Chapter 1 基本特性

1-1 物化性質

It is characterized in terms of its physical, chemical, and biological composition.

常見物化性質表示單位

Basis	Application	Unit
物理性質		
Percent by volume	$\dfrac{Volume\ of\ solution \times 100}{Total\ volume\ of\ solution}$	%(by vol)
Percent by mass	$\dfrac{Mass\ of\ solution \times 100}{Combined\ mass\ of\ solute + solvent}$	%(by mass)
Mass per unit volume	$\dfrac{milligrams}{Liter\ of\ solution}$ 、 $\dfrac{Grams}{Cubic\ meter\ of\ solution}$	$\dfrac{mg}{L}$ 、 $\dfrac{g}{m^3}$
Mass ratio	$\dfrac{Milligrams}{10^6\ milligrams}$	ppm
化學性質		
Molarity	$\dfrac{Moles\ of\ solute}{Liter\ of\ solution}$	$\dfrac{mol}{L}$
Molality	$\dfrac{Moles\ of\ solute}{1000\ grams\ solvent}$	$\dfrac{mol}{Kg}$
Normality	$\dfrac{Milliequivalents\ of\ solute}{Liter\ of\ solution}$	$\dfrac{meq}{L}$

1-2 基本化學

1.電中性(electroneutrality)

$\sum cations = \sum anions$；陽離子之當量總和=陰離子之當量總和

Equivalent weight, $g/_{eq} = \dfrac{molecular\ weight,\ g}{Z}$

利用偏差百分率校正電中性，可接受之偏差範圍 < 5%

$Percent\ difference = 100 \times \left(\dfrac{\sum cations - \sum anions}{\sum cations + \sum anions} \right)$

Example 2-1.

求下列系統中陰、陽離子之電中性？分析結果是否為可接受範圍？

Cation	Conc., mg/L	Anion	Conc., mg/L
Ca^{2+}	82.2	HCO_3^-	220.0
Mg^{2+}	17.9	SO_4^{2-}	98.3
Na^+	46.4	Cl^-	78.0

K$^+$	15.5	NO$_3^-$	25.6

2.化學平衡

$aA＋bB \leftrightarrow cC＋dD$ ；$K = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$ ，k: 平衡常數，[ ]: 莫耳濃度。
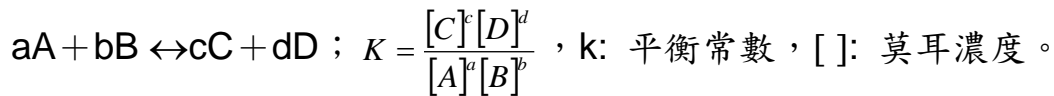
已知反應，平衡常數因溶液之溫度及離子強度而異，而溶液之濃度表示，稀溶液以體積莫耳濃度為主，但離子強度較大之鹽水，以重量莫耳濃度為主。但離子間可能之交互作用，將影響溶液之濃度，故強調非理想狀態時，需應用活性(activity)之觀念。

The activity of an ion is defined as follow.

$\alpha_i = \gamma [C_i]$

α_i : activity of ith ion, mol/L

γ : activity coefficient for the ith ion

C_i = concentration of ith ion in solution, mol/L

因此

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} = \frac{[\alpha_C]^c[\alpha_D]^d}{[\alpha_A]^a[\alpha_B]^b} = \frac{[\gamma_C C]^c[\gamma_D D]^d}{[\gamma_A A]^a[\gamma_B B]^b}$$

3.活性係數之求法

Guntelberg approximation(適合離子強度<0.1 M)：

$$\log \gamma = -\frac{0.5(Z_i)^2 \sqrt{I}}{1+\sqrt{I}} \quad \text{where } Z_i : \text{charge on ith ionic species, } I = \text{ionic strength}$$
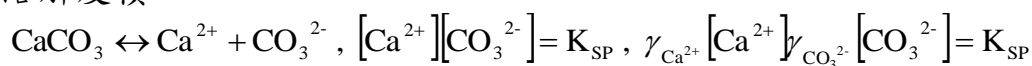
4.離子強度之估算

$$I = \frac{1}{2}\sum C_i Z_i^2$$

where C_i : concentration of the ith species, mole/L $\quad Z_i$: valence number of the ith species

$I = 2.5 \times 10^{-5} \times TDS$
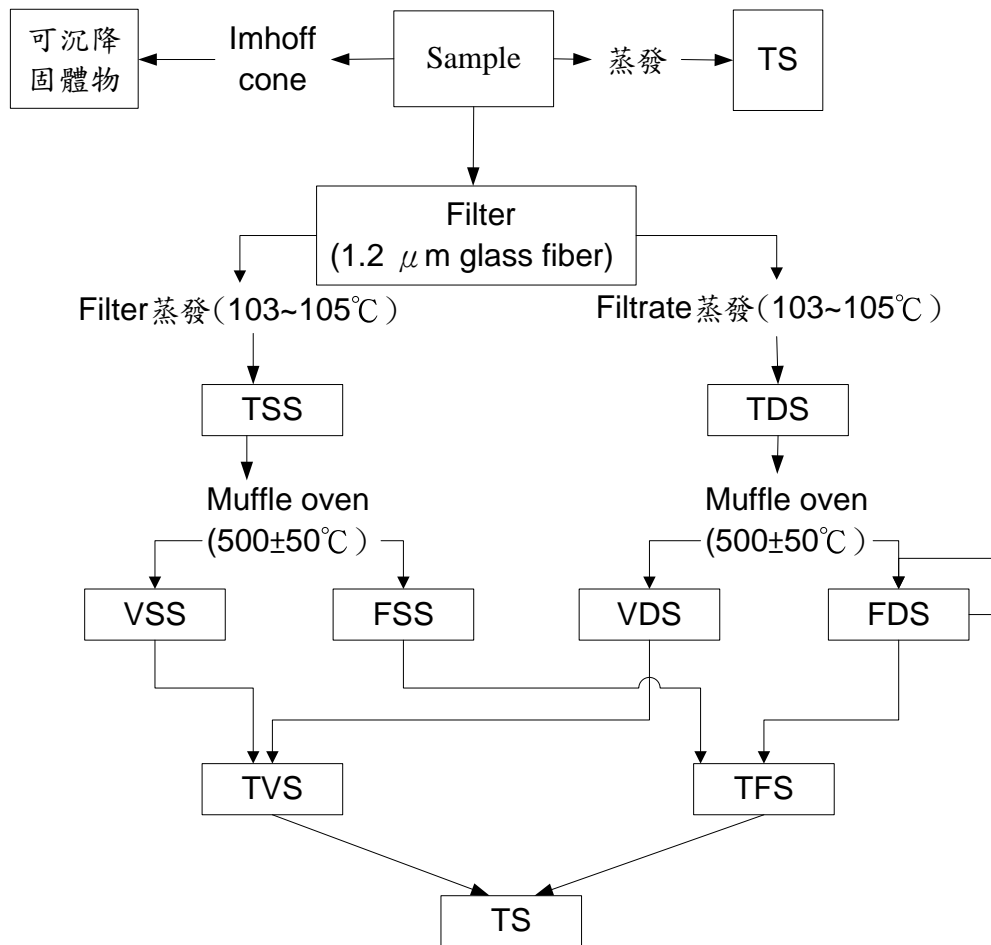
where TDS : total dissolved solids, mg/L

5.溶解度積

$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-}$, $[Ca^{2+}][CO_3^{2-}] = K_{SP}$, $\gamma_{Ca^{2+}}[Ca^{2+}]\gamma_{CO_3^{2-}}[CO_3^{2-}] = K_{SP}$

Example 2-2.求例題 2-1 廢水中一價與二價離子之活性係數各若干？利用兩價離子活性係數，求不生成沉澱之鈣離子最小濃度若干 mg/L？已知 CaCO$_3$ 之 Ksp at 25℃ = 5×10^{-9}

1-3 特性指標

1. Solids

```
可沉降          Imhoff          Sample          蒸發          TS
固體物    ←    cone     ←                  →          →
                              ↓
                         Filter
                    (1.2 μm glass fiber)
         ↓                                    ↓
Filter蒸發(103~105℃)              Filtrate蒸發(103~105℃)
         ↓                                    ↓
       TSS                                  TDS
         ↓                                    ↓
   Muffle oven                          Muffle oven
   (500±50℃)                            (500±50℃)
   ↓         ↓                          ↓         ↓
  VSS       FSS                        VDS       FDS
         ↓        ↓              ↓        ↓
       TVS                              TFS
              ↓                  ↓
                       TS
```

TS：總固體物　TSS：總懸浮性固體物　TDS：總溶解性固體物
VSS：揮發懸浮性固體物　FSS：固定懸浮性固體物
　VDS：揮發溶解性固體物　FDS：固定溶解性固體物
　TVS：總揮發性固體物　　TFS：總固定性固體物

Example 2-3.
　水質分析結果如下，水樣體積 50 mL，求 TS、TVS、TSS 及 TDS。蒸發皿重 52.1533 g，105℃後含蒸發皿之殘留物重 52.189 g，550℃後含蒸發皿之殘留物重 52.1863 g，濾紙重 1.5413 g，105℃後濾紙上之殘留物重 1.5541 g，550℃後濾紙上之殘留物重 1.5519 g。

2. 水溫
Temp↑，DO↓；μ↓
Temp↑，促進細菌活動與化學變化
Optimum temperatures for bacterial activity are in the range from 25 to 35℃

3. Conductivity
　electrical conductivity (EC)，表示單位為 millisiemens per meter (mS/m)

或 micromhos per centimeter (μmho/cm)。1 mS/m = 10 μmho/cm

$TDS(mg/L) \cong EC(\mu mho/cm) \times (0.55 \sim 0.70)$

$I = 1.6 \times 10^{-5} \times EC(\mu mho/cm)$

4. Specific gravity

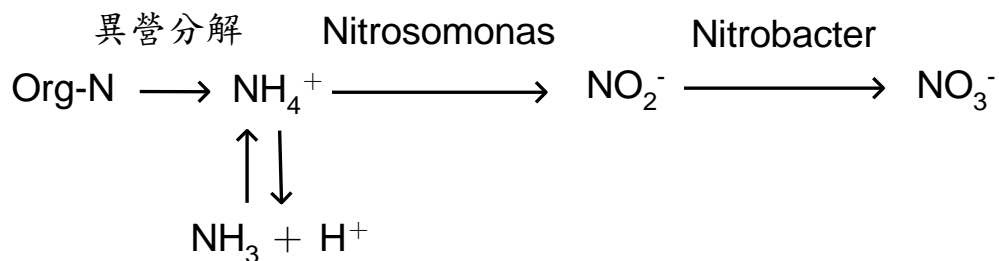$S_w = \dfrac{\rho_w}{\rho_o}$, ρ_w : density of wastewater, ρ_o : density of water

5. pH
pH = -$\log_{10}$ [H$^+$] , pH + pOH = 14

6.鹼度
由 CO_3^{2-}、HCO_3^{-}、OH^{-}所造成，Calcium and magnesium bicarbonates are most common. Alkalinity is expressed in terms of calcium carbonate, mg/L as $CaCO_3$.

7.氮化物(Nitrogen)

$$\text{Org-N} \xrightarrow{\text{異營分解}} NH_4^+ \xrightarrow{\text{Nitrosomonas}} NO_2^- \xrightarrow{\text{Nitrobacter}} NO_3^-$$

$$NH_4^+ \updownarrow NH_3 + H^+$$

TKN=Org-N + NH_3-N

TN=TKN + NO_2^--N + NO_3^--N

8.硫化物
最常見者為 SO_4^{2-}

$$\text{Organic matter} \longrightarrow SO_4^{2-} \xrightarrow{\text{Bacteria}} S^{2-} + H_2O + CO_2$$

$$S^{2-} + 2H^+ \longrightarrow H_2S$$
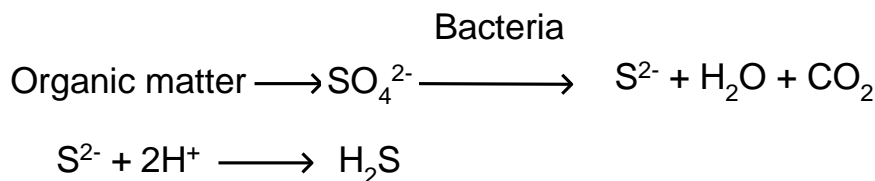
9. Solubility of gases in water
The ideal gas law

PV=nRT,　　R: gas law constant, 0.082057 atm.L/mole.K

Example 2-4.求 1atm, 0℃ 時，每一莫耳氣體所佔體積若干 L？又 9 ppm$_v$ 之 H_2S 氣體，約等於若干 mg/L？

10. Henry's law for dissolved gases

氣體在液體中之平衡或飽和濃度

$P_g = \dfrac{H}{P_T} x_g$ where P_g : mole fraction of gas in air, mole gas/mole of air

H : Henry's law constant, $\dfrac{atm\,(mole\ gas/mole\ air)}{(mole\ gas/mole\ water)}$

P_T : total pressure, usually $1.0\,atm$

x_g : mole fraction of gas in water, mole gas/mole water $= \dfrac{mole\ gas\,(n_g)}{mole\ gas\,(n_g) + mole\ water\,(n_w)}$

Example 2-5. What is the saturation of oxygen in water in contact with dry air at 1 atm and 20℃? (H: 41100 atm)

11. Aggregate organic constituents

常見有機物種類，蛋白質 40~60%、碳水化合物 25~50%、油脂 10%

BOD, COD, TOC, ThOD

(1)BOD$_5$

碳化 BOD；CBOD

氮化 BOD；NBOD

  Oxidation

$COHNS + O_2 + bacteria \rightarrow CO_2 + H_2O + NH_3 + other\ end\ products + energy$

  Synthesis

$COHNS + O_2 + bacteria + energy \rightarrow C_5H_7NO_2\ (new\ cell\ tissue)$
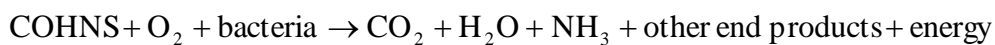
  Endogenous respiration

$C_5H_7NO_2 + 5O_2 \rightarrow 5CO_2 + NH_3 + 2H_2O$
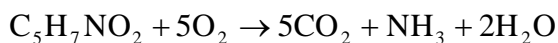
This three oxygen demand is known as the ultimate carbonaceous or first - stage BOD,

and is usually denoted as UBOD

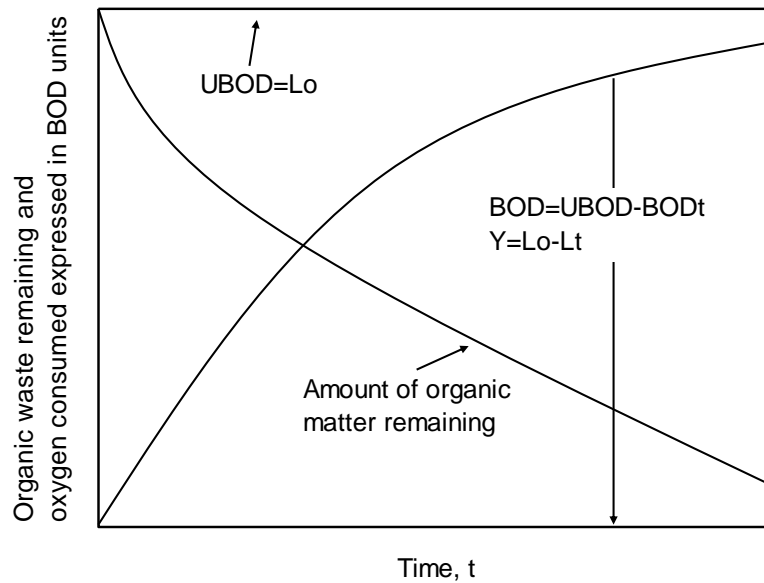有機物分解速率，Phelps $\quad \dfrac{dL}{dt} = -k_1 L$

L：有機物量或所使用氧量，mg/L

t：時間，天

k_1：耗氧係數, 天$^{-1}$

$L_t = L_0 \times e^{-k_1 t}$

$Y = L_0 - L_t = L_0(1 - 10^{-K_1 t}) = L_0(1 - e^{-k_1 t})$, $K_1(base\,10) = \dfrac{k_1(base\,e)}{2.303}$

Y：BOD，mg/L

Lo：Ultimate BOD

Time, t

當溫度介於 20~30℃ 時，$k_{1_T} = k_{1_{20}} \theta^{(T-20)}$，$\theta$ =1.056
當溫度介於 4~20℃ 時，θ =1.135
$L_{(T)} = L_o(1+0.02(T-20))$

Example 2-6. Determine the 1-day BOD and ultimate first-stage BOD for a wastewater whose 5-day 20℃ BOD is 200 mg/L. The reaction constant k (base e) = 0.23 d^{-1}. What would have been the 5-day BOD if the test had been conducted at 25℃?

