **K\_{S,NO2}**:
  + Half-saturation constant for nitrite (for NOB), in **mol/m³**. Represents the substrate affinity.
* **S\_{O2}**:
  + Dissolved oxygen concentration, in **mol/m³**.
* **K\_{S,O2,NOB}**:
  + Oxygen half-saturation constant for NOB (may differ from AOB), in **mol/m³**.
* **X\_{NOB}**:
  + Active biomass concentration of NOB, in **kg/m³** or **mol/m³ (as cells or COD equivalent)**.

**Temperature Correction and Correlation:**  
 theta\_NOB applies to mu\_NOB. For 30 °C, mu\_NOB is multiplied by 1.06^(30–20) = ~1.79.

### **References:**

* Prosser, J.I. (1989). Autotrophic nitrification in bacteria. *Advances in Microbial Physiology*.
* Henze, M. et al. (2000). *Activated Sludge Model No.1*. IWA Publishing.
* Blackburne, R. et al. (2007). Partial nitrification to nitrite using low dissolved oxygen concentration as the main selection factor. *Biodegradation*.
* Siegrist, H., Gujer, W. (1995). *Nitrogen removal in activated sludge systems*. Water Science and Technology.
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* Blackburne et al. (2007). "Ammonia- and nitrite-oxidizing bacteria kinetics."

**Denitrification**

Denitrification is critical for nitrogen removal and climate considerations (due to N₂O emissions). It is the stepwise biological reduction of oxidized nitrogen compounds (primarily nitrate and nitrite) into gaseous nitrogen forms (N₂O and ultimately N₂ gas) and is responsible for removing bioavailable nitrogen from wastewater. This process is primarily carried out by facultative anaerobic heterotrophic bacteria (e.g., *Pseudomonas*, *Paracoccus*), which use nitrate or nitrite as electron acceptors in the absence of oxygen (Knowles, 1982).

Denitrification typically proceeds through four main stages: nitrate reduction to nitrite, nitrite reduction to nitric oxide, nitric oxide reduction to nitrous oxide, and nitrous oxide reduction to nitrogen gas (Payne, 1981). Each step is catalyzed by specific reductase enzymes and is sensitive to environmental conditions such as dissolved oxygen, carbon availability, pH, and temperature (Tiedje et al., 1982).

Reaction 1 – Nitrate Reduction to Nitrite

This reaction reduces nitrate (NO3-) to nitrite (NO2-) under anoxic conditions. Facultative anaerobic heterotrophic bacteria couple the oxidation of organic carbon to the reduction of nitrate. The enzyme involved is nitrate reductase (Nar). This is often the fastest step of denitrification.

**Reference:** Payne, 1981; Tiedje, 1982.

**Chemical Reaction**

NO\_{3}^{-} + 2 \cdot H^{+} + 2 \cdot e^{-} \rightarrow NO\_{2}^{-} + H\_{2}O



### **Example Species:**

**Reactants:**

* Nitrate (NO3-)
* Acetate (CH3COO-)

**Products:**

* Nitrite (NO2-)
* Water (H2O)

**Rate Expression**

r\_{NO3^{-}} = \mu\_{max} \cdot \frac{S\_{NO\_3^{-}}}{K\_{S,NO\_3^{-}} + S\_{NO\_3^{-}}} \cdot \frac{S\_{COD}}{K\_{S,COD} + S\_{COD}} \cdot X\_{DEN}



Explanation of Rate Expression

This is a Monod-based model describing the specific nitrate consumption rate.

* r\_NO3- represents the moles of nitrate consumed per cubic meter reactor volume per second.
* S\_NO3- is the nitrate concentration in mol per cubic meter.
* S\_COD is the readily biodegradable chemical oxygen demand concentration in mol C per cubic meter.
* mu\_max is the maximum specific growth rate of denitrifying biomass.
* K\_S,NO3- is the half-saturation constant for nitrate.
* K\_S,COD is the half-saturation constant for COD.
* X\_DEN is the biomass concentration in kg per cubic meter.

Units of r\_NO3-:  
 mol nitrate consumed per cubic meter reactor volume per second.

The "mol" refers to moles of nitrate removed.

### **Constants**

* mu\_max: maximum growth rate of denitrifiers. Typical range: 0.12 to 0.25 per hour (converted approximately to 3.3e-5 to 6.9e-5 per second). This is the biological maximum rate under optimal substrate and temperature conditions. (Reference: Tiedje, 1982)
* K\_S,NO3-: half-saturation constant for nitrate. Range: 0.1 to 0.5 grams nitrogen per cubic meter. This corresponds to approximately 7e-3 to 3.5e-2 mol nitrate per cubic meter. This is the concentration at which nitrate reduction rate is 50% of mu\_max. (Reference: van Loosdrecht et al., 2002)
* K\_S,COD: half-saturation constant for COD. Range: 20 to 50 grams COD per cubic meter, equivalent to 0.625 to 1.56 mol C per cubic meter. (Reference: Henze et al., 2000)
* theta\_mu: temperature coefficient. Typical value: 1.07. This means that the rate increases by about 7% per degree Celsius. (Reference: Henze et al., 2000)

### **Temperature Correction**

Temperature correction applies to mu\_max. It is described by the Arrhenius relationship:

\mu\_{T} = \mu\_{20} \cdot \theta^{(T - 20)}

where theta is 1.07, T is the reactor temperature in degrees Celsius, and mu\_20 is the reference rate at 20 degrees Celsius.

