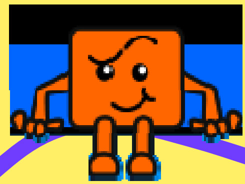
Chapter-4

Prof. Dr. Samir Afifi

Nutrient Removal from wastewaters



Major problems associated with sewage effluent

- Nutrient enrichment (Eutrophication) → Algal Blooms
- Deaeration of the watercourse → oxidation of ammonia
- Nitrate toxicity→ water abstracted as a potable .

Major problems associated with sewage effluent

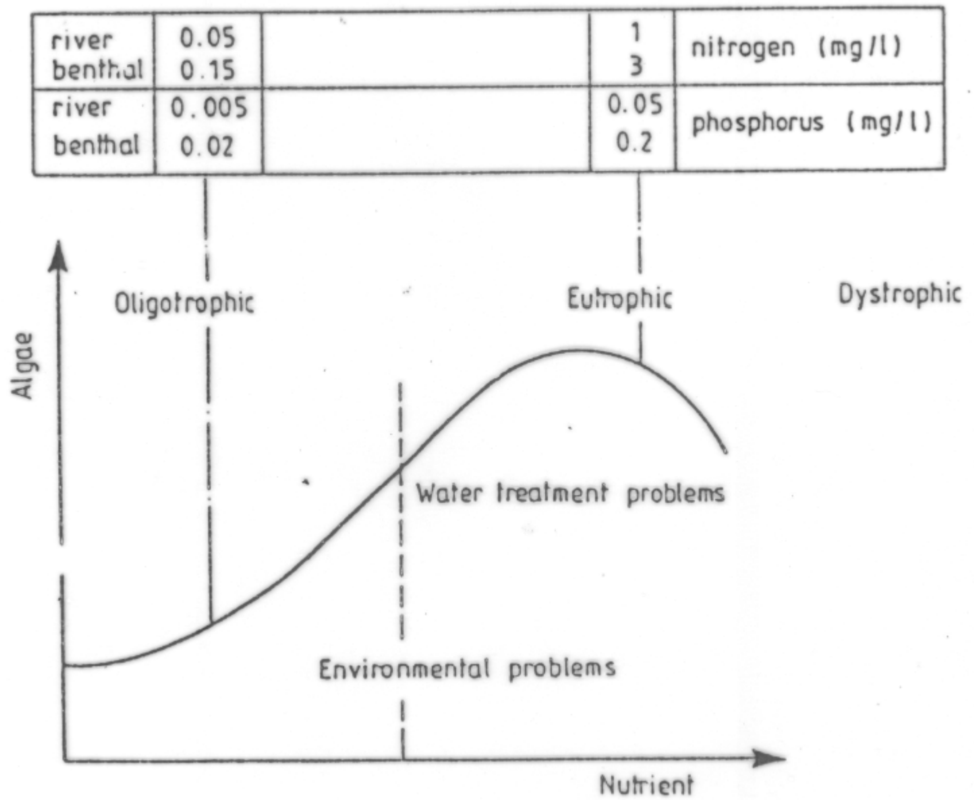
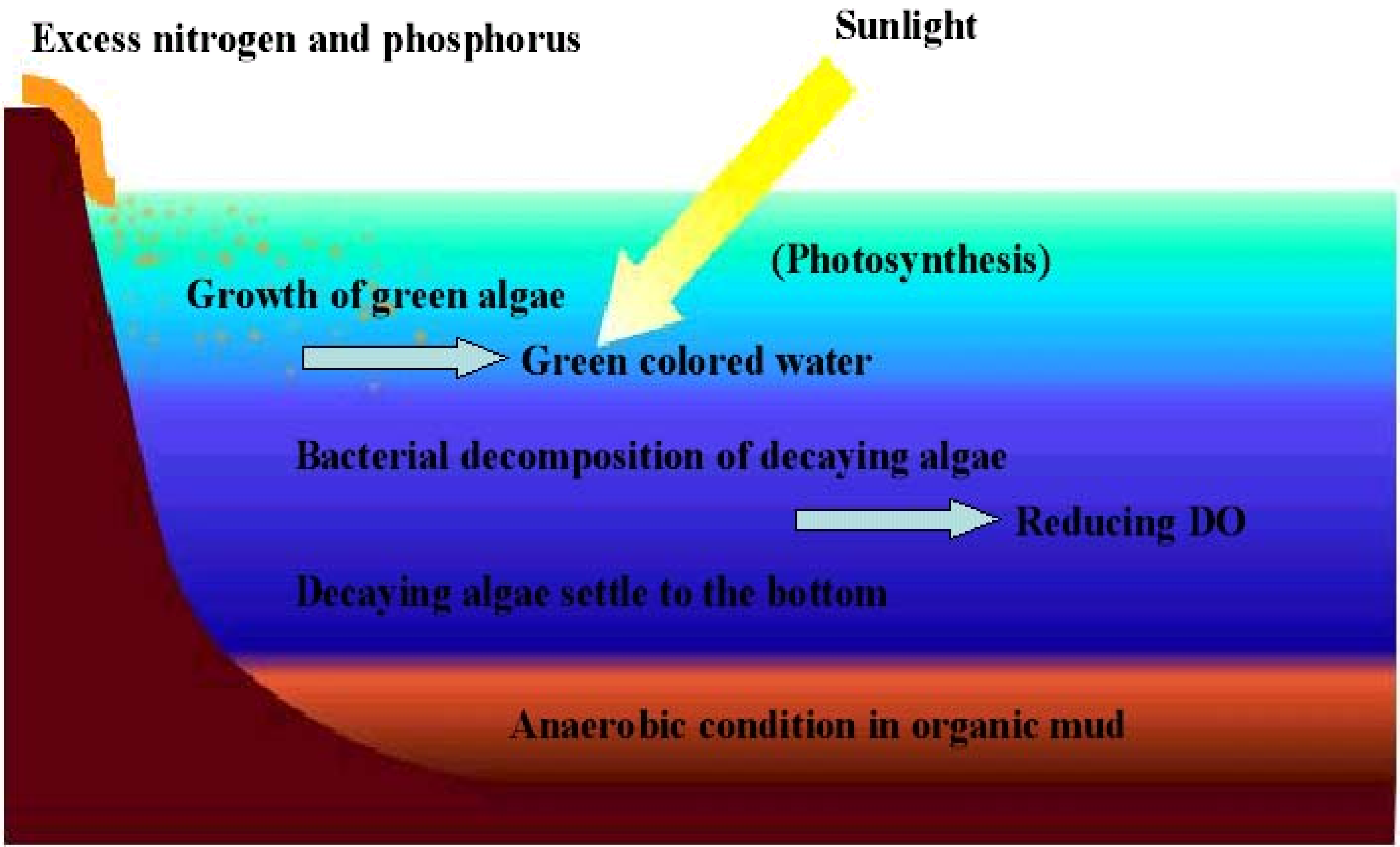