(2)TOC、COD

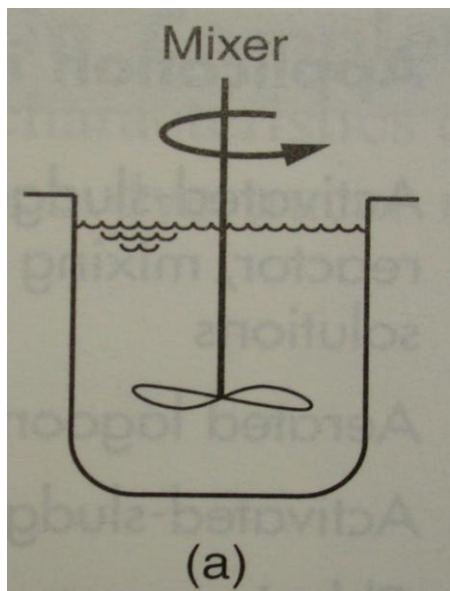Example 2-7. 求化合物 $C_5H_7NO_2$ 之理論 BOD/COD, BOD/TOC 及 TOC/COD 比值？已知 BOD 之耗氧係數為 0.23 d^{-1}(base e)。

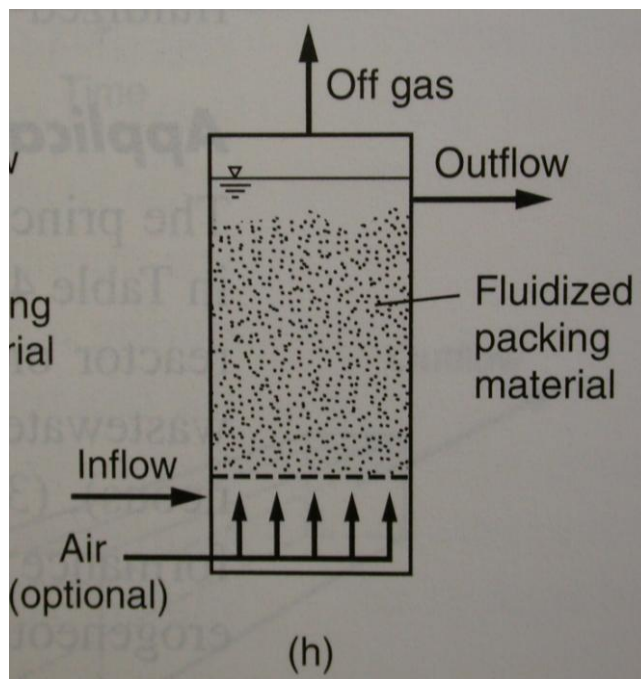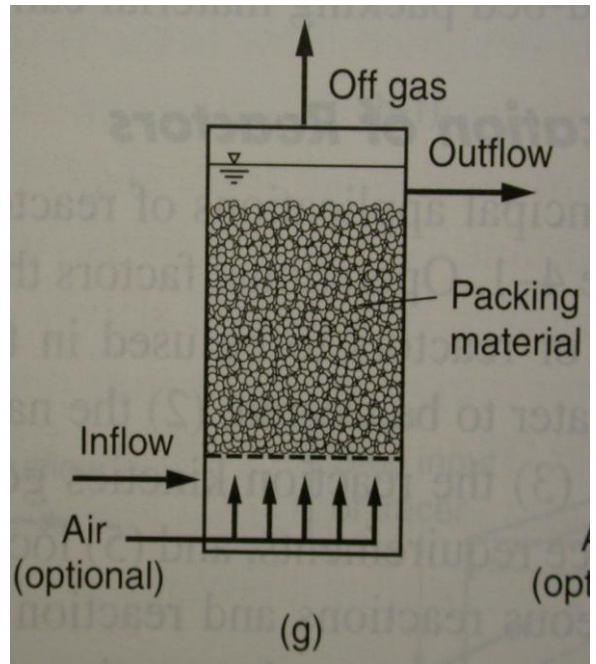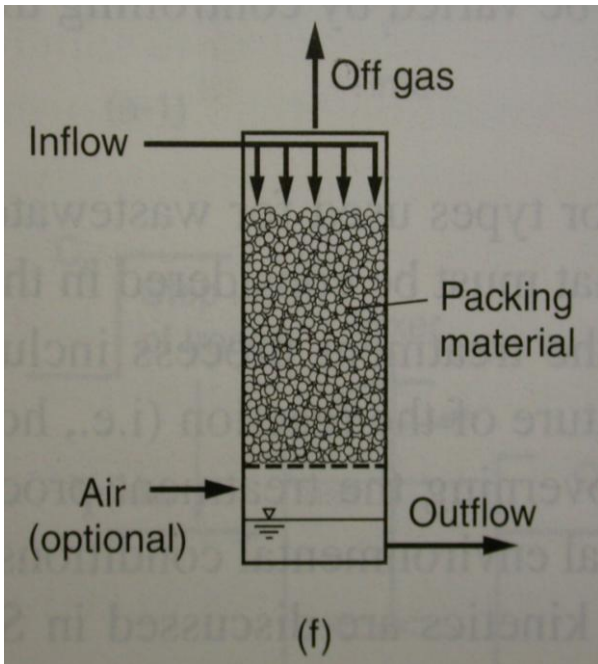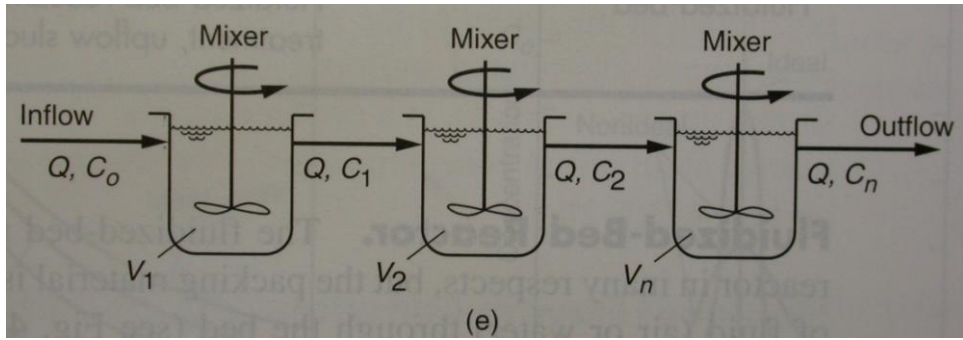# Chapter 2 Introduction to Process Analysis and Selection

前處理主要利用物理、化學及生物等方法。利用物理原理之物理操作單元包括篩除、混合、沉澱、氣體傳輸、過濾及吸附，化學單元程序則藉由化學藥劑之添加及化學反應，使用之方法包含消毒、氧化及沉降。生物單元程序，主要去除生物可分解之有機物，而這些程序皆因溫度及反應器之型式，有很大之差異。

2-1 處理之反應器(Reactor)

1. Types of reactors
(a) batch reactor (b) complete-mix reactor (c) plug-flow open reactor
(d) plug-flow closed reactor (e) complete-mix reactor in series (f) packed-bed reactor (g) packed-bed upflow reactor (h) expended-bed upflow reactor

(e)

Off gas

Inflow

Packing material

Air (optional)

Outflow

(f)

Off gas

Outflow

Packing material

Inflow

Air (optional)

(g)

Off gas

Outflow

Fluidized packing material

Inflow

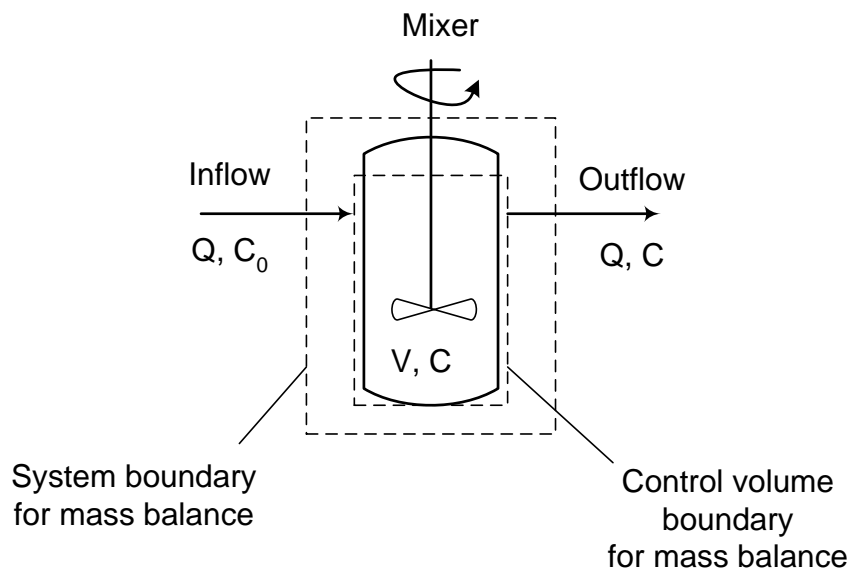Air (optional)

(h)
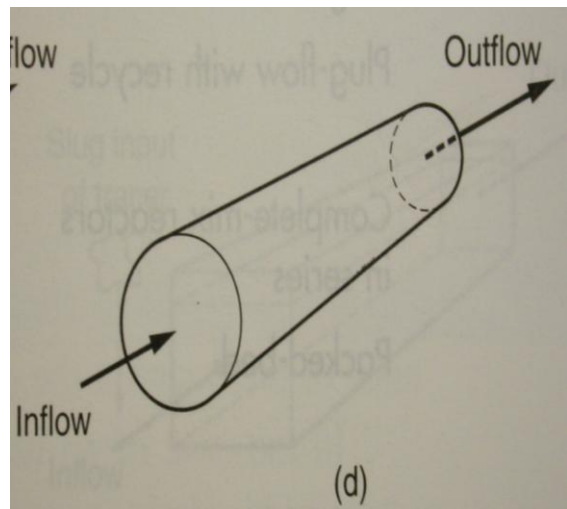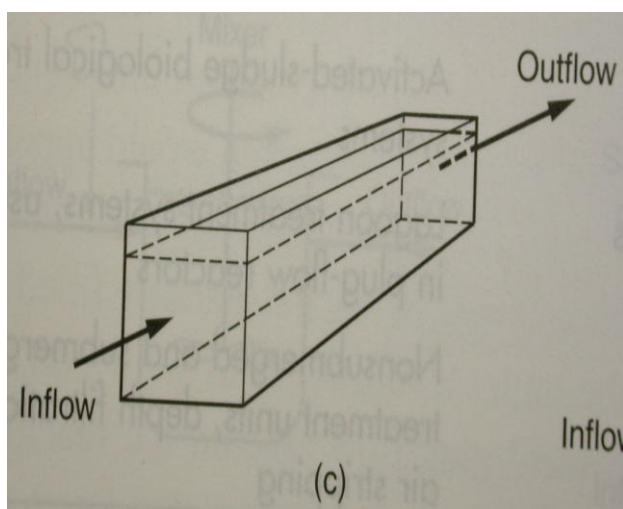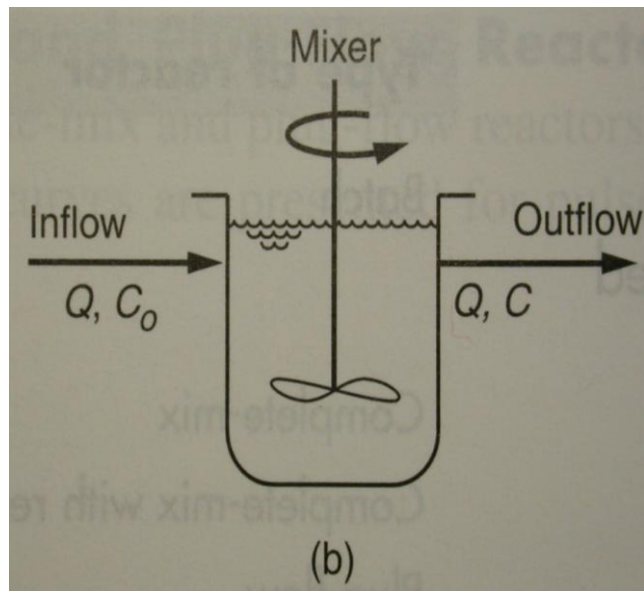
2. Application of reactor

選用反應器需考慮幾項因素，包括水質、反應型態(homogeneous or heterogeneous)、反應動力、所需效率、當地環境狀況、操作維護與建造成本。

2-2 質量平衡分析

1. The Mass-balance Principle

The mass-balance analysis is based on the principle that mass is neither created nor destroyed, but the form of the mass can be altered. (e.g., liquid to gas)

考慮如下反應槽：

Mixer

Inflow
Q, C_0

Outflow
Q, C

V, C

System boundary
for mass balance

Control volume
boundary
for mass balance

| Rate of accumulation of reactant within the system boundary | = | Rate of flow of reactant into the system boundary | - | Rate of flow of reactant of the system boundary | + | Rate of generation of reactant within the system boundary |

Simplified

Accumulation = inflow - outflow + generation

Refer to above figure

9

$$\frac{dC}{dt}V = QC_0 - QC + r_C V, \qquad \text{first - order reaction,} \quad r_C = -kC$$

$$\frac{dC}{dt}V = QC_0 - QC + (-kC)V$$

dC/dt：單位時間反應物濃度變化量，$ML^{-3}T^{-1}$

V：槽體積，L^3

Q：流量，L^3T^{-1}

C_0：反應物進流濃度，ML^{-3}

C：反應物出流濃度，ML^{-3}

r_C：一階反應，$ML^{-3}T^{-1}$

k：速率常數，T^{-1}

Steady-State (long term) Simplification，$\dfrac{dC}{dt} = 0$

$$0 = OC_0 - QC - r_C V$$

$$r_C = \frac{Q}{V}(C - C_0)$$

2-3 Reactions, Reaction rates, and Reaction rate coefficients

1. The stoichiometry of reaction refers to the definition of the quantities of chemical compounds involved in a reaction. The rate at which a substance disappears or is formed in any given stoichiometric reaction is defined as the rate of reaction.

常見兩種處理反應型態：homogeneous and heterogeneous

同相反應又有可逆和不可逆反應，例如

   Simple reactions: A → B ; A + A → C ; aA + bB → C

   Parallel reactions: A + B → C ; A + B → D
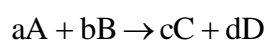
   Consecutive reactions： A + B → C ; A + C → D

   $A \leftrightarrow B$; $A + B \leftrightarrow C + D$

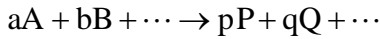異相反應：常發生於一種或多種污物，例如離子交換。系統中若有固相催化劑存在者，亦屬之，例如活性碳吸附

2. Rate of Reaction

  homogeneous：$r = \pm\dfrac{dC}{dt}$

$$aA + bB \rightarrow cC + dD$$

$$-\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

  heterogeneous：$r = \dfrac{1}{S}\dfrac{d[N]}{dt} = \dfrac{moles}{(area)(time)}$

3. Reaction Order

$$aA + bB + \cdots \rightarrow pP + qQ + \cdots$$

$$r = kC^a_A C^b_B C^c_C \cdots C^p_P = kC^n_A$$

$$n = a + b + \cdots + p \ , \ n : \text{overall reaction order}$$

4. Types of rate expressions

$r = \pm k \ (\text{zero - order}) , \text{independent of concentration of reatants}$

$r = \pm kC \ (\text{first - order}) , \text{proportioml to concentration of one of reatants}$

$r = \pm k(C - C_S) \ (\text{first - order})$

$r = \pm kC^2 \ (\text{second - order}) , \text{proportioml to the second power of a single reactant}$

$r = \pm kC_A C_B$

$r = \pm \dfrac{kC}{K + C} \ (\text{saturation or mixed - order})$

積分整理

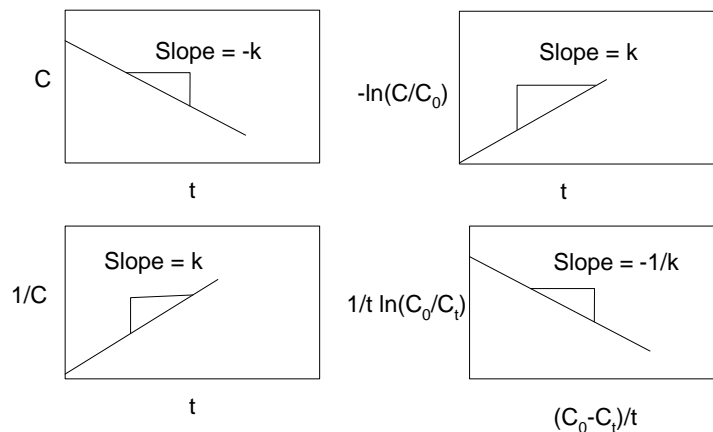$$r_C = \frac{dC}{dt} = -k \ , \ C - C_0 = -kt$$

$$r_C = \frac{dC}{dt} = -kC \ , \ \ln \frac{C}{C_0} = kt$$

$$r_C = \frac{dC}{dt} = -kC^2 \ , \ \frac{1}{C} - \frac{1}{C_0} = kt$$

$$r_C = \frac{dC}{dt} = -\frac{kC}{k + C} \ , \ kt = k \ln \frac{C_0}{C_t} + (C_0 - C_t)$$

微分法求反應階次

$$r_C = \frac{dC}{dt} = -kC^n \ , \ n = \frac{\log(-\dfrac{d[C_1]}{dt}) - \log(-\dfrac{d[C_2]}{dt})}{\log[C_1] - \log[C_2]}$$

Example 2-1. 利用批式反應器進行試驗，獲得如下結果，求此反應階次及反應速率常數。

Time, d	Concentration, [c], mole/L	Time, d	Concentration, [c], mole/L
0	250	5	18
1	70	6	16

2	42	7	13
3	30	8	12
4	23		

2-4 Modeling Treatment Process Kinetics

1. Batch reactor with reaction
已知質量平衡式：

Accumulation = inflow - outflow + generation

$$\frac{dC}{dt}V = QC_0 - QC + r_C V, \quad 因為批式反應,故流量Q=0,若反應為一階反應,則$$

$$\frac{dC}{dt}V = (-kC)V$$

$$\frac{dC}{dt} = (-kC) \Rightarrow \int_{C=C_0}^{C=C} \frac{dC}{C} = -k\int_{t=0}^{t=t} dt = kt$$

$$\frac{C}{C_0} = e^{-kt}$$

2. Complete-mix reactor with reaction

$$\frac{dC}{dt}V = QC_0 - QC + r_C V, \quad 若反應為一階反應,則 \frac{dC}{dt}V + QC - (-kC)V = QC_0$$

$$各除V,並整理為\frac{dC}{dt} + (\frac{Q}{V} + k)C = \frac{Q}{V}C_0,解此一階微分方程$$

$$C = \frac{Q}{V}\frac{C_0}{(k+Q/V)}(1 - e^{-(k+Q/V)t}) + C_0 e^{-(k+Q/V)t}$$

$$當反應為steady-state時, \frac{dC}{dt} = 0$$

$$C = \frac{C_0}{[1+k(V/Q)]} = \frac{C_0}{[1+k\tau]}$$

3. Ideal plug-flow reactor with reaction

$$\frac{C}{C_0} = e^{-k\tau} = e^{-k(V/Q)}$$

Example 2-2. A Complete-mix reactor is to be designed for a first-order reaction, and the required conversion of A is 90%. If the rate constant, k, is 0.35 hr^{-1}, what is the required residence time in hours？ How does this compare to the time for the plug-flow reactor？

2-5 Treatment Processes Involving Mass Transfer(質量傳送處理程序)

to reduce the concentration of a given component in one stream and to increase the concentration in another stream.主要驅動力為壓力或濃度梯度。

1. 質傳基本原理(Basic principle of mass transfer)

$$r = -D_m \frac{\partial C}{\partial x}$$

r : 單位面積單位時間之質傳速率, $ML^{-2}T^{-1}$

D_m : x方向之分子擴散係數, L^2T^{-1}

C : 污染物傳輸濃度, ML^{-3}

x : 距離, L

分子擴散係數 D 與 stokes-Einstein's 擴散定律有關

$$D = \frac{kT}{6\pi\eta r_P} = \frac{RT}{6\pi\eta r_P N}$$

D : 擴散係數, m^2/s

k : Boltzmann常數, 1.3805×10^{-23} J / K

T : 溫度, $K = 273.15 + {}^{\circ}C$

R : 氣體常數, 8.3145 J / mole. K

η : 動黏滯係數, $N.s / m^2$

r_P : 顆粒半徑, m

N : Avogadro's number , 6.02×10^{23} molecules / g - mole

若有一半徑 0.01 μm 之顆粒(如細菌)於 20℃，動黏滯係數為 1.002×10^{-3} N.s/m²，其質傳係數為：

$$D = \frac{8.314 \times (273.15 + 20)}{6 \times 3.14 \times (1.002 \times 10^{-3}) \times 10^{-7} \times (6.02 \times 10^{23})} = 2.143 \times 10^{-8} \text{ cm}^2/s$$
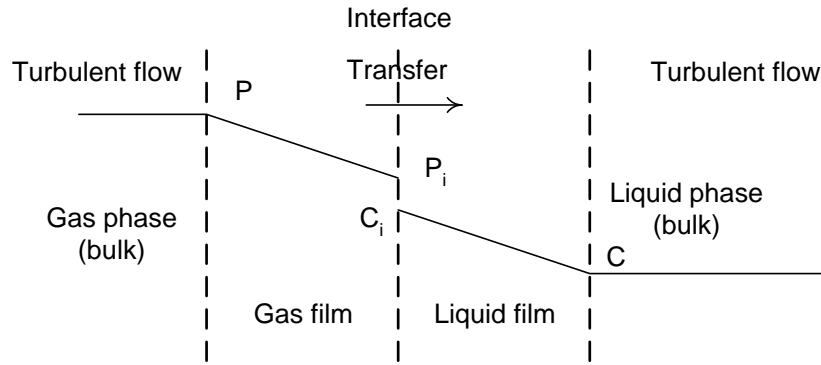
2. 氣-液質傳