Reaction 2 – Nitrite Reduction to Nitric Oxide

This step of denitrification reduces nitrite (NO2-) to nitric oxide (NO). The reaction is catalyzed by the enzyme nitrite reductase (Nir). It is a critical intermediary reduction step and can be rate-limiting under some conditions because NO is a gaseous intermediate that can inhibit further reduction if it accumulates. This step requires electrons provided by the oxidation of organic carbon substrates.

**Reference:** Tiedje, 1982; van Loosdrecht et al., 2002.

**Chemical Reaction:**

NO\_{2}^{-} + 2 \cdot H^{+} + e^{-} \rightarrow NO + H\_{2}O



### **Example Species:**

**Reactants:**

* Nitrite (NO2-)
* Acetate (CH3COO-) as electron donor

**Products:**

* Nitric oxide (NO)
* Water (H2O)

**Rate Expression**

r\_{NO2^{-}} = \mu\_{max} \cdot \frac{S\_{NO\_2^{-}}}{K\_{S,NO\_2^{-}} + S\_{NO\_2^{-}}} \cdot \frac{S\_{COD}}{K\_{S,COD} + S\_{COD}} \cdot X\_{DEN}



### **Explanation of Rate Expression**

This is a Monod model describing nitrite reduction rate.

* r\_NO2- is the moles of nitrite reduced per cubic meter reactor volume per second.
* S\_NO2- represents the nitrite concentration in mol per cubic meter.
* S\_COD is the concentration of soluble readily biodegradable organic carbon (acetate) in mol C per cubic meter.
* mu\_max is the maximum specific growth rate of nitrite-reducing denitrifying biomass.
* K\_S,NO2- is the half-saturation constant for nitrite.
* K\_S,COD is the half-saturation constant for COD.
* X\_DEN is the active biomass concentration in kg per cubic meter.

**Units of r\_NO2-:**  
 mol nitrite consumed per cubic meter per second.

Here the “mol” refers to moles of nitrite removed.

### **Constants** Reference: Henze et al., 2000.

* mu\_max: maximum growth rate of nitrite-reducing bacteria.
  + Typical range: 0.08 to 0.20 per hour (2.2e-5 to 5.6e-5 per second)
  + Reference: Tiedje, 1982.
* K\_S,NO2-: half-saturation constant for nitrite.
  + Range: 0.05 to 0.3 grams N per cubic meter (~3.6e-3 to 2.1e-2 mol per cubic meter).
  + Reference: van Loosdrecht et al., 2002.
* K\_S,COD: half-saturation constant for COD.
  + Range: 20 to 50 grams COD per cubic meter (~0.625 to 1.56 mol C per cubic meter).
  + Reference: Henze et al., 2000.
* theta\_mu: temperature coefficient (applies to mu\_max).
  + Value: 1.07 (meaning ~7% increase in rate per °C).

### **H. Temperature Correction**

Temperature correction uses the Arrhenius relation

\mu\_{T} = \mu\_{20} \cdot \theta^{(T - 20)}

* mu\_20 is the reference maximum growth rate at 20 °C.
* theta is 1.07.
* T is the operating temperature (°C).

## Reaction 3: Nitric Oxide Reduction to Nitrous Oxide

This step reduces nitric oxide (NO) to nitrous oxide (N2O). It is mediated by the enzyme nitric oxide reductase (Nor). NO is a toxic intermediate, and this reduction prevents its accumulation. The step is often rapid if electron donors are present, but it can be inhibited by low COD or by excessive free nitrous acid.

**Reference:** Tiedje, 1982; Richardson et al., 2001.

**Chemical Reaction**

2 \cdot NO + 2 \cdot H^{+} + 2 \cdot e^{-} \rightarrow N\_{2}O + H\_{2}O



### **Example Species**

**Reactants:**

* Nitric oxide (NO)
* Acetate (CH3COO-) as electron donor

**Products:**

* Nitrous oxide (N2O)
* Water (H2O)

**Rate Expression:**

r\_{NO} = \mu\_{max} \cdot \frac{S\_{NO}}{K\_{S,NO} + S\_{NO}} \cdot \frac{S\_{COD}}{K\_{S,COD} + S\_{COD}} \cdot X\_{DEN}



### **Explanation of Rate Expression:**

This is a Monod-type expression describing NO reduction:

* r\_NO is the moles of nitric oxide consumed per cubic meter per second.
* S\_NO is nitric oxide concentration (mol per cubic meter).
* S\_COD is soluble readily biodegradable organic carbon (mol C per cubic meter).
* mu\_max is the maximum specific growth rate of NO-reducing denitrifiers.
* K\_S,NO is the half-saturation constant for NO.
* K\_S,COD is the half-saturation constant for COD.
* X\_DEN is active denitrifying biomass concentration (kg per cubic meter).