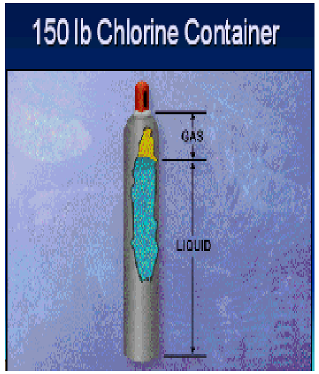
Figure 8.1 Concentrations of nitrogen and phosphorus in surface water and sediments, associated with environmental problems.



Eutrophic lake

Physiochemical methods used for nitrogen removal:

- Ammonia stripping
- Chlorination
- Selective ion-exchange



cont== Physiochemical methods used for nitrogen removal:

Disadvantage:

- High operation costs
- Unreliability

Principal application of biological processes are to:

1) Removal of carbonaceous organic matter
2) Nitrification;
3) Denitrification;
4) Phosphorus removal; and
5) Waste stabilization.

Biological processes considered the most effective and economic process in the field of wastewater treatment

Successful technique for nitrogen removal which occur in the biological nitrogen cycle

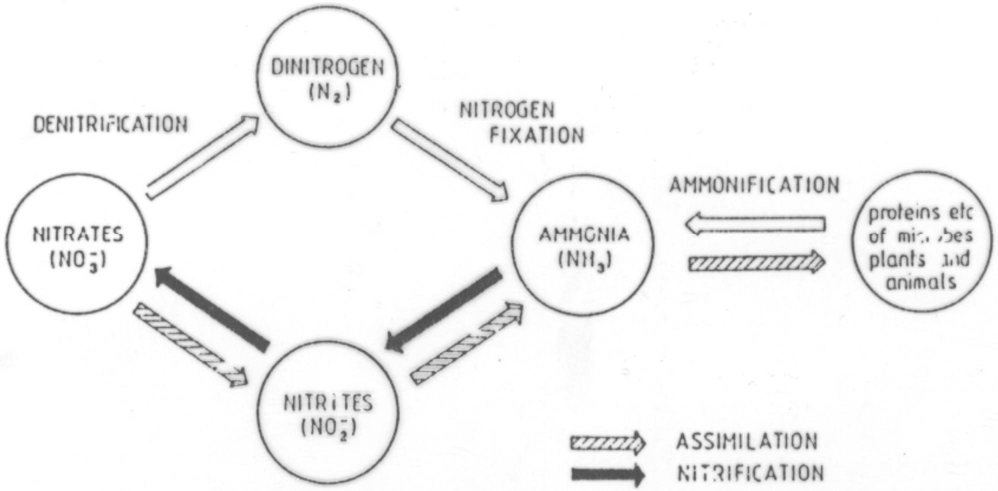


Figure 8.2 Simplified nitrogen cycle showing the nitrogen interconversions which can occur in an aquatic environment.

Nitrogen forms in wastewater

- Organic as protein and nucleic acids
- Urea (OC(NH)2)
- Ammonium ion ($NH^+{}_4$)
- Nitrite and Nitrate

The total nitogen content= total Kjeldahl nitrogen(TKN)

Typical removal efficiencies of total nitrogen in non-nitrifying conventional treatment plants

Treatment stage	Typical concentration (mg/l)	
	Total nitrogen	%Removal
Raw sewage	20-70	-
•Settled sewage	18-60	5-10
•Final effluent (activated sludge)	12-40	10-30
•Final effluent (trickling fillers)	14.45	8-25

Typical removal efficiencies of total nitrogen in non-nitrifying conventional treatment plants

- Up to 30% in biological treatment process removed in cell synthesis
- Small fraction removed in sedimentation process
- Remaining ammonia need additional treatment

Ammonium to nitrate /nitrification- oxygen is needed

Nitrate to N2/De-nitrification- An-aerobic condition

Nitrification

It is biological process by which ammonia is first converted to nitrite and then to nitrate.

Two groups of chemo-Autotrophic bacteria Required

- Nitrosomonas catalyst Ammonia $\rightarrow$ Nitrite
- Nittrobacter for further oxidize Nitrite $\rightarrow$ Nitrate

Nitrification:

Autotroph Metabolism:

$$\text{Organic Nitrogen} \xrightarrow[\text{hydrolysis}]{\text{Bacterial decomposition and}} NH_3$$