雙膜理論(the two-film theory)

$$r = K_G(P_G - P_i) = K_L(C_i - C_L)$$

$r =$ 質傳速率

$K_G =$ 氣膜質傳係數

$K_L =$ 液膜質傳係數

氣液膜質傳係數依氣液介面狀況而異，膜厚度愈小，質傳程度愈大。通常氣膜厚度小於液膜厚度，亦即，$k_L << k_G$.，因此

$r = K_L(C_S - C_L)$

C_S:氣體於界面之平衡濃度

氣體隨時間溶於液相之質傳通量可表示為$r = K_L(C_S - C_t)$

而單位液體體積單位時間之質傳:

$r_v = K_L \dfrac{A}{V}(C_S - C_t) = K_L a(C_S - C_t)$，其中A為接觸面積,V為液體體積,

$K_L a$為volumetric mass transfer coefficient

求解 $K_L a$：

$r_v = \dfrac{dC}{dt} = K_L a(C_S - C_t) , \int_{C_0}^{C_t} \dfrac{dC}{(C_S - C_t)} = K_L a \int_0^t dt$

$\Rightarrow \dfrac{C_S - C_t}{C_S - C_0} = e^{-(K_L a)t}$

Example 2-3. 去氯水收集於 10 m³ 貯存桶，預備再利用。已知其溶氧為 1.5 mg/L，現擬以表面曝氣方式提高溶氧。假設氧氣 K_L 值為 0.03 m/h，貯存桶表面積 400 m²，深 3 m，水溫 20℃(飽和溶氧 9.09 mg/L)。求溶氧提高至 8.5 mg/L 所需時間。

3. 固-液質傳

　(A). adsorption、adsorbent、adsorbate

吸附劑重要特性：(1)its extremely large surface area to volume ratio (2)its preferential affinity for certain constituents in the liquid phase

污水處理常用吸附劑：Granular or powdered activated carbon (GAC or PAC)，描述吸附現象，常用 Freundlich isotherm

$$q_e = \frac{x}{m} = K_f C_e^{1/n}$$
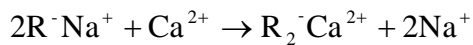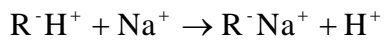
$q_e = $ 吸附容量, M/M

$K_f = $ Freundlich 常數
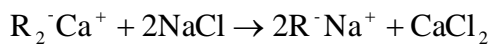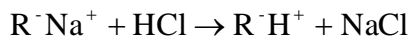
$C_e = $ 平衡時吸附質濃度, ML^{-3}

$1/n = $ Freundlich intensity parameter

Example 2-4. 處理流量 4000 m^3/d，含氯量 0.12 mg/L，今欲以 PAC 處理至 0.05 mg/L，若 Freundlich adsorption isotherm 係數分別 K_f=2.6，$1/n$=0.73，求所需 PAC 量若干 kg/d？
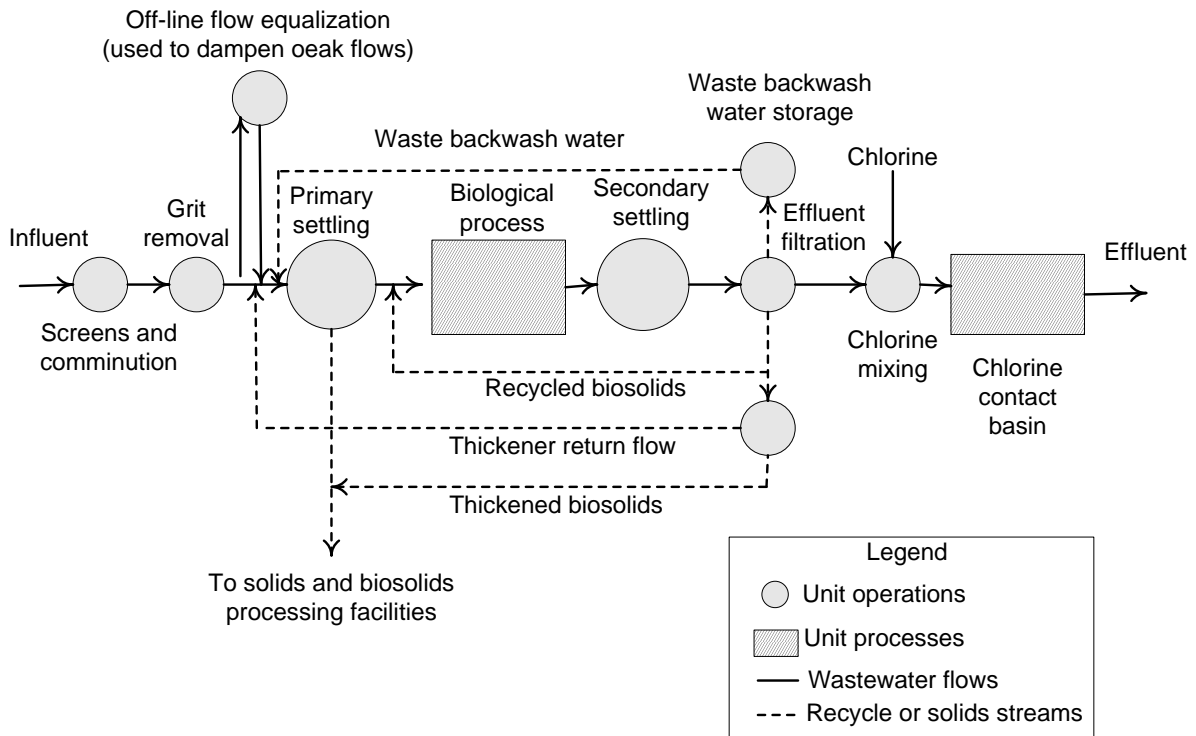
(B). Ion exchange

Reaction

$$R^-H^+ + Na^+ \rightarrow R^-Na^+ + H^+$$

$$2R^-Na^+ + Ca^{2+} \rightarrow R_2^-Ca^{2+} + 2Na^+$$

Regeneration

$$R^-Na^+ + HCl \rightarrow R^-H^+ + NaCl$$

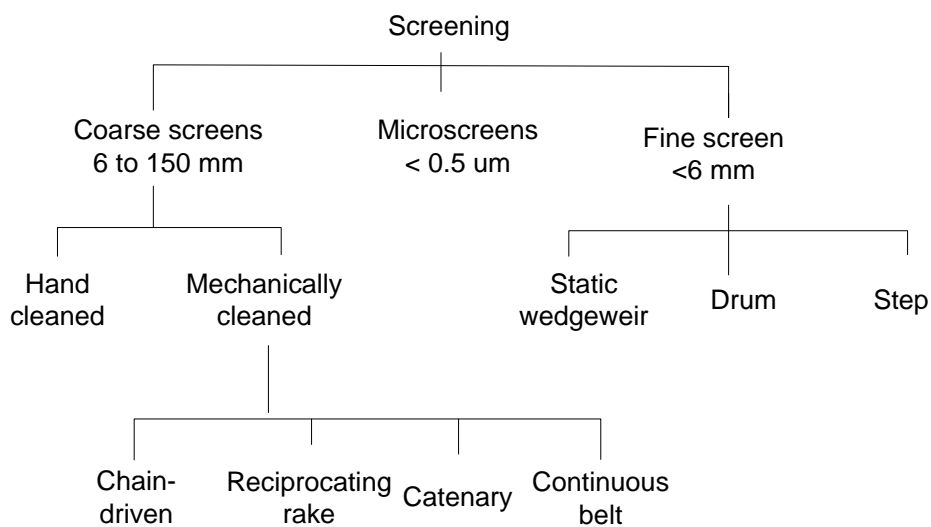$$R_2^-Ca^+ + 2NaCl \rightarrow 2R^-Na^+ + CaCl_2$$

Chapter 3 Pretreatment－Physical Unit Operation

3-1 Screening

篩除為前處理首要之操作單元，目的在於去除大型漂浮物，以保護下游之設備，提高處理程序之效率與可靠性。

Classification of Screens

3-2 Flow Equalization

Flow equalization is a method used to overcome the operational problems caused by flowrate variation, to improve the performance of the downstream processes, and to reduce the size and cost of downsteam treatment facilities.
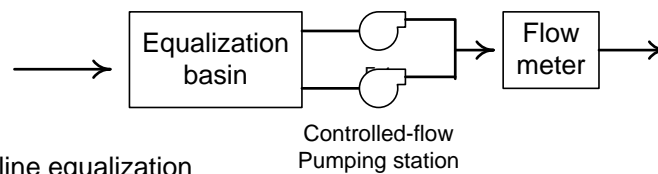
1. 調整池之優點
   (1)避免生物處理之 shock loading 或基質濃度下降，保持 pH 穩定
   (2)提高生物處理出流水水質與終沉池污泥沉降效率
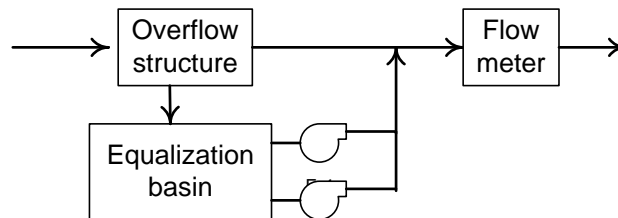   (3)增進生物處理出流水之過濾效能，使反沖洗頻率固定
   (4)提高化學藥劑添加之控制

2. 調整池之缺點
   (1)所需土地面積增加 (2)可能有臭味問題
   (3)增加操作維護費   (4)成本提高
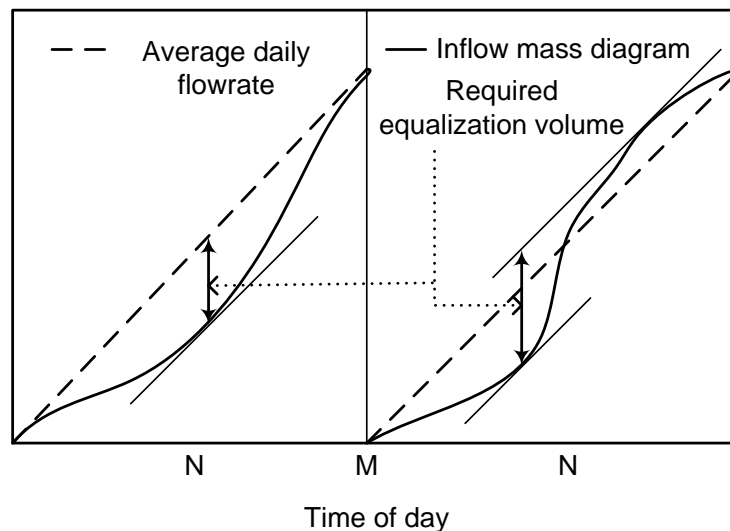
3. 方式

(a) In-line equalization

Controlled-flow
Pumping station

(b) Off-line equalization

Volume requirements for the equalization basin

Example 3-1. For the flowrate data given in the following table, determine the in-line storage volume required to equalize the flowrate.

Time period	Average flowrate during time period, m³/s	Time period	Average flowrate during time period, m³/s
M-1	0.275	N-1	0.425
1-2	0.22	1-2	0.405
2-3	0.165	2-3	0.385
3-4	0.13	3-4	0.35
4-5	0.105	4-5	0.325
5-6	0.1	5-6	0.325
6-7	0.12	6-7	0.33
7-8	0.205	7-8	0.365
8-9	0.355	8-9	0.4
9-10	0.41	9-10	0.4
10-11	0.425	10-11	0.38
11-N	0.43	11-M	0.345

5. Mixing and Air requirements

目的：

   to prevent deposition of solids

   to prevent the wastewater from becoming septic and odorous

to maintain aerobic conditions, air should be supplied at a rate of 0.01 to 0.015 m^3/m^2.min
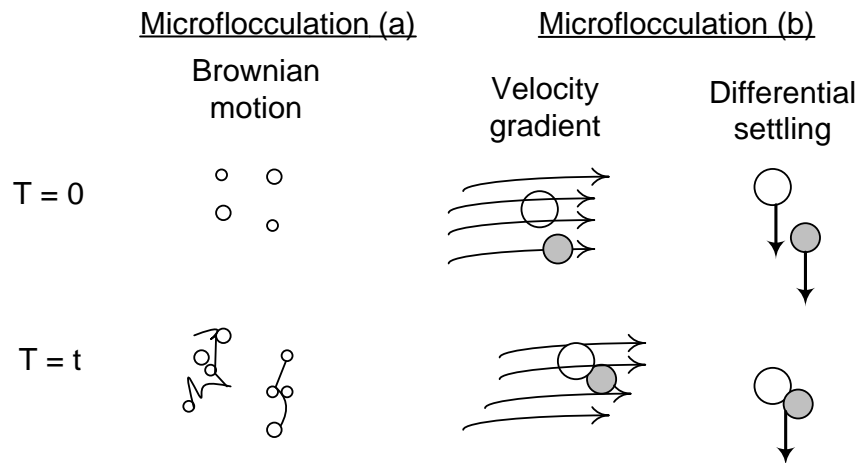
3-3 Mixing and Flocculation

前處理之混合，常應用於(1)水中物質完全混合(2)可溶性液體之混合(3)顆粒混凝(4)懸浮液連續混合(5)熱傳 等方面。大部分操作可分兩類，一為 continuous rapid mixing 方式，另一為 continuous 方式。前者主要應用於化學藥劑添加與可溶性液體混合等方面，如添加消毒劑或添加化學藥劑，增進汙泥脫水。後者則為使系統保持懸浮狀態，例如調和池、生物處理之曝氣槽等。

1. Flocculation in wastewater treatment

(1)Flocculation is a transfer step that brings about the collisions between the destabilized particles needed to form larger particles that can be removed readily by settling or filtration.

(2)主要應用：(1)增進預先處理時之 BOD 及懸浮顆粒去除(2)調理特殊水質(3)增進終沉池功能(4)作為過濾之前處理。Flocculation 分兩種形式，microflocculation 及 macroflocculation。

(3) Microflocculation (also known as perikinetic flocculation) is term used to refer to the aggregation of particles brought about by the random thermal motion of liquid molecules. Microflocculation is significant for particles that are in the size range from 0.001 to about 1 μm. Macroflocculation (also known as orthokinetic flocculation) is the term used to refer to the aggregation of particles greater than 1 or 2 μm.

	Microflocculation (a)	Microflocculation (b)	
	Brownian motion	Velocity gradient	Differential settling

2. Energy dissipation in mixing and flocculation
   1943 Camp and Stein

$$G = (\frac{P}{V\mu})^{1/2}$$

G＝average velocity gradient, T^{-1}, sec^{-1}
P＝power requirement, W (N-m/sec)
V＝flocculator volume, m^3
μ＝dynamic viscosity, N-s/m^2

上式兩邊各乘停留時間(∣=V/Q)，改寫為

$$G\tau = \frac{V}{Q}\sqrt{\frac{P}{\mu V}} = \frac{1}{Q}\sqrt{\frac{PV}{\mu}}$$

Table.

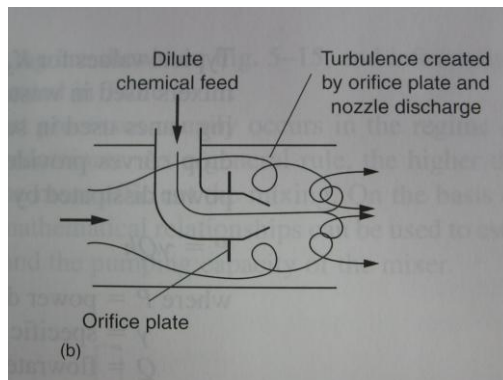| Process	Range of values	
	Detention time	G value, s^{-1}
Mixing	5 - 30 s	500 - 1500
Flocculation	30 - 60 min	50 - 100