### **Units and Interpretation:**

**Units of r\_NO:**  
 mol nitric oxide reduced per cubic meter per second.

“mol” refers to moles of NO removed.

### **Constants:**

* mu\_max:
  + Maximum growth rate of NO reducers.
  + Typical range: 0.05 to 0.15 per hour (1.4e-5 to 4.2e-5 per second).
  + Reference: Richardson et al., 2001.
* K\_S,NO:
  + Half-saturation for NO.
  + Range: 1e-6 to 5e-6 mol per cubic meter.
  + Reference: Richardson et al., 2001.
* K\_S,COD:
  + Half-saturation for COD.
  + Range: 0.625 to 1.56 mol C per cubic meter.
  + Reference: Henze et al., 2000.
* theta\_mu:
  + Temperature coefficient for mu\_max.
  + Value: 1.06.
  + Reference: Tiedje, 1982.

### **Temperature Correction**

Temperature adjustment uses Arrhenius-type relationship:

\mu\_{T} = \mu\_{20} \cdot \theta^{(T - 20)}

* mu\_20: reference mu\_max at 20 °C.
* theta: 1.06.
* T: actual temperature (°C)

### **Reference for this Reaction:**

* Tiedje J.M. (1982). Denitrification.
* Richardson D.J. et al. (2001). *Biochimica et Biophysica Acta*.
* Henze M. et al. (2000). *Activated Sludge Models*.

### **Reference for this Reaction**

* Payne W.J. (1981). *Denitrification*. Wiley-Interscience.
* Tiedje J.M. (1982). Denitrification. *Antonie van Leeuwenhoek*.
* Henze M. et al. (2000). *Activated Sludge Models*. IWA.
* van Loosdrecht M.C.M. et al. (2002). *Biological Wastewater Treatment*. IWA.

### **Reference for this Reaction**

* Tiedje J.M. (1982). Denitrification. *Antonie van Leeuwenhoek*.
* van Loosdrecht M.C.M. et al. (2002). *Biological Wastewater Treatment*. IWA.
* Henze M. et al. (2000). *Activated Sludge Models*. IWA.

Reaction 4: Nitrous Oxide Reduction to Nitrogen Gas

This final denitrification step converts nitrous oxide (N2O) into dinitrogen gas (N2), completing the nitrogen removal process. The enzyme nitrous oxide reductase (Nos) catalyzes this step. This reaction is sensitive to dissolved oxygen and copper limitation, and it is often the slowest in the denitrification pathway under sub-optimal conditions (Tiedje, 1982; Richardson et al., 2009).

### **Chemical Reaction**

N\_{2}O + 2 \cdot H^{+} + 2 \cdot e^{-} \rightarrow N\_{2} + H\_{2}O



### **Example Species**

**Reactants:**

* Nitrous oxide (N2O)
* Acetate (CH3COO-) as electron donor

**Products:**

* Dinitrogen gas (N2)
* Water (H2O)

### **Rate Expression**

r\_{N\_2O} = \mu\_{max} \cdot \frac{S\_{N\_2O}}{K\_{S,N\_2O} + S\_{N\_2O}} \cdot \frac{S\_{COD}}{K\_{S,COD} + S\_{COD}} \cdot X\_{DEN}



**Explanation of Rate Expression**

This Monod-type expression models N2O reduction:

* r\_N2O is the moles of N2O consumed per cubic meter per second.
* S\_N2O is nitrous oxide concentration (mol per cubic meter).
* S\_COD is soluble readily biodegradable carbon (mol C per cubic meter).
* mu\_max is the maximum growth rate of N2O reducers.
* K\_S,N2O is the half-saturation constant for N2O.
* K\_S,COD is the half-saturation constant for COD.
* X\_DEN is active denitrifying biomass concentration (kg per cubic meter).

### **Units and Interpretation**

Units of r\_N2O:  
 mol nitrous oxide reduced per cubic meter per second.

**Constants**

* mu\_max:
  + Maximum specific growth rate of N2O reducers.
  + Typical range: 0.03 to 0.12 per hour (8.3e-6 to 3.3e-5 per second).
  + Reference: Richardson et al., 2009.
* K\_S,N2O:
  + Half-saturation constant for N2O.
  + Range: 5e-7 to 1e-6 mol per cubic meter.
  + Reference: Richardson et al., 2009.
* K\_S,COD:
  + Half-saturation for COD.
  + Range: 0.625 to 1.56 mol C per cubic meter.
  + Reference: Henze et al., 2000.
* theta\_mu:
  + Temperature coefficient for mu\_max.
  + Value: 1.07.
  + Reference: Tiedje, 1982.

### **Temperature Correction**

Temperature dependence is described by:

\mu\_{T} = \mu\_{20} \cdot \theta^{(T - 20)}

* mu\_20: Reference mu\_max at 20 °C.
* theta: 1.07.
* T: Temperature (°C).