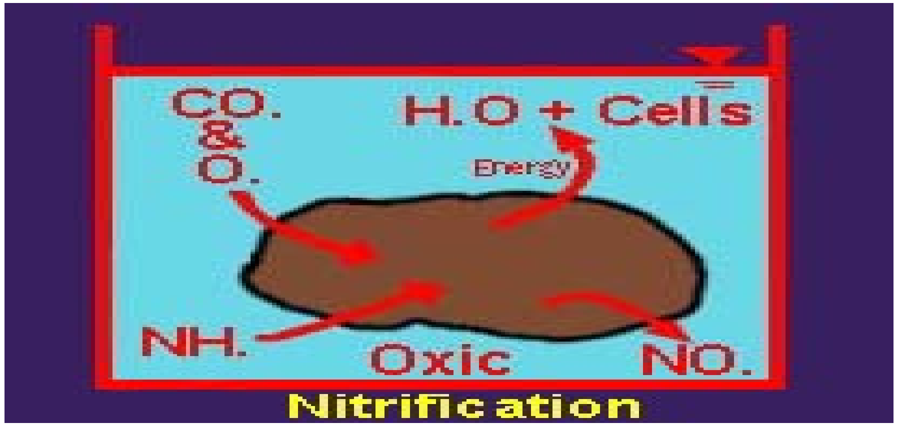
$$\left.\begin{array}{l} NH_3 + O_2 \longrightarrow NO_2^- + \text{Energy} \\ NO_2^- + O_2 \longrightarrow NO_3^- + \text{Energy} \end{array}\right\} \text{Nitrification}$$

cont== Nitrification:

Reaction for the oxidation of ammonia:

$$NH^{+}_{4} + 1.83\ O_2 + 1.98\ HCO^{-}_{3} \rightarrow$$
$$0.021\ C_5H_7NO_2 + 1.041\ H_2O + 0.98\ NO_3 + 1.88\ H_2CO_3$$

- Reaction provide the bacteria with energy
- Carbon is assimilated via the calvin cycle



Information of Design of nitrifying wastewater treatments plants

1) Cell Yield (Y) of nitrifying very low compared with heterotrophs

- 1 mol of NH^{+}_{4} nitrogen oxidized only 0.021 mol of nitrifier (Biomass)
- 18g N-NH^{+}_{4}=133*0.021/18=0.13g cells/g N-NH^{+}_{4}
- 1g NH^{+}_{4} contains 14/18=0.77g n
- 0.17 cell produced/g NH+4

2) Oxygen requirment:

1.83 mol O_2 for every mole of ammonium removed.

Thus 1g of ammonium nitrogen required 4.2g oxygen for its removal.

3) Removal of bicarbonate associated with a reduction in the alkalinity.

Each mole of NH^{+}_{4} oxidized removes 1.98 mol of bicarbonate

There will be a drop in the pH of the mixed liquor

Important Remarks

- *Nitrifying bacteria are slower growing than the heterotrophic bacteria, which comprises the greater proportion of the biomass in both fixed film and suspended growth systems.*

- *The key requirement for nitrification to occur is that the process should be so controlled that the net rate of accumulation of biomass, and hence, the net rate of withdrawal of biomass from the system, is less than the growth rate of the nitrifying bacteria*

- *Nitrification process carried out by strictly aerobic*

Application of Nitrification in treatment plants

1. Nitrification by single-stage activated sludge:

A. calculation of sludge age

B. Application of safety factors

C. Calculation of oxygen requirments

Cont==Application of Nitrification in treatment plants

2. Nitrification using a two-sewage activated sludge process.

3. Nitrification in trickling filter.

Nitrification by single- stage activated sludge:

<u>A- Calculation of sludge age:</u>

- Nitrifying bacteria energetically inefficient, their growth is very slow
- Nitrifying bacteria sensitive to a wide range of environmental condition

- The important factors affecting their growth rate

- Substrate concentration
- Temperature
- Dissolved oxygen
- pH. value

- Sludge age required to ensure that they do not wash out of the reactor
- Oxidation of ammonia to nitrite is the rate-limiting step in the nitrification process
- So, sludge age required for defining effluent standards

- Effluent of temperature on the nitrification process

- Above 20 C , nitrification occur at sludge age lower than 3 days
- Temperature falls to 10 C , sludge age in excess of 8 days needed for nitrification