Example 3-2. 求槽體積 2800 m^3，G 值 100/s，水溫 15(μ=1.139 × 10^{-3} N.s/m^2 時之理論所需提供之能量？
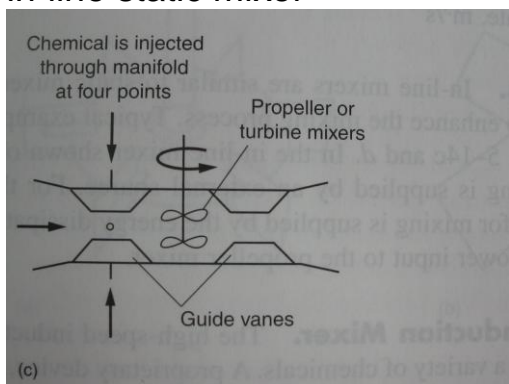
Types of Mixers used for rapid mixing in wastewater treatment
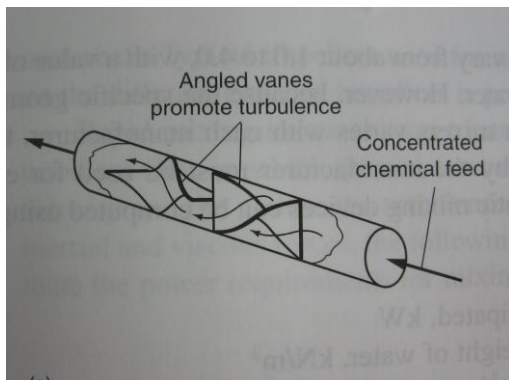
in-line static mixer

in-line static mixer with orifice

in-line mixer
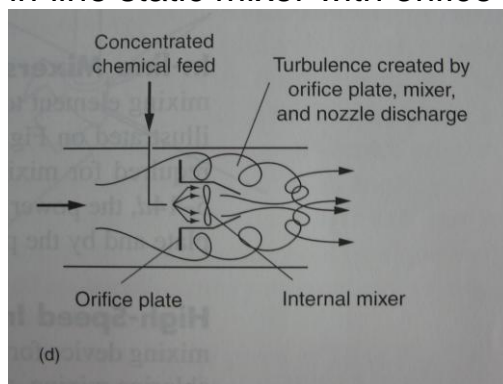
in-line static mixer with internal mixer
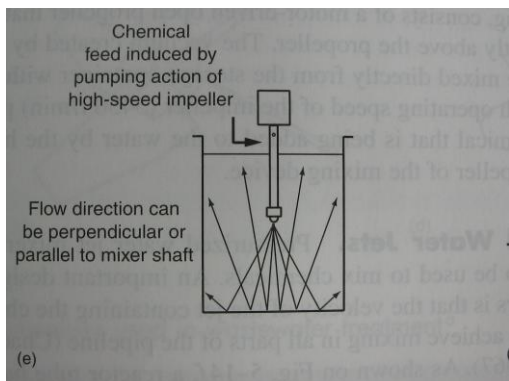
high-speed induction mixer reactor tube
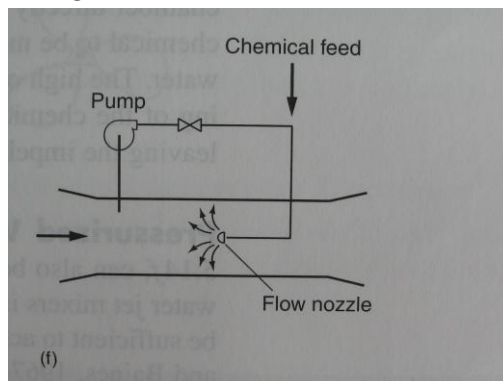
pressurized water jet mixer with
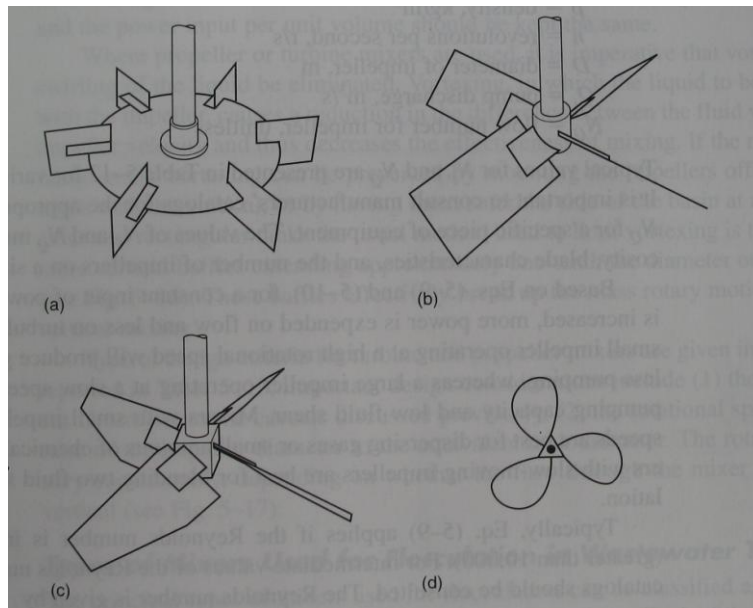
Typical impeller used for mixing in wastewater treatment facilities

3. Types of Mixers used for flocculation in wastewater treatment
(a)主要型式包括三種：static mixers, paddle mixers, turbine and propeller mixers.

Over and under baffles

Note: Spacing of over and under baffles can be varied to alter the energy input to the water

Paddle mixers are driven by variable-speed drives. A disadvantage of paddle flocculators is that the supports and bearings for the paddles are submerged

Paddles

Reduced-speed gear drive

Motor

Turbine mixer

Note: Pumping action of impeller is important with turbine mixers

Baffle

(c)

(b)Power in a mechanical paddle system can be related to the drag force on the paddles as follows.

$$F_D = \frac{C_D A \rho v_p^2}{2}$$

$$P = F_D v_p = \frac{C_D A \rho v_p^3}{2}$$
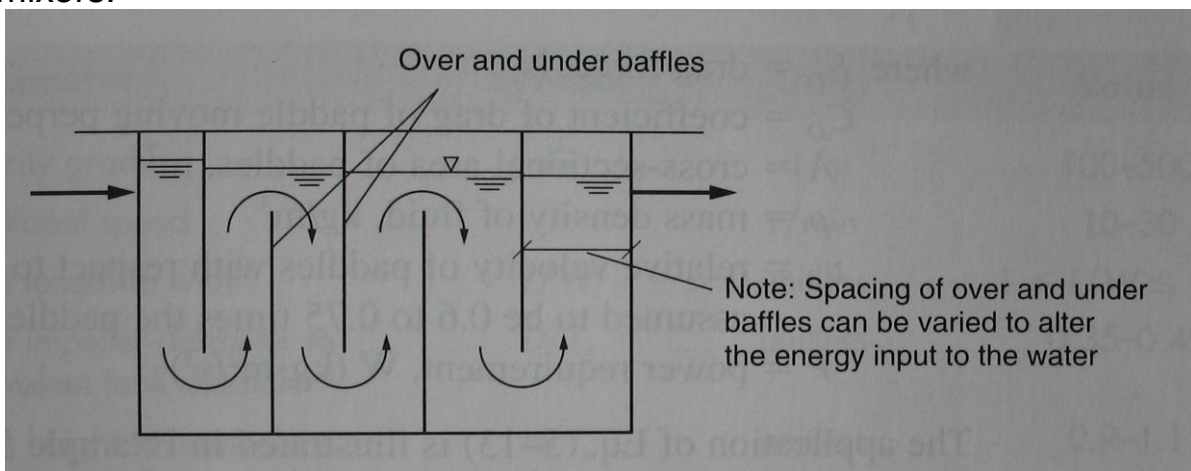
where F_D = drag force, N

C_D = coefficient of drag paddle moving perpendicular to fluid

A = cross - sectional area of paddle, m^2

ρ = mass density of fluid, kg/m^3

v_p = relative velocity of paddle with respect to the fluid, m/s, usually assumed to be 0.6 to 0.75 times the paddle - tip speed

P = power requirement, W $(kg.m^2/s^3)$

Example 3-3. Determine the theoretical power requirement and the paddle area required to achieve a G value of 50/s in a tank with a volume of 3000 m^3. Assume that the water temperature is 15℃, 0.6 m/s, and the

relative velocity of the paddle v_p is 0.75 v.

4. Types of mixers used for continuous mixing in wastewater treatment
常用於生物處理提供所需溶氧或使混合液懸浮

Pneumatic mixing

$$P_c = KQ_a \ln(\frac{h+10.33}{10.33})$$

P_c = air presure at the point of discharge, kN/m^2 K = constant;1.689

Q_a = air flow rate at atmospheric pressure, m^3/min

h = air pressure at the point of discharge expressed in meters of water, m

3-4 Gravity Separation Theory

Sedimentation is the term applied to the separation of suspended particles that are heavier than water, by gravitational settling. The terms sedimentation and settling are used interchangeably. A sedimentation basin may also be referred to as a sedimentation tank, clarifier, settling basin, or settling tank. On the basis of the concentration and the tendency of particles to interact, four types of gravitational settling can occur: (1) discrete particle, (2) flocculent, (3) hindered (also called zone), and (4) compression.

1. Particle settling theory
單顆粒沉降遵循 Newton and Stokes 沉澱理論，即考慮重力與摩擦力(或 drag)之關係。
The gravitational force:
    $F_G=(\rho_p - \rho_w)gV_p$
    Where F_G: gravitational force, MLT^{-2} (kg.m/s^2)
          ρ_p: density of particle, ML^{-3} (kg/m^3)
          ρ_w: density of water, ML^{-3} (kg/m^3)
          g: acceleration due to gravity, LT^{-2} (9.81 m/s^2)
          V_p: Volume of particle, L^3 (m^3)
The frictional drag force:

$$F_d = \frac{C_d A_p \rho_w \upsilon_p^2}{2}$$

where F_d : frictional drag force, MLT^{-2} (kg.m/s^2)

    C_d : drag coefficient (unitless)

    A_p : cross-sectional or projected area of particles in direction of flow, L^2 (m^2)

    υ_p : particle settling velocity, LT^{-1} (m/s)

Equating the gravitational force to the frictional drag force for spherical particles yields Newton's law:

$$\upsilon_{p(t)} = \sqrt{\frac{4g}{3C_d}(\frac{\rho_p - \rho_w}{\rho_w})d_p} \approx \sqrt{\frac{4g}{3C_d}(sg_p - 1)d_p}$$

where υ_p : terminal velocity of particle, LT^{-1} (m/s)

　　　d_p : diameter of particle, L (m)

　　　sg_p : specific gravity of the particle

拖曳係數(C_d)依流況而異，即為 Reynolds number 之函數。通常可分三個區域：laminar (N_R<1), transitional (N_R=1 to 2000), and turbulent (N_R>2000)

$$N_R = \frac{\upsilon_p d_p \rho_w}{\mu} = \frac{\upsilon_p d_p}{v}$$

雷諾數與拖曳係數之關係：

$$C_d = \frac{24}{N_R} + \frac{3}{\sqrt{N_R}} + 0.34$$

若為非球型顆粒，則

$$\upsilon_{p(t)} = \sqrt{\frac{4g}{3C_d\phi}(\frac{\rho_p - \rho_w}{\rho_w})d_p} \approx \sqrt{\frac{4g}{3C_d\phi}(sg_p - 1)d_p}$$

where ϕ : shape facyor

　1.0 for spheres; 2.0 for sand grains

　up to and greater than 20 for fractal floc.

當 Laminar region 時；Stokes' law

$$\upsilon_{p(t)} = \frac{g(\rho_p - \rho_w)d_p^2}{18\mu} \approx \frac{g(sg_p - 1)d_p^2}{18v}$$

μ : dynamic viscosity, MTL^2 ($N.s/m^2$)

v : kinematic viscosity, L^2T^{-1} (m^2/s)

當 Turbulent region 時

$$\upsilon_{p(t)} = \sqrt{3.33g(\frac{\rho_p - \rho_w}{\rho_w})d_p} \approx \sqrt{3.33(sg_p - 1)d_p}$$

Example 3-4. Determine the terminal settling velocity for a sand particle with an average diameter of 0.5 mm, a shape factor of 0.85, and a specific gravity of 2.65, settling in water at 20℃. At this temperature, the kinematic viscosity value is 1.003×10^{-6} m^2/s.
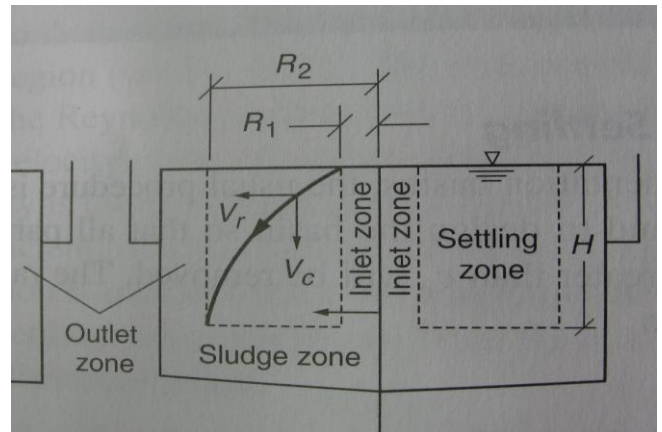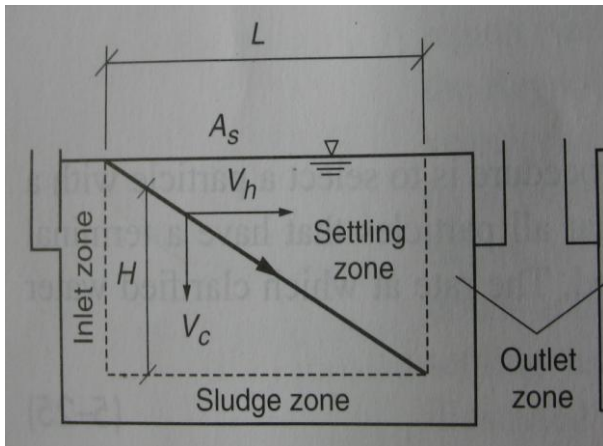
3-5 Grit removal

Removal of grit from wastewater may be accomplished in grit chambers, or by the centrifugal separation of solids. Grit chambers are designed to remove grit, consisting of sand, gravel, cinders, or other heavy solid material that have subsiding velocity or specific gravities substantially greater than those of the organic putrescible solids in wastewater. Grit chambers are provided to (1) protect moving mechanical equipment from abrasion and accompanying abnormal wear; (2) reduce formation heavy deposits in pipelines, channels, and conduits; and (3) reduce the frequency of digester cleaning caused by excessive accumulations of grit.

3-6 Primary sedimentation

沉澱處理主要目的為去除可沉降固體物及漂浮物質，以降低懸浮固體物含量。沉澱池可為矩形或圓形，並至少需保有兩池以上，以方便維修。

1.Design consideration and performance

a.停留時間(detention time)

一般初沉池停留時間為 1.5~2.5 h，若低於 0.5~1 h，將使 SS 去除率降低。另外水溫低時，因水黏滯性提高，沉降效果亦會降低，因此需提高停留時間，例如水溫 10℃時，欲達 20℃時之沉降效果，停留時間需相對提高 1.38 倍。

$$T = \frac{V}{Q} = \frac{L \times W \times H}{Q}$$

T : detention time Q : flowrate V : volume

L : length W : width H : depth

b.表面負荷率(Surface loading rates)

又稱為 overflow rate，定義為 cubic meters per square meter of suface area per day。表示單位為 $m^3/m^2.d$，一般設計值為 30~50 $m^3/m^2.d$。

c.Scour velocity

為避免沉降之顆粒再度揚起，水平流速應足夠低。

Camp (1936)

$$V_H = \left[\frac{8 k (s-1) g d}{f} \right]^{1/2}$$

V_H : horizontal velocity that will just produce scour, m/s

k : constant (0.04 ~ 0.06)

s : specific gravity of particles

g : acceleration due to gravity, 9.81 m/s^2

d : diameter of particles, m

f : Darcy - Weisbach friction factor (0.02 ~ 0.03)

d.BOD and TSS removal

初沉池對於 BOD 及 TSS 之去除效率，依停留時間及其濃度而異，其效率如下表示：

$$R = \frac{t}{a + b t}$$
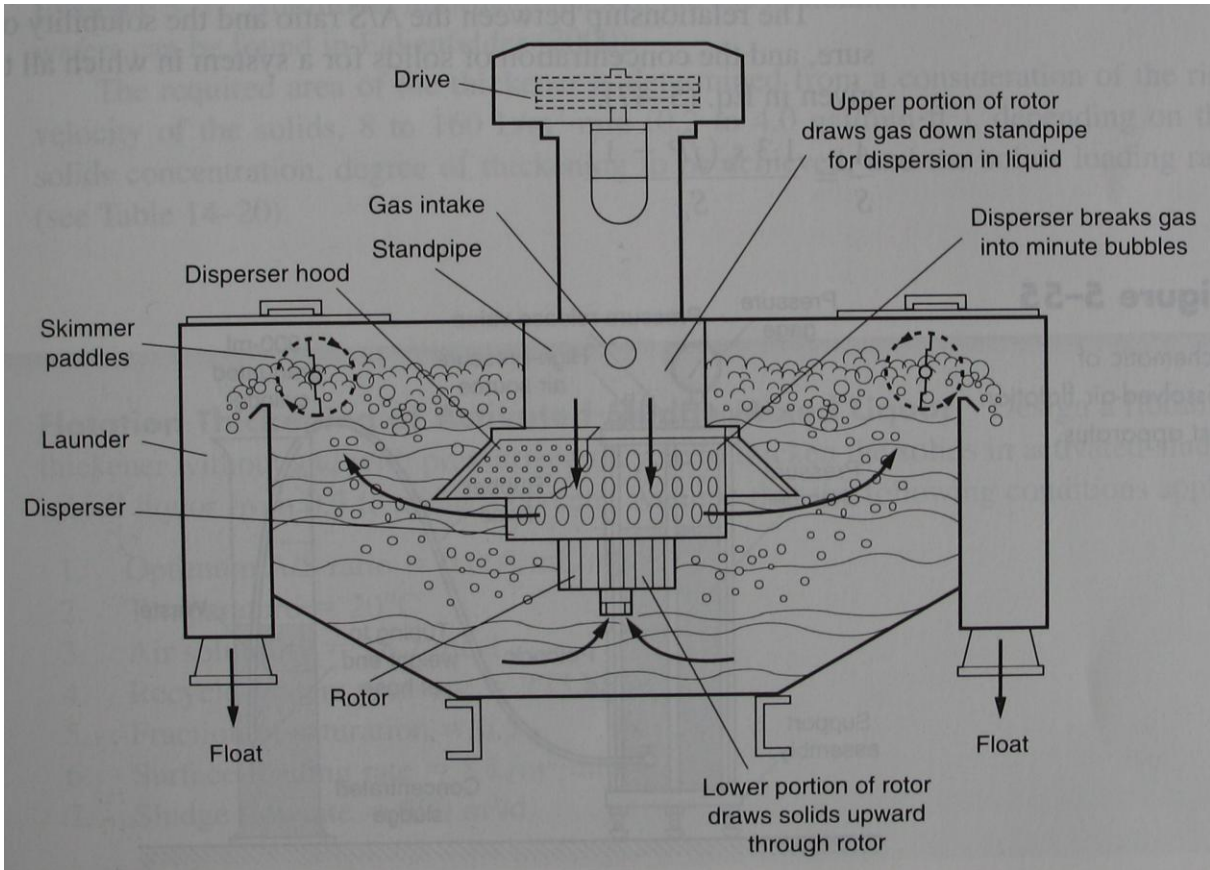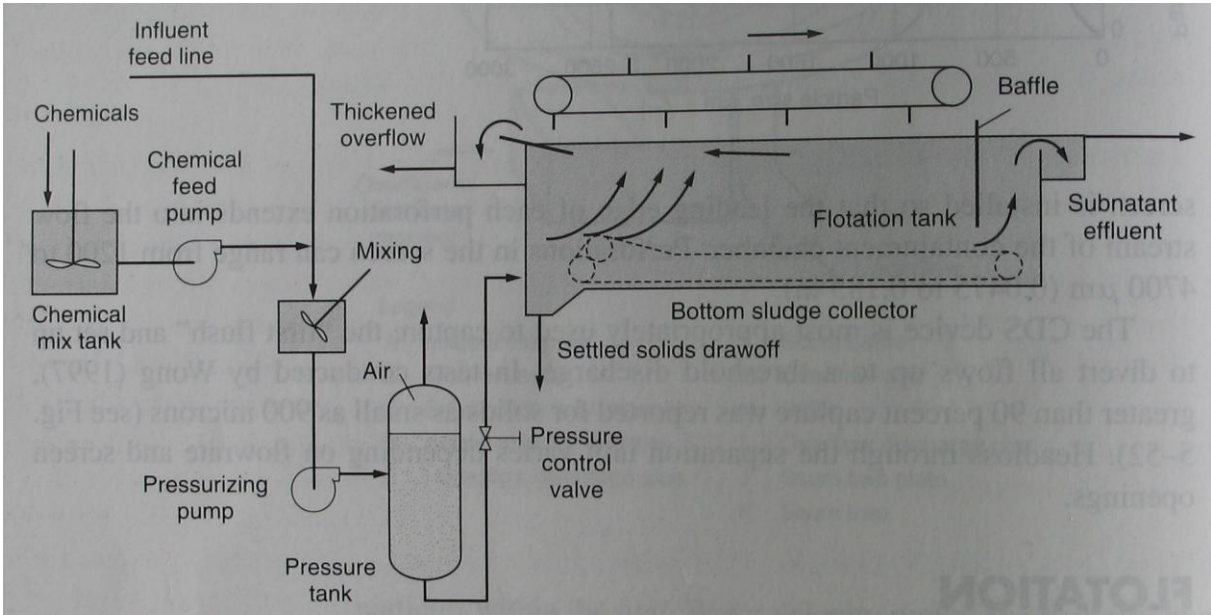
R : expected removal efficiency

t : nominal detention time T

a, b : empirical constants; For BOD, a = 0.018, b = 0.02; For TSS, a = 0.0075, b = 0.014