Combined References

1. Henze, M., Grady, C.P.L., Gujer, W., Marais, G.v.R., & Matsuo, T. (2000). *Activated Sludge Models ASM1, ASM2, ASM2d and ASM3*. IWA Publishing. Link
2. Tchobanoglous, G., Burton, F.L., Stensel, H.D., et al. (2014). *Wastewater Engineering: Treatment and Resource Recovery*, 5th Ed. McGraw-Hill.
3. Richardson, D.J., Felgate, H., Watmough, N.J., Thomson, A.J., & Baggs, E.M. (2009). Mitigating the environmental impact of nitrous oxide. *Nature Reviews Microbiology*, 7(7), 527–536. DOI
4. Grady, C.P.L., Daigger, G.T., Love, N.G., & Filipe, C.D.M. (1999). *Biological Wastewater Treatment*. CRC Press.
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### **Reference for this Reaction**

* Payne W.J. (1981). *Denitrification*. Wiley-Interscience.
* Tiedje J.M. (1982). Denitrification. *Antonie van Leeuwenhoek*.
* Henze M. et al. (2000). *Activated Sludge Models*. IWA.
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### **Reference for this Reaction**

* Tiedje J.M. (1982). Denitrification. *Antonie van Leeuwenhoek*.
* van Loosdrecht M.C.M. et al. (2002). *Biological Wastewater Treatment*. IWA.
* Henze M. et al. (2000). *Activated Sludge Models*. IWA.

## **Combined Variable List (Plain Text)**

Below is a **merged variable index** for all denitrification reactions:

* S\_NO3: Nitrate concentration (mol/m³)
* S\_NO2: Nitrite concentration (mol/m³)
* S\_N2O: Nitrous oxide concentration (mol/m³)
* S\_COD: Readily biodegradable carbon (mol C/m³)
* X\_DEN: Active denitrifying biomass (kg/m³)
* μ\_max: Maximum specific growth rate (s⁻¹)
* K\_S,NO3: Half-saturation constant for nitrate (mol/m³)
* K\_S,NO2: Half-saturation constant for nitrite (mol/m³)
* K\_S,N2O: Half-saturation constant for nitrous oxide (mol/m³)
* K\_S,COD: Half-saturation constant for COD (mol/m³)
* θ: Temperature correction coefficient (dimensionless)
* T: Temperature (°C)
* r\_NO3: Rate of nitrate reduction (mol/m³·s)
* r\_NO2: Rate of nitrite reduction (mol/m³·s)
* r\_N2O: Rate of nitrous oxide reduction (mol/m³·s)

**Acetogenesis**

Acetogenesis is the conversion of volatile fatty acids (VFAs) such as propionate and butyrate into acetate, CO2, and hydrogen gas. This step is essential because methanogens predominantly consume acetate and hydrogen, linking acidogenesis to methanogenesis (Batstone et al., 2002). Acetogenic bacteria are strictly anaerobic and sensitive to hydrogen partial pressure. When hydrogen accumulates, the Gibbs free energy becomes less favorable, resulting in process inhibition (McCarty & Smith, 1986).

Acetogenesis is performed primarily by syntrophic bacteria such as Syntrophobacter and Syntrophomonas spp. These organisms rely on low hydrogen partial pressure maintained by hydrogenotrophic methanogens to render their reactions thermodynamically favorable (Appels et al., 2008). The kinetics are typically modeled using a Monod expression with volatile fatty acids as the limiting substrate. The process is slower than acidogenesis due to stricter thermodynamic constraints and lower μ\_acet. Temperature corrections are critical for accurately predicting acetogenic activity, as small temperature shifts can significantly impact the delicate balance between hydrogen production and consumption (Batstone et al., 2002).

Acetogenesis performance varies widely across treatment units. In primary clarifiers and collection tanks, acetogenesis is often negligible because retention time and biomass concentrations are too low. In anaerobic reactors (e.g., anaerobic tanks or anaerobic membrane bioreactors), higher solids retention time enables syntrophic communities to stabilize hydrogen pressure, promoting higher rates of acetogenesis (Appels et al., 2008). This process is typically suppressed in aerobic and anoxic tanks due to oxygen inhibition. Membrane bioreactors can support higher acetogenic biomass concentrations due to biomass retention, resulting in improved conversion of VFAs to acetate compared to conventional reactors (Batstone et al., 2002).

**Chemical Reaction:**

C3H6O2 + 2 \cdot H2O \rightarrow C2H4O2 + CO2 + 3 \cdot H2

**Example Species:**

**Reactants:**

* Propionate: C3H6O2
* Butyrate: C4H8O2
* Water: H2O

**Products:**

* Acetate: C2H4O2
* Hydrogen: H2
* Carbon dioxide: CO2
* Biomass (generic): C5H7O2N

**Rate Expression:**

r\_{acet} = \mu\_{acet} \cdot \frac{S\_{VFA}}{K\_{S,VFA} + S\_{VFA}} \cdot X\_{acet}

**Units and Moles Clarification:**

* Units of r\_acet: mol·m^-3·s^-1
* The moles refer to **moles of volatile fatty acids consumed** per cubic meter per second.
* This includes all short-chain VFAs (e.g., propionate, butyrate), generally expressed as an acetate-equivalent mass.