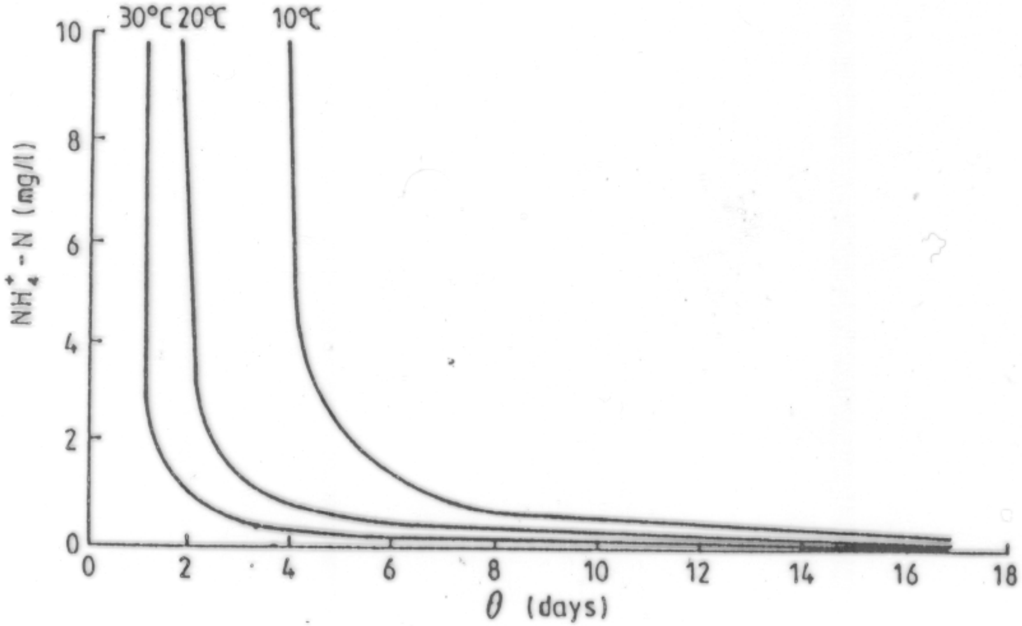


Figure 8.3 The effects of temperature on the sludge age required to produce a given effluent standard for a nitrifying activated sludge.

- A large seasonal temperature difference leads to summer/winter ammonia effluent standard.

B. <u>Application of safety factors</u>

- Applied to sludge age method in wide fluctuation in TKN loading
- Ammonia removal from wastewater follows a zero-order reaction

- Removal rate dependant on :
  - Ammonia concentration
  - Population of nitrifiers in mixed liquor
- Nitrifying bacteria do not respond to nitrogen concentration increase

- Safety factors used to compensate for this by permitting the build-up of a nitrifying population
- Safety factors calculated as the ratio of the peak to average TKN loading of the influent