Example 3-5. 水處理流量 20000 CMD，尖峰流量 50000 CMD，試設計矩形沉澱池。已知表面負荷率為 40 m^3/m^2.d，池深 4 m，池寬 6 m，顆粒粒徑 100 μm。另外，求其 BOD 與 TSS 去除率，和 scour velocity。

3-7 Flotation

Flotation is a unit operation used to separate solid or liquid particles from a liquid phase. Separation is brought about by introducing fine gas (usually air) bubbles into the liquid phase. The bubbles attach to the particulate matter, and the buoyant force of the combined particle and gas bubbles is great enough to cause the particle to rise the surface. Once the particles have been floated to the surface, they can be collected by a skimming operation. 常用於懸浮物質去除和濃縮生物污泥，分兩種方式：dissolved-air flotation(DAF)、dispersed-air flotation

Influent feed line

Chemicals

Chemical feed pump

Chemical mix tank

Mixing

Thickened overflow

Air

Pressurizing pump

Pressure tank

Pressure control valve

Baffle

Flotation tank

Bottom sludge collector

Settled solids drawoff

Subnatant effluent

Drive

Upper portion of rotor draws gas down standpipe for dispersion in liquid

Gas intake

Standpipe

Disperser hood

Disperser breaks gas into minute bubbles

Skimmer paddles

Launder

Disperser

Rotor

Float

Float

Lower portion of rotor draws solids upward through rotor

Chapter 4 Pretreatment－Chemical unit processes

4-1 Role of chemical unit processes in wastewater treatment

The principal chemical unit processes used for wastewater treatment include (1)chemical coagulation, (2)chemical precipitation, (3)chemical disinfection, (4)chemical oxidation, (5)advanced oxidation processes, (6)ion exchange, and (7)chemical neutralization, scale control, and stabilization.

1. Fundamentals of chemical coagulation

Colloidal particles found in wastewater typically have a net negative surface charge. The size of colloids (about 0.01 to 1 μm) is such that the attractive forces between particles are considerably less than the repelling forces of the electrical charge. Under these stable conditions, Brownian motion (i.e., random movement) keeps the particles in suspension. Brownian motion is brought about by the constant thermal bombardment of the colloidal particles by relatively small water molecules that surround them. Coagulation is the process of destabilizing colloidal particles so that particle growth can occur as a result of particle collisions.

In general, a coagulant is the chemical that is added to destabilize the

colloidal particles in wastewater so that floc formation can result. A flocculent is a chemical, typically organic, added to enhance the flocculation process. Typical coagulants and flocculents include natural and synthetic organic polymer, metal salts such as alum or ferric sulfate, and prehydrolized metal salts such as ployaluminum chloride (PACl) and polyiron chloride (PICl)

2.混凝機制

(1)charge neutralization

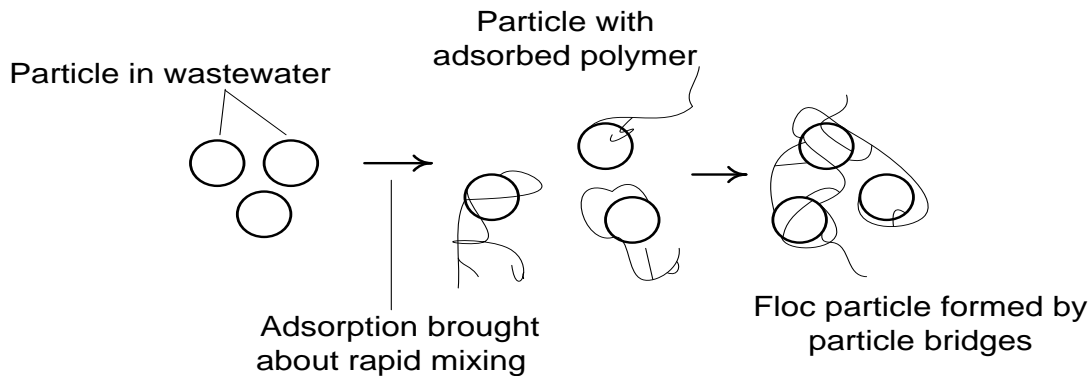陽離子型聚電解質吸附於膠體表面，可中和或降低膠體表面負電性，有效降低相斥電位。Coodination compounds
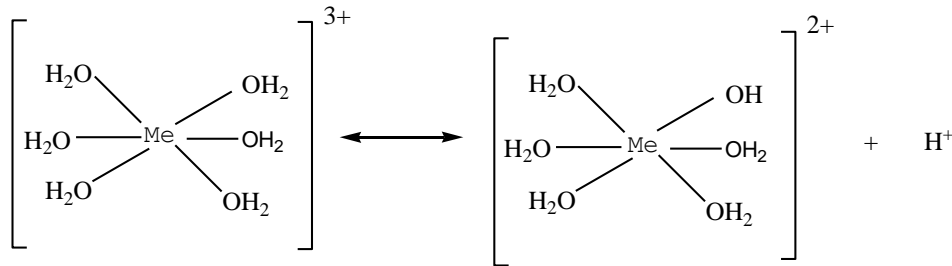
(2)polymer bridge formation

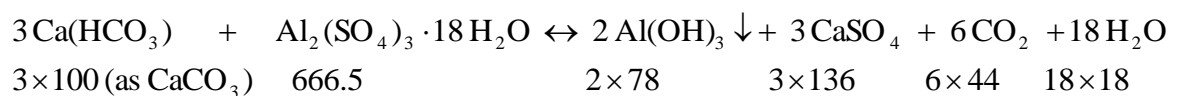polymer(通常為 anionic and nonionic)提供許多吸附位址，藉 polymer 長鏈結構形成架橋作用。

(3)charge neutralization and polymer bridge formation

陽離子型高分子聚電解質，除吸附於膠體表面外，並形成架橋現象。

Particle in wastewater

Particle with adsorbed polymer

Adsorption brought about rapid mixing

Floc particle formed by particle bridges

3. Chemical reaction in wastewater precipitation application

鋁鹽(Alum)

$$3\,Ca(HCO_3) + Al_2(SO_4)_3 \cdot 18\,H_2O \leftrightarrow 2\,Al(OH)_3 \downarrow + 3\,CaSO_4 + 6\,CO_2 + 18\,H_2O$$

$3 \times 100\,(\text{as } CaCO_3)$　666.5　　　　　　　2×78　　　3×136　　6×44　　18×18

$$1\,\text{mg/L} \left[\frac{3\,(100\,\text{g/mole})}{666.5\,\text{g/mole}} \right] = 0.45\,\text{mg/L}$$

Example 4-1. 已知汙水流量 1000 m³/d，TSS 含量 220 mg/L，鹼度 136 mg/L as CaCO₃。初沉池 TSS 去除率 60%，加入硫酸鋁(加量：40 kg/1000 m³)

後，TSS 去除率提高為 85%。求生汙泥與化學汙泥產生量各若干 kg/d？石灰(CaO)需要量若干 kg/1000 m^3？又混合汙泥比重為 1.03，含水率 94%，求混合汙泥之生成體積若干 m^3/d？

4-2 Chemical precipitation for removal of heavy metals and dissolved inorganic substances

去除水中重金屬之方式，包括化學沉降法、活性碳吸附、離子交換及逆滲透。其中以化學沉降法最常用，沉降物又以金屬之 OH^-、S^{2-}、CO_3^{2-}為主。感興趣之重金屬包括 arsenic、barium、cadmium、copper、mercury、nickel、selenium、及 zinc 等，去除原理為藉 lime 與 caustic 之添加至一最適 pH 值，使形成之金屬氫氧化物有最小溶解度，而沉降去除。

例如：

| Disinfectant	Half reaction	pK$_{sp}$
Cadmium hydroxide	$Cd(OH)_2 \rightarrow Cd^{2+} + 2OH^-$	13.93
Zinc hydroxide	$Zn(OH)_2 \rightarrow Cd^{2+} + 2OH^-$	16.7
Copper hydroxide	$Cu(OH)_2 \rightarrow Cu^{2+} + 2OH^-$	19.66
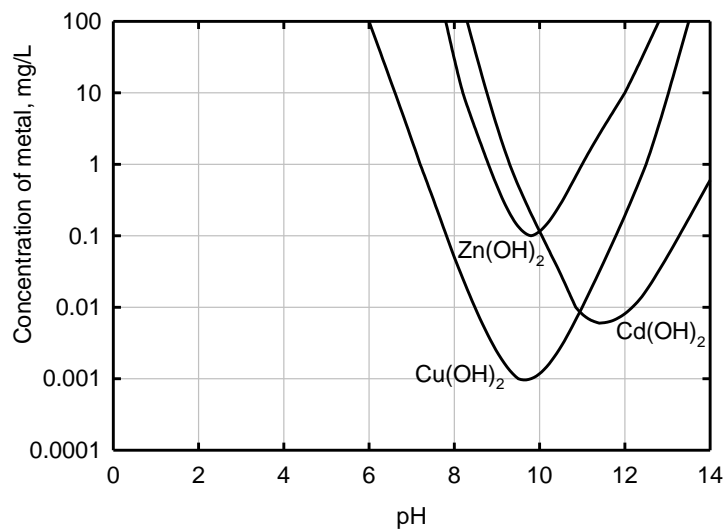
4-3 Chemical oxidation

Chemical oxidation in wastewater treatment typically involves the use of oxidizing agents such as ozone (O_3), hydrogen peroxide (H_2O_2), permanganate (MnO_4^-), chloride dioxide (ClO_2), chlorine (Cl_2) or (HOCl), and oxygen (O_2), to bring about change in the chemical composition of a compound or a group of compounds. Advanced oxidation process (AOPs) in which the free hydroxyl radical (HO^o) is used as a strong oxidant to

destroy specific organic constituents and compounds that can not be oxidized by conventional oxidants such as ozone and chlorine.
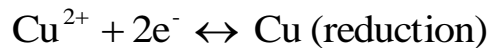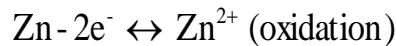
1. Fundamental of chemical oxidation

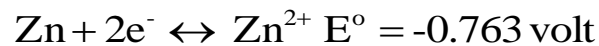(1). Oxidation-reduction reaction

又稱為 redox reaction。In oxidation-reduction reactions both electrons are changed as are the oxidation states of the constituents involved in the reaction. For example, consider the following reaction:

$$Cu^{2+} + Zn \leftrightarrow Cu + Zn^{2+}$$
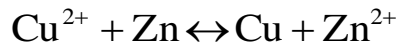
In the above reaction copper change from a +2 to zero oxidation state and the zinc changes from a zero to a +2 state, oxidation-reduction reactions can be separated into two half reaction. The two half reactions are as follows:

$$Zn - 2e^- \leftrightarrow Zn^{2+} \text{ (oxidation)}$$

$$Cu^{2+} + 2e^- \leftrightarrow Cu \text{ (reduction)}$$

(2). Half-reaction potentials

$$Zn + 2e^- \leftrightarrow Zn^{2+} \quad E^o = -0.763 \text{ volt}$$

$$Cu^{2+} + 2e^- \leftrightarrow Cu \quad E^o = 0.34 \text{ volt}$$

E^o: standard potential

(3). Reaction potentials

半反應電位可以用來預測一個反應是否進行，亦即測其總反應電位

$$E^o_{reaction} = E^o_{reduction} - E^o_{oxidation}$$

$$E^o_{reaction} = E^o_{Cu^{2+}, Cu} - E^o_{Zn^{2+}, Zn}$$
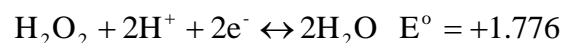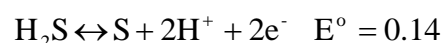
$$E^o_{reaction} = 0.34 - (-0.763) = +1.103 \text{ volts}$$

總反應電位為正值，表示反應會進行，但若為 $Cu + Zn^{2+} \leftrightarrow Cu^{2+} + Zn$，則

$$E^o_{reaction} = E^o_{Zn^{2+}, Zn} - E^o_{Cu^{2+}, Cu} = (-0.763) - 0.34 = -1.103 \text{ volts}$$

總反應電位為負值，表示反應會以逆方向進行

Example 4-2. Determine whether hydrogen sulfide (H_2S) cab be oxidized with hydrogen peroxide (H_2O_2). The pertinent half reactions are as follows

$$H_2S \leftrightarrow S + 2H^+ + 2e^- \quad E^o = 0.14$$

$$H_2O_2 + 2H^+ + 2e^- \leftrightarrow 2H_2O \quad E^o = +1.776$$

(4). Equilibrium constants for redox equations

利用 Nernst 方程式,可求得平衡常數

$$\ln K = \frac{n\,F\,E^{o}_{reduction}}{R\,T} \quad ; \quad \log K = \frac{n\,F\,E^{o}_{reduction}}{2.303\,R\,T}$$

K : equilibrium constant

n : number of electrons exchanged in the overall reaction

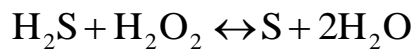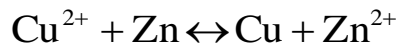F : Faraday's constant = 96485 coulomb/g. eq

R : universal gas constant = 8.3144 J/mole. k

T : temperature, K (273.15 + °C)

例如, at 25°C

$$\log K = \frac{n\,(96485)\,E^{o}_{reduction}}{(2.303)\,(8.3144)\,(273.15 + 25)} = \frac{n\,E^{o}_{reduction}}{0.0592}$$

Example 4-3. 求下列氧化還原反應之平衡常數各為何?

$$Cu^{2+} + Zn \leftrightarrow Cu + Zn^{2+}$$

$$H_2S + H_2O_2 \leftrightarrow S + 2H_2O$$

(5).應用－chemical oxidation of nonbiodegradable organic compounds

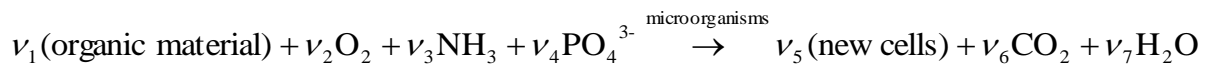| Chemical	Use	Dosage, kg/kg destroyed	
		range	typical
chlorine	BOD reduction Secondary effluent	1.0~3.0	2.0
ozone	COD reduction Secondary effluent	3.0~8.0	6.0

Chapter 5 Fundamentals of biological treatment

5-1 Overview of biological wastewater treatment

1. Objectives of biological treatment
生物處理之目的包括(1)transform (i.e., oxidize) dissolved and particulate biodegradable constituents into acceptable end products, (2)capture and incorporate suspend and nonsettleable colloidal solids into a biological floc or biofilm, (3)transform or remove nutrients, such as nitrogen and phosphorous, and (4)in some cases, remove specific trace organic constituents and compounds.

2. Role of microorganisms in wastewater treatment
生物處理藉各種微生物作用,去除溶解性及粒狀含碳 BOD,並使有機物穩定化。微生物中以細菌扮演主要角色。微生物以 O_2、NH_3、PO_4^{3-} 為營養鹽,進行氧化程序,將有機物轉化為簡單終產物。其中 new cells 代表氧化程序產生之 biomass。

$$\nu_1(\text{organic material}) + \nu_2 O_2 + \nu_3 NH_3 + \nu_4 PO_4^{3-} \xrightarrow{\text{microorganisms}} \nu_5(\text{new cells}) + \nu_6 CO_2 + \nu_7 H_2O$$

3. Some useful definitions

Term	Definition
Metabolic function	
Aerobic (oxic) processes	Biological treatment processes that occur in the presence of oxygen.
Anaerobic processes (厭氧接觸法、厭氧消化、厭氧流體化床、upflow anaerobic sludge blanket)	Biological treatment processes that occur in the absence of oxygen
Anoxic processes	硝酸鹽氮於缺氧狀態下生物轉化為氮氣之程序，This process is also known as denitrification。
Facultative processes	Biological treatment processes in which the organisms can function in the presence or absence of molecular oxygen.
Combined aerobic/anoxic/anerobic processes	好氧、厭氧及兼氣等程序組合一起，以完成特定處理目的。
Treatment processes	
Suspended-growth processes (activated-sludge process, 1913 developed)	微生物將有機物或其他物質轉化成氣體或細胞組織，係以懸浮狀態為主。
Attached-growth processes (Trickling filters; Rotating biological contactors; packed-bed reactors)	微生物將有機物或其他物質轉化成氣體或細胞組織，係以附著在擔體(medium)狀態為主，如濾石、塑膠板等。此程序又稱為 fixed-film processes。
Treatment functions	
Biological nutrient removal	去除氮、磷脂生物處理程序
Nitrification	The two-step biological process by which ammonia is first to nitrite and then to nitrate.
Denification	將 nitrate 還原成氮或其他氣體終產物之生物處理程序。
substrate	生物處理過程,微生物可轉化之營養鹽或有機物

Mixed lipuor suspended solid (MLSS)
Mixed lipuor volatile suspended solid (MLVSS)

5-2 Composition of microorganisms

1. 生物處理利用之微生物，係由 mixed communities 組合而成，其中包含多種之微生物，包括 bacteria、protozoa、fungi、rotifers, and possibly algae。有時，可能僅某些特定微生物便能完成處理程序。微生物依特性可分為原核生物(prokaryotes)與真核生物(Eukaryotes)，除細菌與藍綠藻之外屬原核生物，其餘微生物皆屬真核生物。原核生物約含 80%水分與 20%乾物，乾物重中 90%為有機物，10%為無機物。常用經驗化學式為 $C_5H_7O_2N$ (Hoover and Porges, 1952)，如果考慮磷元素，也可使用 $C_{60}H_{87}O_{23}N_{12}P$。