**Constants and Typical Ranges**

**μ\_acet**

* Maximum specific growth rate of acetogenic bacteria
* Typical range: 0.1 – 0.5 1/day
* Reference: Batstone et al. (2002)

**K\_S,VFA**

* Half-saturation constant for volatile fatty acids
* Typical range: 5.0 × 10^-4 – 1.0 × 10^-3 mol·m^-3
* Reference: Batstone et al. (2002)

**b\_acet**

* Decay rate of acetogenic biomass
* Typical range: 0.02 – 0.06 1/day
* Reference: Batstone et al. (2002)

**Temperature Correction Details**

**θ\_acet**

* Temperature coefficient for μ\_acet
* Typical value: 1.03 – 1.06 (dimensionless)
* Applies specifically to μ\_acet
* Temperature range: 15–35 °C
* Reference: Batstone et al. (2002)

## **References (Combined)**

* Batstone, D. J., Keller, J., Angelidaki, I., Kalyuzhnyi, S. V., Pavlostathis, S. G., Rozzi, A., Sanders, W. T., Siegrist, H., & Vavilin, V. A. (2002). The IWA Anaerobic Digestion Model No. 1 (ADM1). *Water Science & Technology*, 45(10), 65–73. <https://iwa-network.org/publications/anaerobic-digestion-model-no-1-adm1/>
* Appels, L., Baeyens, J., Degrève, J., & Dewil, R. (2008). Principles and potential of the anaerobic digestion of waste-activated sludge. *Progress in Energy and Combustion Science*, 34(6), 755–781. <https://doi.org/10.1016/j.pecs.2008.06.002>
* McCarty, P. L., & Smith, D. P. (1986). Anaerobic wastewater treatment. *Environmental Science and Technology*, 20(12), 1200–1206. <https://pubs.acs.org/doi/10.1021/es00154a001>

**Acidogenesis:**

Acidogenesis is the second stage of anaerobic digestion, following hydrolysis. In this process, fermentative acidogenic bacteria convert soluble organic monomers (such as glucose, amino acids, and fatty acids) into volatile fatty acids (VFAs) including acetate, propionate, and butyrate, as well as CO₂, H₂, and small amounts of alcohols. Acidogenesis is crucial because it creates substrates required for later stages (acetogenesis and methanogenesis) (Batstone et al., 2002). The reaction environment is strictly anaerobic and sensitive to pH (optimally near 6.0). The process rate is influenced by temperature, substrate concentration, and hydrogen partial pressure (Batstone et al., 2002).

**Collection Tank:** Acidogenesis is minor due to short retention time and higher oxygen ingress.  
 **Primary Clarifier:** Limited; partial acidification can occur in settled sludge.  
 **Anoxic Tank:** Typically negligible; nitrate presence inhibits acidogenesis.  
 **Aerobic Tank:** Aerobic conditions fully suppress acidogenic activity.  
 **Membrane Reactor:** If operated anaerobically, acidogenesis is significant, especially with recirculated sludge.  
 **Clear Water Tank:** Essentially none; fully clarified and oxygenated effluent.

**Chemical Reaction:**

C6H12O6 \rightarrow C2H4O2 + CO2 + H2

This represents glucose conversion to acetic acid, CO₂, and hydrogen.

### **Example Species**

* **Reactant:** Glucose – C6H12O6
* **Products:**
  + Acetic Acid – C2H4O2
  + Carbon Dioxide – CO2
  + Hydrogen – H2

Note: Depending on substrate, VFAs can also include propionic acid (C3H6O2) and butyric acid (C4H8O2).

**Rate Expression**

Monod-type kinetics are used to describe acidogenesis. The general form is:

r\_acid = \mu\_acid \cdot \frac{S}{K\_S + S} \cdot X

Where (Batstone et al. ,2002):

* r\_acid is the acidogenesis rate, expressed in **mol of substrate converted per m³ reactor volume per second** (mol·m⁻³·s⁻¹).
* **Moles refer to reactant glucose (C6H12O6) degraded per unit time.**
* S is substrate concentration (mol·m⁻³).
* X is active biomass concentration (mol biomass equivalents·m⁻³).

This rate accounts for substrate limitation but does not explicitly include hydrogen partial pressure inhibition in this form (though some models add a hydrogen inhibition term).

### **Constants and Their Meaning**

**Maximum specific growth rate (mu\_acid):**

* Value: 0.8 day⁻¹
* SI Units: 9.26 × 10⁻⁶ s⁻¹
* Refers to: Maximum conversion rate per unit biomass
* Source: Batstone et al., 2002

**Half-saturation constant (K\_S):**

* Value: 50 mg COD·L⁻¹ (0.050 kg COD·m⁻³)
* Refers to: Concentration of soluble substrate at which rate is half maximal
* Source: Batstone et al., 2002

**Yield coefficient (Y):**

* Value: 0.1 mol biomass·mol substrate⁻¹
* Refers to: Moles of biomass generated per mole of glucose degraded
* Source: Batstone et al., 2002

**Decay coefficient (b):**

* Value: 0.02 day⁻¹
* SI Units: 2.31 × 10⁻⁷ s⁻¹
* Refers to: Biomass decay rate
* Source: Batstone et al., 2002

**Theta (Temperature Correction Factor):**

* Value: 1.07 per °C
* Refers to: Correction applied to μ\_acid per degree deviation from 35 °C
* Typical operational range: 15–45 °C
* Source: Batstone et al., 2002

### **Typical Ranges**

**mu\_acid:** 0.5–1.5 day⁻¹ depending on substrate (glucose higher, amino acids lower)  
 **K\_S:** 20–100 mg COD·L⁻¹ (0.02–0.1 kg·m⁻³)  
 **Temperature:** 30–37 °C optimal mesophilic range  
 **pH:** 5.5–6.5 for maximal activity  
 **Reference:** Batstone et al., 2002; Angelidaki et al., 1993

### **Temperature Correction**

**Theta = 1.07 per °C**  
 This means for each degree Celsius above or below reference temperature (usually 35 °C), the rate increases or decreases by ~7%.  
 **Reference:** Batstone et al., 2002

**References cited:** Batstone et al. (2002), Angelidaki et al. (1993), McCarty (1964)

### **List of References**

* Batstone, D. J., et al. (2002). *The IWA Anaerobic Digestion Model No.1 (ADM1)*. IWA Publishing.
* Angelidaki, I., et al. (1993). "A mathematical model for dynamic simulation of anaerobic digestion of complex substrates." *Biotechnology and Bioengineering*.
* McCarty, P. L. (1964). "Anaerobic waste treatment fundamentals." *Public Works*.

## **Phosphate Uptake (Enhanced Biological Phosphorus Removal)**

**Description:**  
 Phosphate accumulating organisms (PAOs) incorporate phosphate aerobically as polyphosphate.

**Chemical Reaction:**  
 PO₄³⁻ + BODₛ + O₂ → poly-P + CO₂ + biomass

r\_pao = μ\_PAO ⋅ (PO4 / (K\_PO4 + PO4)) ⋅ (BOD\_s / (K\_BOD + BOD\_s)) ⋅ (O2 / (K\_O + O2))

μ\_PAO = 1.16×10^-5 s^-1

K\_PO4 = 0.01 kg/m³

Reference: Oehmen et al. (2007)

\*\*Membrane Reactor

**Membrane Fouling (Optional Process)**

**Description:**  
 Accumulation of soluble microbial products and colloids on membrane surfaces, reducing permeability. Usually modeled empirically or via cake layer resistance.

**Empirical Fouling Rate Expression (if needed):**

r\_foul = k\_foul ⋅ C\_solids ⋅ TMP

* k\_foul = fouling coefficient (system-specific, m³/(N·s))
* C\_solids = solids concentration (kg/m³)
* TMP = transmembrane pressure (Pa)

Fouling is often **not included** in biological mass balances but critical for filtration design.

**Reference:** Le-Clech et al. (2006)

## **Chlorine Decay (If Disinfection is Applied)**

**Description:**  
 Residual chlorine applied for disinfection decays over time via reaction with organics and self-decomposition.

**Chemical Reaction:**  
 Cl₂ → Cl⁻ + byproducts

**Reaction Rate Expression (First-order decay):**

r\_cl = k\_cl ⋅ Cl

**Constants:**

* k\_cl = 1.39×10^-6 s^-1 (approximate, varies widely)

**Reference:** Hua & Reckhow (2007)

## **Fermentation**

Fermentation is the anaerobic transformation of soluble and particulate organic matter into volatile fatty acids (VFAs), alcohols, hydrogen gas, ammonia, and carbon dioxide. This process generates the substrates for acidogenesis and methanogenesis. Fermentative bacteria initiate this process in environments where oxygen is absent. Substrate availability, biomass concentration, and temperature all strongly influence the reaction rate (McCarty & Smith, 1986; Batstone et al., 2002).

Fermentation efficiency varies greatly between units. In collection tanks and clarifiers, low biomass concentration and short retention time limit VFA generation (Tong & McCarty, 1991). Anoxic tanks can see partial inhibition by nitrate, while membrane bioreactors retain fermentative biomass and improve lipid degradation (Batstone et al., 2002). Higher temperatures (e.g., 35 °C) can nearly double mu\_F across all substrates (Grady et al., 2011).

Reaction 1 – Fermentation of Soluble Glucose

Fermentative bacteria convert glucose into ethanol and CO₂ under strictly anaerobic conditions. The main bacteria are *Zymomonas mobilis* and *Clostridium* species (Batstone et al., 2002)

**Chemical Reaction**

C\_6H\_{12}O\_6 \quad \rightarrow \quad 2 \cdot CH\_3CH\_2OH \quad + \quad 2 \cdot CO\_2



**Rate Expression**

r\_{fermentation,glucose} \quad = \quad \mu\_{F,glucose} \cdot \frac{S\_{glucose}}{K\_{S,glucose} \quad + \quad S\_{glucose}} \cdot X\_F



**Example Species:**

* Reactant: Glucose — C6H12O6
* Products: Ethanol — C2H6O, CO2

**Units of Reaction Rate:**  
mol glucose consumed per m3 per second.

**Constants (plain text):**

* mu\_F,glucose: Maximum specific growth rate = 1.5 per day.
  + Refers to growth on glucose.
  + Typical range: 0.8–2.0 per day.
  + Reference: Batstone et al., 2002.
* K\_S,glucose: Half-saturation constant = 2.1e-4 mol per m3.
  + Refers to soluble glucose.
  + Typical range: 1.0e-4 – 4.0e-4 mol per m3.
  + Reference: McCarty & Smith, 1986.
* X\_F: Biomass concentration in kg per m3.