2. Environmental Factors
影響微生物生長與生存之重要因子為溫度與 pH。除少數微生物之外，大部分符合下列所示。

Type	Temperature (℃) & pH range	Optimum (℃)& pH range
Psychrophilic	10~30	12~18
Mesophilic	20~50	25~40
Thermophilic	35~75	55~65
pH	4.0~9.0	6.5~7.5

5-3 Introduction to microbial metabolism

1. 為持續繁殖，微生物需有能源、碳源與無機元素作為合成新細胞之用，其中之無機元素如 nitrogen、phosphorous、sulfur、potassium、calcium、and magnesium 等。碳源可從有機碳或 CO_2 獲得。Organisms that use organic carbon for the formation of new biomass are called *heterotrophs*, while organisms that derive cell carbon from carbon dioxide are called *autotrophs*. 碳源獲取碳源須進行還原程序，需消耗能量，自營性微生物比異營性微生物消耗更多能量，因此其生長速率與細胞產率較低。

2. 微生物進行細胞合成所需能量，可從光反應或化學氧化反應獲得。能從光反應獲取能量之微生物稱為 *phototrophs*，能從化學氧化反應獲取能量之微生物稱為 *chemotrophs*。*Phototrophs* 可為異營性，如 sulfur-reducing bacteria，亦可為自營性，如 algae and photosynthetic bacteria，同樣 *chemotrophs*，可分異營性(protozoa、fungi, and most bacteria)及自營性 (nitrifying bacteria)。亦即，*Chemoautotrophs* obtain energy from the oxidation of reduced inorganic compounds, such as ammonia, nitrite,

ferrous iron, and sulfide. *Chemoheterotrophs* usually derive their energy from the oxidation of organic compounds.
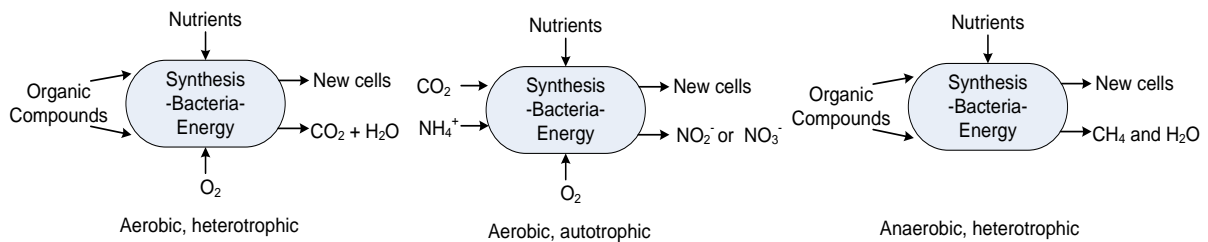
3. 微生物獲取能量，藉氧化還原反應間之電子傳遞完成，亦即須具備 electron donor 與 electron acceptor 間之反應，電子接受者可能是細胞外之分子氧或內呼吸作用 (endogenous)之細胞。Organism that generate energy by enzymy-mediated electron transport to an external electron acceptor are said to have a respiratory metabolism. The use of an internal electron acceptor is termed fermentative metabolism and is less efficient energy-yielding process than respiration.進行發酵作用之異營性微生物，比進行呼吸作用之異營性微生物，有較低生長速率與細胞產率。

4. 細菌依碳源、終產物、接受/釋出電子之分類

Type of bacteria	Common reaction name	Carbon source	Electron donor (substrate oxidized)	Electron acceptor	products
Aerobic heterotrophic	Aerobic oxidation	Organic compounds	Organic compounds	O_2	CO_2、H_2O
Aerobic autotrophic	Nitrification	CO_2	NH_3^-、NO_2^-	O_2	NO_2^-、NO_3^-
	Iron oxidation	CO_2	$Fe(\text{II})$	O_2	$Fe(\text{III})$
	Sufur oxidation	CO_2	H_2S、S^o、$S_2O_3^{2-}$	O_2	SO_4^{2-}
Facultative heterotrophic	Denitrification Anoxic reaction	Organic compounds	Organic compounds	NO_2^-、NO_3^-	N_2、CO_2、H_2O
Anaerobic heterotrophic	Acid fermentation	Organic compounds	Organic compounds	Organic compounds	Volatile fatty acids (VFAs)
	Iron reduction	Organic compounds	Organic compounds	$Fe(\text{III})$	$Fe(\text{III})$、CO_2、H_2O

| Sulfate reduction | Organic compounds | Organic compounds | SO_4^{2-} | H_2S、CO_2、H_2O |
| Methanogenesis | Organic compounds | Volatile fatty acids (VFAs) | CO_2 | Methane |

5-4 Microbial growth kinetics

1. 生物處理效率因基質利用率及微生物生長狀態而異，基質泛指生物可降解之 COD(biodegradable COD; bCOD)或 UBOD，其可能為溶解性、膠體及顆粒狀有機、無機物質。微生物以二分裂法(Binary fission)無性生殖方式，進行繁殖。The time required for each division, which is termed the generation time, can vary from days to less than 20 min.在批式反應槽中，細菌之生長方式，如下圖說明：

(A) The lag phase. Upon addition of the biomass, the lag phase represents the time required for the organisms to acclimate to their new environment before significant cell division and biomass production occur. During the lag phase enzyme induction may be occurring and/or the cells may be acclimating to change in salinity, pH, or temperature.

(B) The exponential-growth phase. During the exponential-growth phase, bacterial cells are multiplying at their maximum rate, as there is no limitation due to substrate or nutrients. The biomass growth curve increases exponentially during this period.

(C) The stationary phase. 此階段，生物質量濃度隨時間保持穩定，細菌不再以對數方式生長，部分細菌死亡，降低生物質量濃度。
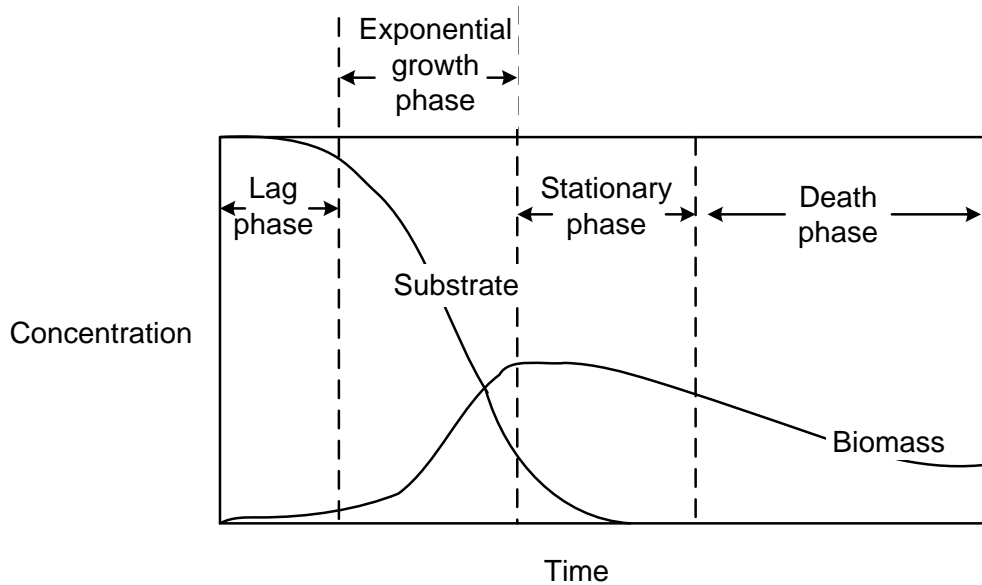
(D) The death phase. 基質消耗殆盡，細菌大量死亡。

Figure. Batch process biomass growth phases with changes In substrate and biomass versus time

2. Rate of utilization of soluble substrates

$$r_{su} = -\frac{k\,X\,S}{K_s + S}$$

r_{su} : rate of substrate concentration change due to utilization, $g/m^3 \cdot d$

k : maximum specific substrate utilization rate, g substrate/g microorganisms.d

X : biomass (microorganism) concentration, g/m^3

S : growth - limiting substate concentration in solution, g/m^3

K_s : half - velocity constant,

    substrate concentration at one - half the maximum specific substrate utilization, g/m^3

3. Biomass yield:

定義為 the ratio of the amount of biomass produced to the amount of substrate consumed. 例如，好氧異營反應，biomass yield 表示為 g biomass/g organic substrate, 好氧自營硝化反應，biomass yield 可表示為 g biomass/g NH_4-N oxidized, 揮發性脂肪酸(volatile fatty acids, VFAs)厭氧降解反應，biomass yield 表示為 g biomass/g VFAs used.不管好氧或厭氧生物處理，由於有機物種類多，因此一般 biomass yield 通常表示為 g biomass/g BOD removed 或 g biomass/g COD removed。

$$\text{Biomass yield } Y = \frac{\text{g biomass produced}}{\text{g substrate utilized (i.e., consumed)}}$$

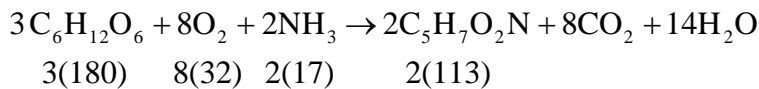$$\mu_m = kY, \quad k = \frac{\mu_m}{Y}$$

$$r_{su} = -\frac{\mu_m X S}{Y(K_s + S)}$$

4. Measuring biomass growth

由於 biomass 大部分為有機物質，因此可利用揮發性懸浮固體物(VSS)、particulate COD (total COD minus soluble COD)，或蛋白質、DNA、ATP 等來表示其濃度，有時也可利用濁度表示，其中以 VSS 最常被使用。

5. Estimating biomass yield and oxygen requirements from stoichiometry
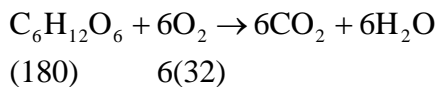
以 glucose ($C_6H_{12}O_6$)為例作為說明，而細胞之化學式以 $C_5H_7O_2N$ 為代表：

忽略營養鹽之影響，glucose 合成為細胞之反應式為：

$$3C_6H_{12}O_6 + 8O_2 + 2NH_3 \rightarrow 2C_5H_7O_2N + 8CO_2 + 14H_2O$$

$$\quad 3(180) \quad 8(32) \quad 2(17) \qquad 2(113)$$

理論上單位1 g glucose 可合成0.42 g細胞

$$Y = \frac{\Delta(C_5H_7O_2N)}{\Delta(C_6H_{12}O_6)} = \frac{2(113 \text{ g/mole})}{3(180 \text{ g/mole})} = 0.42 \text{ g cells/g glucose used}$$

但因為 glucose 可用 COD 表示：

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

$$(180) \qquad 6(32)$$

$$COD = \frac{\Delta(O_2)}{\Delta(C_6H_{12}O_6)} = \frac{6(32 \text{ g/mole})}{(180 \text{ g/mole})} = 1.07 \text{ g } O_2/\text{g glucose}$$
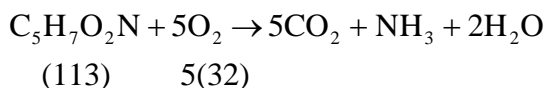
因此，

$$Y = \frac{0.42 \text{ g cells}}{\text{g glucose}} \times \frac{\text{g glucose}}{1.07 \text{ g COD}} = 0.39 \text{ g cells/g COD used}$$

另外，所需氧量為：

$$\frac{\text{Oxygen consumed}}{\text{Glucose as COD}} = \frac{8(32 \text{ g } O_2/\text{mole})}{3(180 \text{ g/ mole})(1.07 \text{ g COD/g glucose})} = 0.44 \text{ g } O_2/\text{g COD used}$$

而 biomass 相當之 COD 量為：

$$C_5H_7O_2N + 5O_2 \rightarrow 5CO_2 + NH_3 + 2H_2O$$

$$\quad (113) \qquad 5(32)$$

$$COD = \frac{\Delta(O_2)}{\Delta(C_5H_7O_2N)} = \frac{5(32 \text{ g/mole})}{(113 \text{ g/mole})} = 1.42 \text{ } O_2/\text{g cells}$$
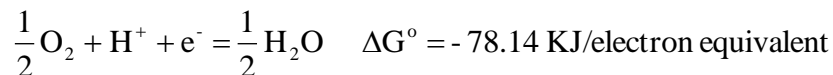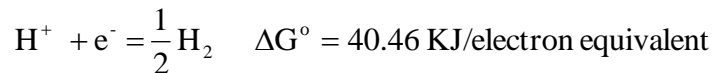
6. Estimating biomass yield from bioenergetics

大部分生物質量產率(biomass yield)皆由實驗室、模型廠或實廠系統求得。但另有一種依據熱力學原理之 bioenergetics 方法，同樣可求得 biomass yield。

化學反應有關能量之變化，可用熱力學加以描述，亦即能量變化，表示為 Gibbs free energy，ΔG^o (標準狀態下，pH=7.0，25℃)。ΔG^o 有正、負值，

$\triangle G^o$ 之計算可利用反應物與生成物半反應之標準自由能求得，半反應係指轉移 1 mole 電子之氧化-還原及合成反應。若反應結果，致使$\triangle G^o$為負值，代表 release energy，係為 exergonic reaction，若為正值，則為 endergonic reaction，表示不會自發反應(will not occur spontaneously)，亦即需要能量，才能使反應進行。

Example 5-1. Determine the free energy resulting from the oxidation of hydrogen by molecular oxygen. 已知半反應及其$\triangle G^o$如下：

$$H^+ + e^- = \frac{1}{2}H_2 \quad \triangle G^o = 40.46 \text{ KJ/electron equivalent}$$

$$\frac{1}{2}O_2 + H^+ + e^- = \frac{1}{2}H_2O \quad \triangle G^o = -78.14 \text{ KJ/electron equivalent}$$

微生物藉由酵素催化放熱反應，以獲取有效能量。約有 40~80%能量被利用，其餘則轉換熱能。例如好氧消化反應，由於生物好氧作用及釋出能量，可使系統溫度由 20℃上升至 60℃。

7. Rate of biomass with soluble substrates

微生物生長速率隨基質利用率而增加，但微生物衰減速率(decay)亦與存在之微生物成正比例。亦即：

$$r_g = -Yr_{su} - k_dX = Y\frac{kXS}{K_s + S} - k_dX$$

r_g : net biomass production, $gVSS/m^3.d$

Y : synthesis yield coefficient, $gVSS/g\ bCOD$

k_d : endogenous decay coefficient, $g\ VSS/g\ VSS.d$

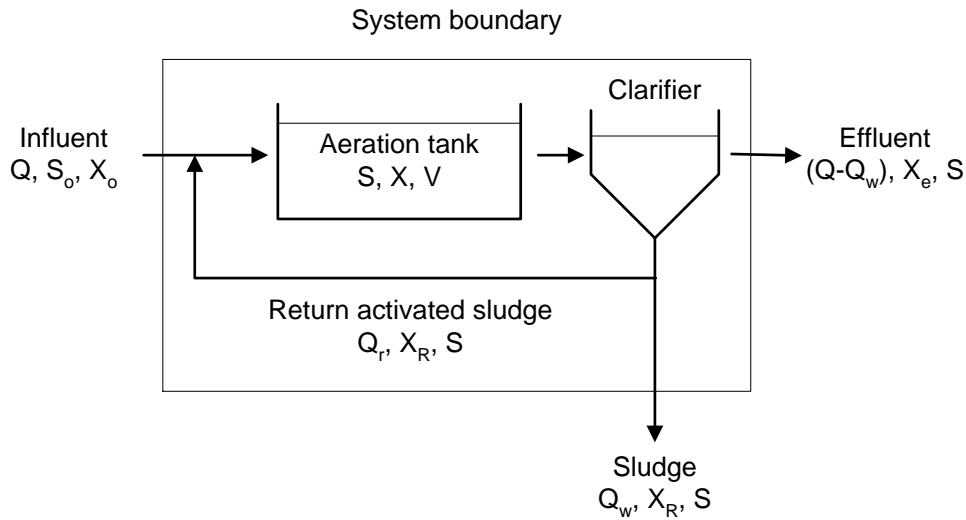式子兩邊各除X，則

$$\mu = \frac{r_g}{X} = Y\frac{kS}{K_s + S} - k_d$$

μ : specific biomass growth rate, $g\ VSS/g\ VSS.d$

Example 7-2. 已知進流水之 bCOD 為 300 g/m^3，VSS 為 50 g/m^3，進流水流量 1000 m^3/d，而反應槽之微生物濃度 2000 g/m^3，槽體積 105 m^3，槽中 bCOD 為 15 g/m^3。若基值利用率為 5 d^{-1}，微生物衰減係數 0.1 d^{-1}，半飽和常數 40 g/m^3，微生物產率 0.4 d^{-1}。求淨生物質量產率(r_g)若干？

5-5 Modeling suspended growth treatment processes

本節主要在於建立生物質量與基質平衡模式，以預測出流水基質濃度、生物質量濃度、污泥產量及所需氧量。

1. Biomass mass balance

Accumulation = inflow - outflow + generation

$$\frac{d\,X}{d\,t}\,V = QX_o - \left[(Q-Q_w)X_e - Q_wX_R\right] + r_gV$$

$\dfrac{d\,X}{d\,t}$: 反應槽生物質量變化速率, $gVSS/m^3.d$

V : 反應槽體積, m^3

Q : 進流水流量, m^3/d

X_o : 進流水生物質量, $gVSS/m^3$

Q_w : 廢棄污泥流量, m^3/d

X_e : 出流水生物質量, $gVSS/m^3$

X_R : 回流生物質量濃度, $gVSS/m^3$

r_g : 淨生物質量產率, $gVSS/m^3.d$

若進流水生物質量濃度低至可以忽略且系統為 steady state(dX/dt=0), 則

$$(Q - Q_w)X_e + Q_wX_R = r_gV \qquad 而已知\ r_g = -Yr_{su} - k_dX$$

$$\frac{(Q - Q_w)X_e + Q_wX_R}{V\,X} = -Y\frac{r_{su}}{X} - k_d$$

定義：solids retention time (SRT)

$$SRT = \frac{V\,X}{(Q - Q_w)X_e + Q_WX_R}$$

因此,

$$\frac{1}{SRT} = -Y\frac{r_{su}}{X} - k_d \text{ , 而其中}(-\frac{r_{su}}{X})\text{又稱為 specific substrate utilization rate , U.}$$

亦即

$$U = \frac{r_{su}}{X} = \frac{Q(S_o - S)}{VX}$$

Q : 水流量, m^3/d

S_o : 進流水基質濃度, $gBOD/m^3$

S : 出流水基質濃度, $gBOD/m^3$

另外，

$$\frac{1}{SRT} = \mu \text{ , 而 } \mu = Y\frac{kS}{K_s + S} - k_d$$

$$\frac{1}{SRT} = \frac{YkS}{K_s + S} - k_d \text{ , 則}$$

$$S = \frac{K_s\left[1 + (k_d)SRT\right]}{SRT(Yk - k_d) - 1}$$

2. Substrate mass balance

Accumulation = inflow - outflow + generation

$$\frac{dS}{dt}V = QS_o - QS + r_{su}V$$

steady-state $dS/dt = 0$

$$S_o - S = (\frac{V}{Q})(\frac{kXS}{k_s + S}) \quad \tau = \frac{V}{Q}$$

$$X = (\frac{SRT}{\tau})\left[\frac{Y(S_o - S)}{1 + (k_d)SRT}\right]$$

3. Design and operating parameters
(1) Food to microorganism ratio

$$\frac{F}{M} = \frac{\text{total applied substrate rate}}{\text{total microbial biomass}} = \frac{QS_o}{VX} = \frac{S_o}{\tau X}$$