**Temperature Correction:**

* Theta\_F,glucose = 1.04 (dimensionless), range: 1.03–1.06.
  + Refers to sensitivity of mu\_F to temperature.

Reaction 2 – Fermentation of Soluble Proteins

Proteins are hydrolyzed and fermented to VFAs, CO2, and ammonia. Proteolytic bacteria such as *Bacteroides* mediate this pathway (Grady et al., 2011).

**Chemical Reaction**

C\_{4.4}H\_{7.3}O\_{1.6}N \quad \rightarrow \quad VFAs \quad + \quad NH\_3 \quad + \quad CO\_2



**Reaction Rate**

r\_{fermentation,protein} \quad = \quad \mu\_{F,protein} \cdot \frac{S\_{protein}}{K\_{S,protein} \quad + \quad S\_{protein}} \cdot X\_F



**Example Species:**

* Reactant: Casein hydrolysate (approx. C4.4H7.3O1.6N)
* Products: Acetate (C2H4O2), Propionate (C3H6O2), NH3, CO2

**Units of Reaction Rate:**  
 mol protein degraded per m3 per second.

**Constants (plain text):**

* mu\_F,protein: 0.7 per day.
  + Refers to growth on soluble proteins.
  + Typical range: 0.5–1.0 per day.
  + Reference: Batstone et al., 2002.
* K\_S,protein: 3.1e-4 mol per m3.
  + Refers to soluble protein.
  + Typical range: 2e-4 – 5e-4 mol per m3.
  + Reference: McCarty & Smith, 1986.
* X\_F: Biomass in kg per m3.

**Temperature Correction:**

* Theta\_F,protein: 1.04 (dimensionless), range: 1.03–1.06.

Reaction 3 – Fermentation of Lipids

Lipids are slowly hydrolyzed and fermented, producing VFAs and hydrogen, which can inhibit subsequent methane formation (Batstone et al., 2002).

**Chemical Reaction**

C\_{57}H\_{104}O\_6 \quad \rightarrow \quad VFAs \quad + \quad H\_2 \quad + \quad CO\_2

**Chemical Reaction**

C\_{57}H\_{104}O\_6 \quad \rightarrow \quad VFAs \quad + \quad H\_2 \quad + \quad CO\_2

Reaction Rate Expression

r\_{fermentation,lipid} \quad = \quad \mu\_{F,lipid} \cdot \frac{S\_{lipid}}{K\_{S,lipid} \quad + \quad S\_{lipid}} \cdot X\_F



**Example Species:**

* Reactant: Tripalmitin — C57H104O6
* Products: Acetate, Propionate, CO2, H2

**Units of Reaction Rate:**  
 mol lipid degraded per m3 per second.

**Constants (McCarty & Smith, 1986):**

* mu\_F,lipid: 0.3 per day.
  + Refers to fermentative growth on lipids.
  + Typical range: 0.2–0.5 per day.
  + Reference: Batstone et al., 2002.
* K\_S,lipid: 4.6e-4 mol per m3.
  + Refers to soluble lipid.
  + Typical range: 3e-4 – 6e-4 mol per m3.
  + Reference: .
* X\_F: Biomass in kg per m3.

**Temperature Correction:**

* Theta\_F,lipid: 1.03, range: 1.02–1.04.

## **Variable Index**

* S\_glucose: Concentration of soluble glucose, mol per m3.
* S\_protein: Soluble protein, mol per m3.
* S\_lipid: Soluble lipid, mol per m3.
* X\_F: Fermentative biomass, kg per m3.
* mu\_F: Maximum specific growth rate, per day.
* K\_S: Half-saturation constant, mol per m3.
* Theta\_F: Temperature coefficient (dimensionless).

## **📚 References**

* Batstone DJ et al., 2002. IWA Anaerobic Digestion Model No.1.
* McCarty PL, Smith DP, 1986. Anaerobic Wastewater Treatment Fundamentals.
* Grady CP et al., 2011. Biological Wastewater Treatment, 3rd Ed.
* Tong Z, McCarty PL, 1991. Hydrolysis Kinetics in Anaerobic Digestion.

# **PAC Adsorption**

PAC (Powdered Activated Carbon) adsorption is a physicochemical process in which dissolved contaminants adhere to the porous surface of PAC particles. This process is often used in clarifiers and membrane tanks to improve removal of micropollutants and soluble organics. Adsorption onto PAC is a two-step process: external film mass transfer of the contaminant to the particle surface, followed by surface binding (Kuo et al., 2012).

Adsorption kinetics are typically described by Langmuir or Freundlich isotherms, and rate expressions depend on the PAC dose, contaminant concentration, and mass transfer limitations (Kuo et al., 2012). PAC can adsorb a wide range of compounds including soluble BOD, phenols, and pesticides. The rate is often controlled by the availability of surface sites (Langmuir kinetics). The term C denotes the dissolved concentration of the contaminant. PAC dosage is crucial: higher PAC concentrations increase the number of available adsorption sites, enhancing removal efficiency.

PAC adsorption performance varies substantially between reactor types. In collection tanks, short retention times limit equilibrium achievement, leading to lower removal efficiency (Kuo et al., 2012). Clarifiers can improve contact time but may suffer from PAC carryover with sludge. Membrane reactors are particularly effective because microfiltration retains both the PAC and adsorbed contaminants, enhancing removal and preventing desorption downstream (Weber & DiGiano, 1996). Temperature has minimal effect, but higher temperatures can slightly increase diffusion rates and marginally improve kinetics.

# **Adsorption of Soluble Contaminant onto PAC**

## **Chemical Reaction**

This represents reversible binding of a dissolved contaminant to the activated carbon surface.

Contaminant\_{(aq)} \quad + \quad PAC\_{(s)} \quad \leftrightarrow \quad Contaminant{-}PAC\_{(s)}



r\_{ads} \quad = \quad k\_{ads} \cdot PAC \cdot \frac{C}{1 \quad + \quad K\_{ads} \cdot C}



## **Example Species**

**Reactants:**

* Phenol: C6H5OH
* Soluble BOD (modeled as C6H12O6)
* Micro-pollutants (e.g., Atrazine: C8H14ClN5)

**Products:**

* Phenol-PAC complex
* BOD-PAC complex

These complexes are not fully specified chemically but are often generically referred to as Contaminant-PAC\_{(s)} in literature.

## **Units of Reaction Rate**

The rate r\_ads is measured as:  
 mol contaminant adsorbed per m3 liquid per second.

**Important note:**  
 The mols refer specifically to **contaminant removed from solution phase**, not to PAC mass or site occupancy.

## **Constants (plain text)**

* k\_ads: Adsorption rate constant.
  + Value: 3.0e-4 m3 per mol per second.
  + Refers to mass transfer-limited binding of dissolved contaminant onto PAC.
  + Typical range: 1e-4 – 5e-4 m3 per mol per second.
  + Reference: Kuo et al., 2012.
* K\_ads: Langmuir equilibrium constant.
  + Value: 1.2e2 m3 per mol.
  + Refers to affinity of contaminant for PAC.
  + Typical range: 1e2 – 3e2 m3 per mol.
  + Reference: Weber & DiGiano, 1996.
* PAC: PAC concentration.
  + Units: kg per m3.
  + Typical operating range: 0.05 – 1.0 kg per m3.
  + Reference: Kuo et al., 2012.

## **Temperature Correction**

Adsorption kinetics are generally less temperature-sensitive than biological reactions. However, temperature affects both diffusion coefficients and equilibrium constants (Weber & DiGiano, 1996). A commonly used correction factor is:

* Theta\_ads = 1.01 (dimensionless).
  + Range: 1.00 – 1.02.
  + Refers to the minor sensitivity of k\_ads to temperature increases.

## **Typical Ranges**

* k\_ads: 1e-4 to 5e-4 m3/mol/s.
* K\_ads: 1e2 to 3e2 m3/mol.
* PAC dose: 0.05–1.0 kg/m3.
* Operating temperatures: 10–35 °C.

## **Variable Index**

* C: Concentration of dissolved contaminant (mol/m3).
* PAC: Powdered Activated Carbon concentration (kg/m3).
* k\_ads: Adsorption rate constant (m3/mol/s).
* K\_ads: Langmuir equilibrium constant (m3/mol).
* r\_ads: Rate of adsorption (mol/m3/s).
* Theta\_ads: Temperature coefficient for adsorption kinetics.

## **📚 References**

* Kuo WC, et al., 2012. Lipase-producing microbes in wastewater: Environmental Technology.
* Weber WJ, DiGiano FA, 1996. Adsorption Processes for Water Treatment.
* Grady CP, Daigger GT, Love NG, Filipe CDM, 2011. Biological Wastewater Treatment.

Temperature Correlation

The temperature empirical model is used in many wastewater models (e.g. ASM1) and assumes exponential behavior over small temperature ranges (10–30 °C). It is **not based on activation energy**, and is used when data is limited

k\_T = k\_{T\_0} \cdot \theta^{(T - T\_0)}



**Where**:

* k\_T: rate constant at temperature T (in °C)
* k\_{T\_0}: rate constant at reference temperature T\_0 (usually 20 °C)
* θ: empirical temperature coefficient (dimensionless, usually between **1.03–1.07**)
* T: operating temperature in °C
* T\_0: reference temperature in °C

The exponential term in the Arrhenius equation is linearly approximated over the narrow biological temperature range (10-30 degC) using the empirical form:

\theta^{(T - T\_0)}



To avoid theta approximations and use a temperature correlation based on reaction energies, the Arrhenius equation can be used:

k\_T = k\_{T\_0} \cdot \exp\left( \frac{-E\_a}{R} \cdot \left( \frac{1}{T} - \frac{1}{T\_0} \right) \right)