(2) Specific substrate utilization rate

$$\frac{1}{SRT} = Y(\frac{F}{M})\frac{E}{100} - k_d \qquad E : \text{BOD removal efficiency , } E,\% = \frac{S_o - S}{S_o} \times 100$$

(3) Organic volumetric loading rate

$$L_{org} = \frac{Q S_o}{V \times 1000 \, g/kg}$$

L_{org} : 體積負荷, $kgBOD/m^3.d$

S_o : 進流水BOD濃度, g/m^3

(5) 需氧量

R=a`Y+b`Z

R:攝氧率；kg/d

a`:去除 1kg BOD 所需氧量轉換係數, $kgO_2/kgBOD$，(0.35~0.65)

b`:內呼吸所需氧量轉換係數, $kgO_2/kgMLSS.d$，(0.05~0.24)

Y:BOD 去除量=Q×(BOD 進流－BOD 出流)×10^{-3}；kgBOD/d

Z:曝氣槽微生物量=MLSS×V×10^{-3}, kg

Q:水量；CMD、V: 曝氣槽体積, m^3

(6) 污泥量

X=(Q×SS 進流×SS 去除率×10^{-3})＋(a×BOD 進流xBOD 去除率xQ×10^{-3})
－(b×MLSS×V×10-3)

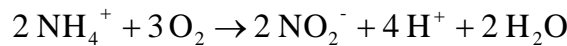X:總剩餘污泥量；kg/d

a:去除 BOD 之污泥轉換率(0.5~0.8)

b:体內自行氧化率(0.01~0.1 day^{-1})

5-6 Biological nitrification

1. Nitrification is the term used to describe the two-step biological process in which ammonia (NH_4^+-N) is oxidized to nitrite (NO_2^--N) and nitrite is oxidized to nitrate (NO_3^--N). 生物硝化處理，主要目標在於(1)保護承受水體，避免溶氧降低及降低氨氮對魚類之毒性，(2)去除氮化物，避免水體 eutrophication，(3)提高水之再利用。
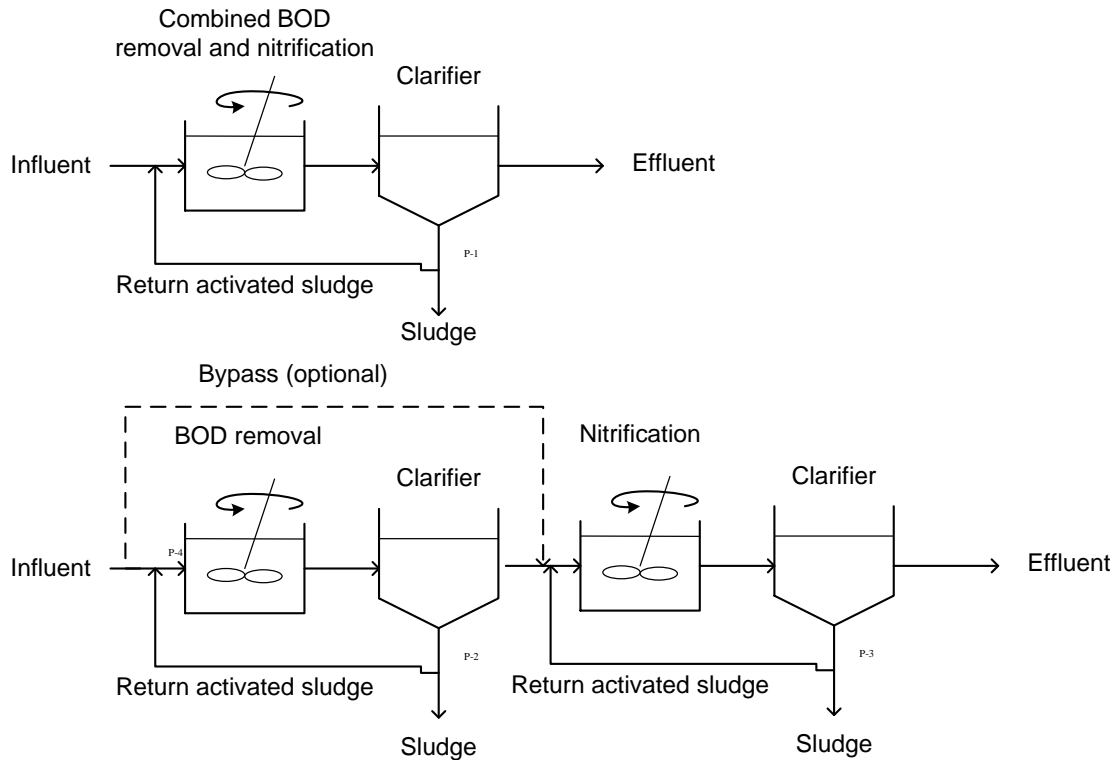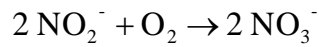

2. 生物處理去除 BOD 之餘，同時能進行硝化作用。由於硝化菌比去除 BOD 之異營菌，生長較為緩慢，因此欲完成硝化作用，需有較長之水力與固體停留時間。硝化菌屬好氧自營性，主要包括 *Nitrosomonas* (ammonia→nitrite)與 *Nitrobacter* (nitrite→nitrate)兩種菌屬(Winogradsky，1891 年分離而得)，其他尚有 *Nitrosococcus*、*Nitrosospira*...等亦有能力將 ammonia 氧化成 nitrite，而 *Nitrococcus*、*Nitrospira* 也能將 nitrite 氧化成 nitrate。
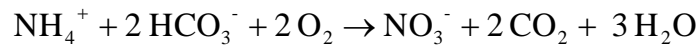
Nitroso- bacteria :

$$2\,NH_4^+ + 3\,O_2 \rightarrow 2\,NO_2^- + 4\,H^+ + 2\,H_2O$$

Nitro- bacteria :

$$2\,NO_2^- + O_2 \rightarrow 2\,NO_3^-$$

Total oxidation reaction :

$$NH_4^+ + 2\,O_2 \rightarrow NO_3^- + 2\,H^+ + H_2O$$
$$\quad 14 \qquad 2 \times 32$$

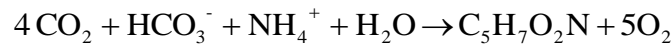所需鹼度

$$NH_4^+ + 2\,HCO_3^- + 2\,O_2 \rightarrow NO_3^- + 2\,CO_2 + 3\,H_2O$$
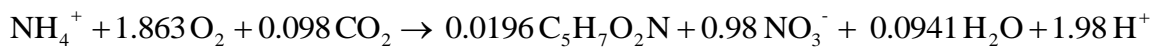$$\quad 14 \qquad 2 \times 100 \text{ as } CaCO_3$$

3. 理論上，氧化每克 N 需 4.57 克 O_2，而其所需鹼度為 7.14 克。然而，部分 ammonia ion 將代謝成為細胞組織，如下式之表示：

$$4\,CO_2 + HCO_3^- + NH_4^+ + H_2O \rightarrow C_5H_7O_2N + 5\,O_2$$

因此，考慮氨氮轉化為硝酸鹽、細胞合成反應與氧氣還原成水分子，有研究提出實際反應式為：

$$NH_4^+ + 1.863\,O_2 + 0.098\,CO_2 \rightarrow 0.0196\,C_5H_7O_2N + 0.98\,NO_3^- + 0.0941\,H_2O + 1.98\,H^+$$

由上式得知，氧化每克 N 需 4.25 克 O_2 以及 7.07 克鹼度，氧化每克 N 生成 0.16 克新細胞。因此，鹼度、溫度、BOD 濃度、N 濃度、毒性化合物、pH 與溶氧，是影響生物硝化作用之重要因子。其中，溶氧低於 0.5 mg/L 時，生物硝化作用受抑制。適合 pH 值為 7.5~8.0，pH 低於 6.8 時，生物硝化作用亦受抑制。
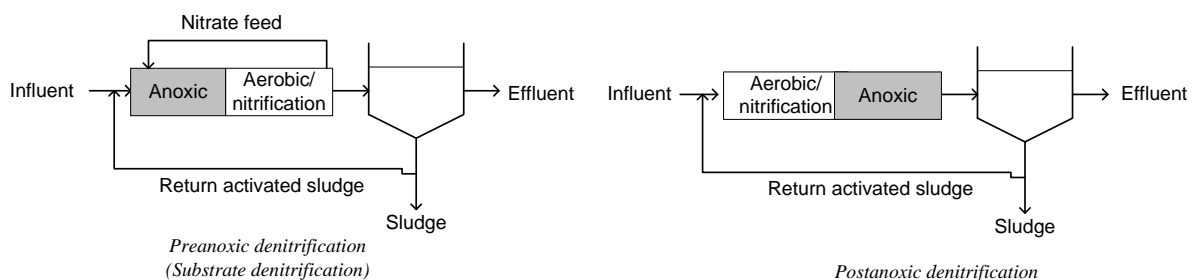
5-7 Biological denitrification

1. The biological reduction of nitrate to nitric oxide, nitrious oxide, and nitrogen gas is termed denitrification. 生物脫硝作用係生物脫氮(biological nitrogen removal)之一部分，生物脫氮包括 nitrification 與 denitrification 兩作用。水中去除氮化物，尚有 ammonia stripping, breakpoint chlorination, ion exchange 等方式，生物脫氮與此三種方式比較，屬於較為經濟且常用之方法，生物脫氮目的在於避免成受水體優養化，另外可避免補注地下水時，地下水硝酸鹽濃度過高。

2. Two modes of nitrate can occur in biological processes, and these are termed assimilating and dissimilating nitrate reduction.
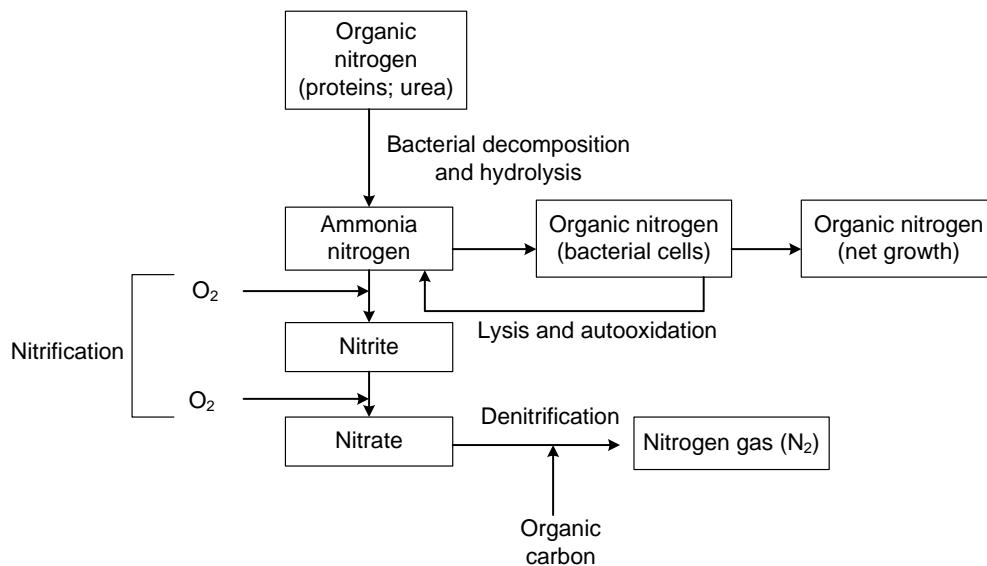
3. 兩種生物脫硝處理流程，preanoxic denitrification 與 postanoxic denitrification。preanoxic denitrification，最常見於都市污水之生物脫氮處理，係由 Ludzak-Ettinger 程序改良而來(U.S. EPA, 1993)，又稱為 MLE 程序。進流污水之 BOD，作為有機碳源，而第二槽之好氧生物硝化產生之硝酸鹽作為第一槽脫硝作用之基質，以進行厭氧生物脫硝作用，此方式又稱為基質脫硝程序(substrate denitrification)。

第二種程序，稱為 postanoxic denitrification。當第一槽同時進行 BOD 去除時，此槽生物硝化作用需藉助內呼吸作用(亦即增長停留時間)，因此反應速率低於 preanoxic denitrification。另外，常須添加如 metahanol 或 acetate 等，作為有機碳源，以提升第二槽脫硝速率。

Preanoxic denitrification
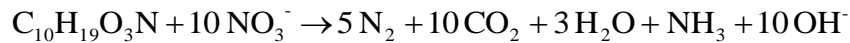*(Substrate denitrification)*

Postanoxic denitrification

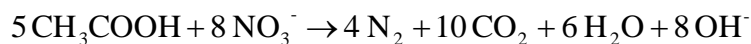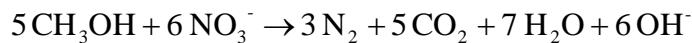## 4. Stoichiometry of biological denitrification

生物脫硝作用係脫硝菌利用 nitrate 或 nitrite 做為電子接受者，進行有機基質之生物氧化作用，亦即在缺氧或低溶氧狀況下，脫硝菌分泌 nitrate reductase enzyme，增進電子轉移至 nitrate，使 nitrate 行還原作用，以完成脫硝作用，nitrate 還原反應如下表示：
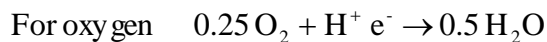
$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$
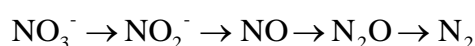
生物脫氮作用中，常見三種電子提供者(electron donnor)，包括(1)進流水中生物可分解 COD(bsCOD)，(2)內呼吸期生成之生物可分解 COD，(3)外加碳源，如甲醇或醋酸。若以 $C_{10}H_{19}O_3N$ 代表生物可分解 COD，則脫硝反應可表示為：
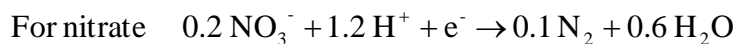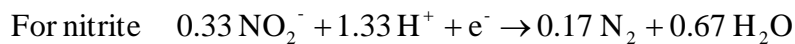
$$C_{10}H_{19}O_3N + 10\,NO_3^- \rightarrow 5\,N_2 + 10\,CO_2 + 3\,H_2O + NH_3 + 10\,OH^-$$

甲醇或醋酸為碳源時：

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

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

由上述反應式，可知脫硝作用每還原(nitrate nitrogn reduced)1 g 之 N，會產生 3.57 g alkalinity (as $CaCO_3$)。而所需外加碳量，利用如下方程式計算，硝酸鹽時為 $2.86\,g\,O_2/g\,NO_3^-\text{-}N$，而亞硝酸鹽時為 $1.71\,g\,O_2/g\,NO_2^-\text{-}N$。有研究指出(Barth et al., 1968)，脫硝作用約需 $4\,g\,BOD/g\,NO_3^-\text{-}N$ reduced.

For oxygen $0.25\,O_2 + H^+\,e^- \rightarrow 0.5\,H_2O$
0.25×32

For nitrate $0.2\,NO_3^- + 1.2\,H^+ + e^- \rightarrow 0.1\,N_2 + 0.6\,H_2O$
0.2×14

For nitrite $0.33\,NO_2^- + 1.33\,H^+ + e^- \rightarrow 0.17\,N_2 + 0.67\,H_2O$
0.33×14

但實際外加碳量，依系統操作狀況與碳源種類而異，一般可依如下公式估算：

$$g\,bsCOD/g\,NO_3^-\text{-}N = \frac{2.86}{1\text{-}1.42\,Y_n} \qquad Y_n : net\ biomass\ yield, g\ VSS/g\ bsCOD_r$$

5-8 Biological phosphorous removal

1. 磷為優養化限制因子，進行生物除磷，可避免承受水體優養化。以往，磷去除常採用鋁鹽或鐵鹽之化學混凝方法，但自 1980 年代起，成功發展生物除磷方式，其優點為降低處理成本與產生較少汙泥量。生物除磷主要原理係將磷 incorporated into cell biomass，再將污泥沉降去除。在厭氧狀態下，磷積蓄菌(Phosphorous accumulating organisms, PAOs)代謝醛酵產物(揮發性脂肪酸)並加以儲存，同時伴隨釋出磷，但在好氧環境下，PAOs 攝取更多水中溶解性磷酸鹽，並以聚磷酸鹽(polyphosphate)型式儲存於細胞內，亦即，好氧狀態，PAOs 吸收之磷含量高於在厭氧時所釋出之磷，而增殖污泥則於沉澱池沉降去除，如此循環，達到水中去磷之效果。處理流程

圖如下所示，一般厭氧槽需有 0.5~1 小時之污泥停留時間，好氧槽則需 2~40 天。
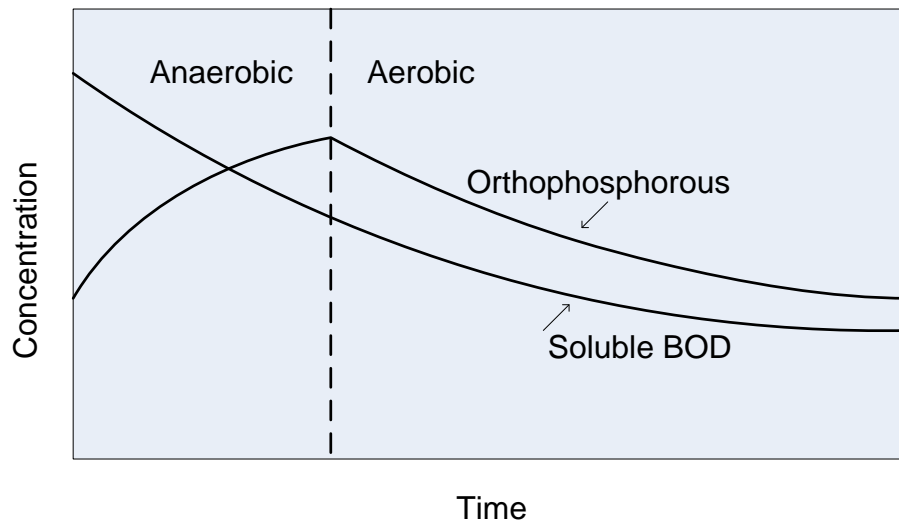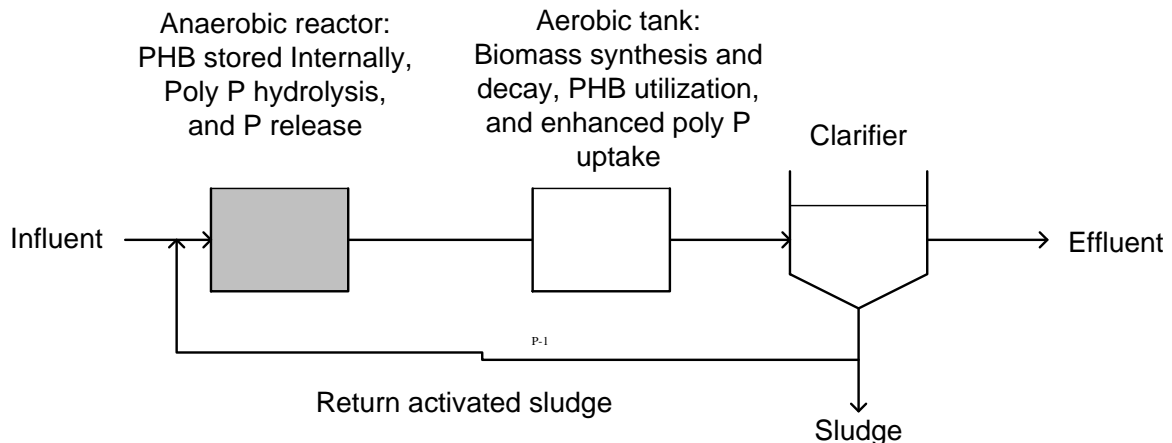
2. 生物去磷之影響因子

分三大類：環境因子、系統操作條件、基質種類及特性

(1)溶氧：好氧段溶氧應維持 2 mg/L 以上，以保持 PAOs 之活性。

(2)溫度：影響不明顯。

(3)pH：pH 低於 6.5 時，PAOs 活性降低，低於 5.0，活性全失。

(4)污泥停留時間：太長，發生內呼吸作用，裂解釋出磷，污泥磷含量降低。

(5)厭氧段水力停留時間：視進流有機物特性而異，1~2 小時足以釋出磷。

(6)好氧段水力停留時間：1~2 小時左右，但有機碳濃度高或較難分解者，需加長水力停留時間。

(7)有機碳源：易生物分解有機碳，可促進厭氧/好氧之 PAOs 交替代謝作用，因此 COD/P 之比值愈高，磷在厭氧/好氧兩段之去除率愈高。

(8)抑制物質：脫硝作用會對磷釋出造成抑制作用。

7-10 Anaerobic fermentation and oxidation

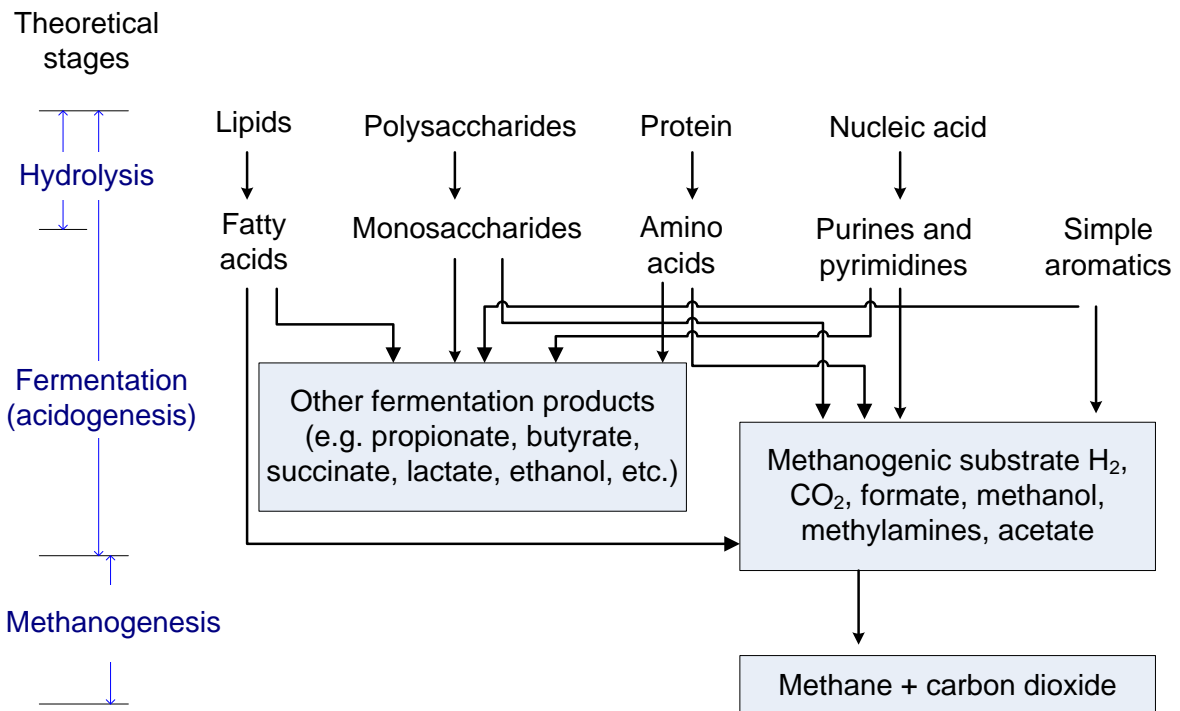# Chapter 6 Anaerobic biological treatment

6-1 厭氧醱酵

1. 與好氧生物處理比較，厭氧生物處理主要優點為不需曝氣、污泥產量低，以及可回收能源。厭氧生物處理之優缺點，整理如下：

優點	缺點
所需能量低	啟動時間長
污泥產量低	需添加鹼度或特定離子
所需營養鹽低	需後續好氧生物處理，以符合放流水標準
可生成生質能源，CH_4、H_2	無法去除 N、P
大部分有機物皆可代謝	溫度低，反應速率慢
長時間未進料，當再添加基質時，反應依然良好	可能產生臭味及腐蝕性氣體
	對毒性物質敏感

2. 17 世紀科學家發現 Biogas(生物沼氣 marsh gas，甲烷)。Marsh gas is methane, a product of anaerobic biological degradation of organic materials.

   3.

3. 由於厭氧醱酵程序無法獲得滿意的處理水質，通常厭氧醱酵程序後面需連結好氧程序。基本厭氧醱酵程序，包括三個步驟，(1)Hydrolysis；(2)Fermentation (also known as acidogenesis)；(3)Methanogenesis，如下圖所示。The first step for most fermentation processes, in which particulate material is converted to soluble compounds that can then be hydrolyzed further to simple monomers that are used by bacteria that perform fermentation.

Theoretical stages					
	Lipids	Polysaccharides	Protein	Nucleic acid	
Hydrolysis	Fatty acids	Monosaccharides	Amino acids	Purines and pyrimidines	Simple aromatics

Other fermentation products (e.g. propionate, butyrate, succinate, lactate, ethanol, etc.)

Methanogenic substrate H$_2$, CO$_2$, formate, methanol, methylamines, acetate

Fermentation (acidogenesis)

Methanogenesis

Methane + carbon dioxide

5. 第二步驟為酸化。酸化程序將胺基酸、糖、脂肪酸、單醣、核酸醱酵為乙酸鹽、丙酸鹽、丁酸鹽、氫氣、CO$_2$ 等中間產物。第三步驟為甲烷化，甲烷菌(methanogenic organisms)再將中間產物轉化成 CH$_4$ 及 CO$_2$。
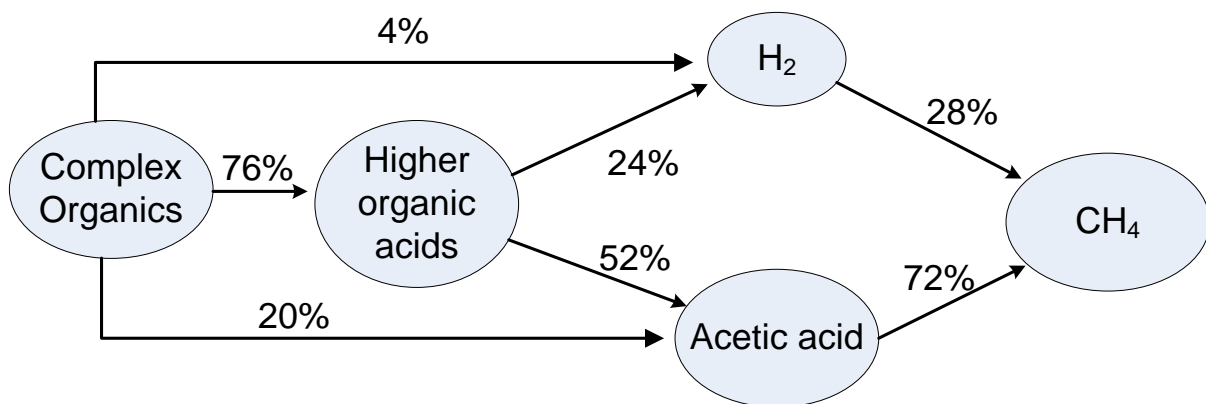
6-2 處理原理

1. 厭氧醱酵作用主要優點是低污泥產量與產生可用能源甲烷。

2. 環境影響因子
(1) Temperature
大部分厭氧醱酵程序初期溫度控制為 50~60℃，後期溫度控制為 30~35℃。
As temperature increases the rate of reaction generally increase. For biological systems the rate increases are usually not as great as for chemical reactions. Methane has been produced at temperatures down to 10℃ or lower, but for reasonable rates of methane production, temperature should be maintained above 20℃.

(2) pH

The most important process control parameter is pH.甲烷生成菌最適 pH 值為 6~8，接近 7 左右。因為甲烷生成菌生長速率低於酸生成菌，因此厭氧系統需維持穩定之 pH 值，但由於系統不斷產生有機酸與 CO_2，故需足夠鹼度以控制系統 pH 值，常用之鹼劑包括 lime、sodium bicarbonate 與 sodium carbonate。

(3) Mixing

Mixing is an important factor in pH control and maintenance of uniform environmental condictions. Without adequate mixing, unfavorable microenvironments can develop. Mixing distributes buffering agents throughout the reactor and prevents local buildup of high concentrations of intermediate metabolic products that can be inhibitory to methanogens.

(4) Ammonia and sulfide control

高濃度 NH_3 對厭氧醱酵程序會產生抑制作用，NH_3 比 NH_4^+ 對厭氧菌毒性更大。當系統 pH 值偏高時，NH_3 之形成佔優勢，容易造成系統失敗，因此，需添加酸劑加以控制。

另外，系統若含過量 sulfate (SO_4^{2-})，亦會影響厭氧醱酵程序。原因為 sulfate 會被還原為 sulfide (S^{2-})，過量 sulfide 對甲烷菌造成毒性。解決方式為加入鐵鹽，使形成 iron sulfide 沉澱物。
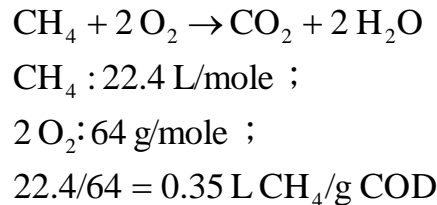
(5) Nutrient requirements

酸化菌與甲烷菌對於基質之需求，低於好氧菌。一般而言，活性污泥系統之 COD：N：P(重量比)為 100：5：1，但相同基質情形下，厭氧代謝之 COD：N(重量比)為 250：5。
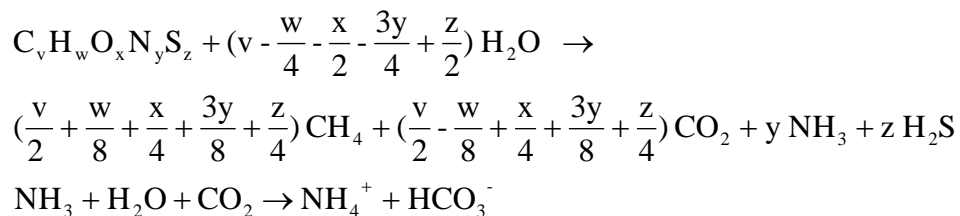
(6)固體產生量與停留時間

大部分厭氧醱酵程序，甲烷菌在 35℃ 之最低汙泥停留時間為 3~5 day，但欲維持生物系統穩定操作，最低汙泥停留時間約需乘上 3~20 倍之安全係數。

6-3 厭氧產氣潛能

1. 理論上，厭氧醱酵每 g 之 COD 可以產生 0.35 L 之甲烷 (0℃ and 1 atm)，如下方程式所示。而正常狀況下，厭氧醱酵程序產生之氣體約含有 60~70%的甲烷與 30~40%的 CO_2，其餘為少量之 H_2、H_2S、NH_3、H_2O 等氣體。

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$$
$$CH_4 : 22.4\ L/mole ；$$
$$2\,O_2 : 64\ g/mole ；$$
$$22.4/64 = 0.35\ L\ CH_4/g\ COD$$

厭氧反應通式

$$C_v H_w O_x N_y S_z + (v - \frac{w}{4} - \frac{x}{2} - \frac{3y}{4} + \frac{z}{2})\,H_2O \rightarrow$$

$$(\frac{v}{2} + \frac{w}{8} + \frac{x}{4} + \frac{3y}{8} + \frac{z}{4})\,CH_4 + (\frac{v}{2} - \frac{w}{8} + \frac{x}{4} + \frac{3y}{8} + \frac{z}{4})\,CO_2 + y\,NH_3 + z\,H_2S$$

$$NH_3 + H_2O + CO_2 \rightarrow NH_4^+ + HCO_3^-$$

Example 6-1. 厭氧醱酵程序，操作溫度 35℃，已知處理流量 3000 CMD，生物可分解之 COD 濃度為 5000 g/m^3。若生物可分解之 COD 去除率為 95%，且汙泥產量為 0.04 g VSS/g COD used，求 COD 轉換成甲烷量若干 g/d？提示：$COD_{in} = COD_{eff} + COD_{VSS} + COD_{Methane}$。甲烷產量若干 m^3/d (35℃，1 atm)？

2. 1979 年開發生化甲烷潛能(Biochemical methane potential, BMP)指標，用以測量甲烷產生量。BMP 為樣品於溫度 35℃，厭氧狀況下，培養 30 天或氣體停止產氣後，產生之氣體體積量。BMP 代表最大甲烷產生量，甲烷產生率與基質去除率、流量之關係式如下：

$$Q_m = Q\,(S_{TO} - S_{Te})\,M = Q\,E\,M\,S_{TO}$$
$$\text{where } Q_m = \text{is the quantity of methane per unit time}$$
$$Q = \text{is influent flow rate}$$
$$S_{TO} = \text{is the total influent COD (suspended + soluble)}$$
$$S_{Te} = \text{is the total effluent COD (suspended + soluble)}$$
$$E = \text{is an efficiency factor (ranging from 0 to 1) ; } 06 \sim 0.9$$
$$M = \text{is the volume of } CH_4 \text{ produced per unit of COD removed}$$

由於其他損失，實際之 M 值常低於 BMP 理論值。

3. 厭氧醱酵程序

(1)完全混合流(Complete mix process)

水力停留時間等於固體物停留時間。固體物停留時間控制在 15~30 天之間，可維持系統穩定性。無污泥迴流，適合於處理高固體物與高有機物，但出流水所含污泥進行濃縮處理，較為困難。一般體積負荷(Volumetric organic loading)控制在 1~5 kg COD/m^3.d 之間。

(2)厭氧接觸(Anaerobic contact process)

系統具污泥迴流設計，因而水力停留時間小於固體物停留時間，反應槽體積可降低。迴流污泥前，可利用重力沉降、氣提、真空脫氣或添加混凝劑，進行污泥分離與濃縮。系統體積負荷(Volumetric organic loading)控制在 1~8 kg COD/m^3.d 之間，水力停留時間則維持在 0.5~5 天。
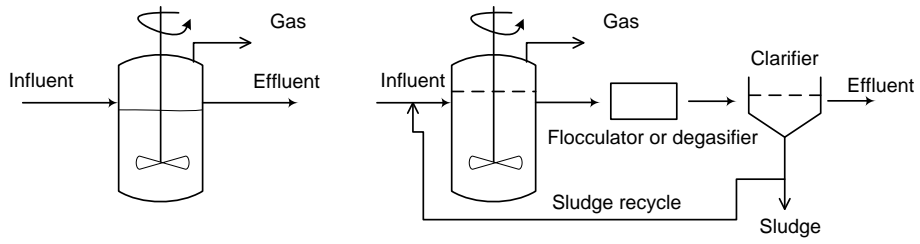
(3) Anaerobic sequencing batch reactor

厭氧醱酵與固液分離，在同一反應器中進行。系統主要有四個步驟，包含進流、反應、沉降與出流。反應階段，每小時攪拌數分鐘，確保基質與固體物分布均勻。系統體積負荷(Volumetric organic loading)控制在 1.2~2.4 kg COD/m^3.d 之間，水力停留時間則維持在 0.25~0.5 天。

(4)上流式厭氧污泥床(Upflow sludge blanket reactor process, UASB)

1970 年代晚期，由荷蘭 Lettinga 團隊開發出來。之後，McCarty 團隊 (Stanford University, early 1980s)與 Angenent (Iowa State University, late 1990s)陸續開發出其他改良式。

UASB 廢水自反應器底部分散進入，向上流動，經過顆粒化污泥氈。與其他方式比較，UASB 主要特性為能承受更大體積負荷。系統設計主要項目包含 the influent distribution system、the gas-solids separator、the effluent withdrawal design。系統體積負荷(Volumetric organic loading)控制在 12~20 kg COD/m^3.d 之間(30~35℃)，水力停留時間則維持在 4~8 小時。上流速度為 2 m/h。
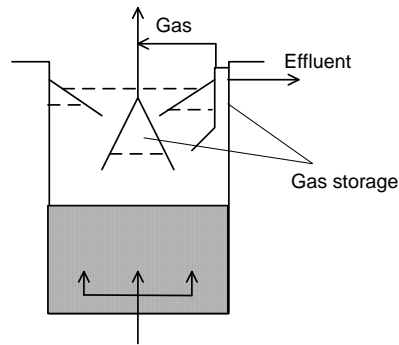
(a) Complete mix

(b) Anaerobic contact process
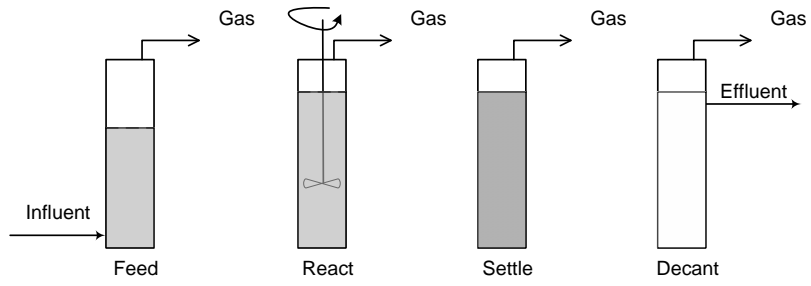
(c) Anaerobic sequencing batch reactor (ASBR)

(d) Anaerobic sludge blanket processes (UASB)