peak TKN loading

Safety factors = ----------------------------

Average TKN loading

- Applying safety factors above 2.5 value not economic

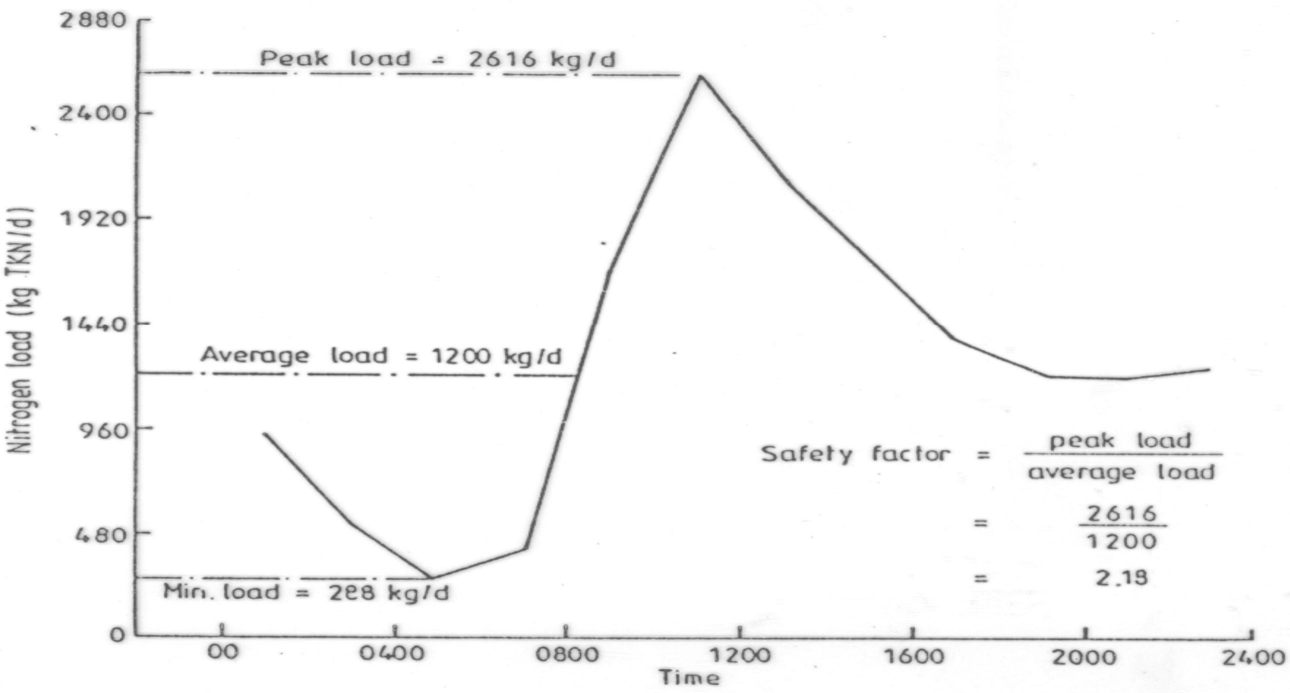


Figure 8.4 Diurnal variations in ammonia loading on a wastewater treatment plant, illustrating the calculation of a safety factor to apply to the sludge age required for nitrification.

C. Calculation of oxygen requirements:

- Oxygen demand requirements modified to meet both NOD and BOD

1. <u>Oxygen demand requirment for BOD:</u>

BOD_u:

$CHO + O_2 \rightarrow CO_2 + H_2O + E$

1.47 kg is requirement for 1 kg organic material in influent (BOD_5 to BOD_u)

O_2 requirement (kg O_2/d) = 1.47 {Q(S_0-Se)}

BOD$_5$:

- $CHON + O_2 \rightarrow CO_2 + H2O + (C_5H_7NO_2)$

(Bacterial Growth-sludge)

- $C_5H_7NO_2 + 5\ O_2 \rightarrow 5\ CO_2 + 2H_2O + NH_3$

1.42 kg is requirements for each kg solid produced

O_2 requirements for BOD_5 (kg O_2/d)=

$1.47\ \{Q(S_0\text{-}Se)\}\text{-}1.42\Delta S$

ΔS= daily solid production(kg/d)

2. Oxygen Demand Requirement for NOD:

$NH^+_4 + 2O_2 \rightarrow NO_3^- + H_2O$

4.2 kg O_2 for each kg of nitrogen (TKN) oxidied

Nitrogenous oxygen Demand (kg O_2/d) =4.2Q (N_0-Ne)

Where:

Q= influent flow rate (m3/d)

N_e= average effluent TKN (kg/m3)

N_0 = the net influent TKN-TKN used in cell synthesis(kg/m3)

TKN cell synthesis/d = 0.2 daily solids production {Δ X}

N_0 = net influent TKN – 0.2ΔX

NOD (kg O2/d) = 4.2Q {(influent TKN-0.2 ΔX) - N_e)

Nitrification using a two-stage activated sludge process

As Nitrification bacteria are:

- Slow growing
- Requirement for long sludge ages
- Requirement high dissolved oxygen
- Susceptible to inhibition by others (heterophophic bacteria)

For the separation of carbonaceous removal and nitrogen removal into separate previal each through:

- Increased process efficiency
- Land saving in addition
- Inhibitory harmful compounds in the influent in the first stage

Option for two-stage process

- Mechanically aerated for first step followed by
- Diffused aerator second stage or
- Nitrifiying trickling filter

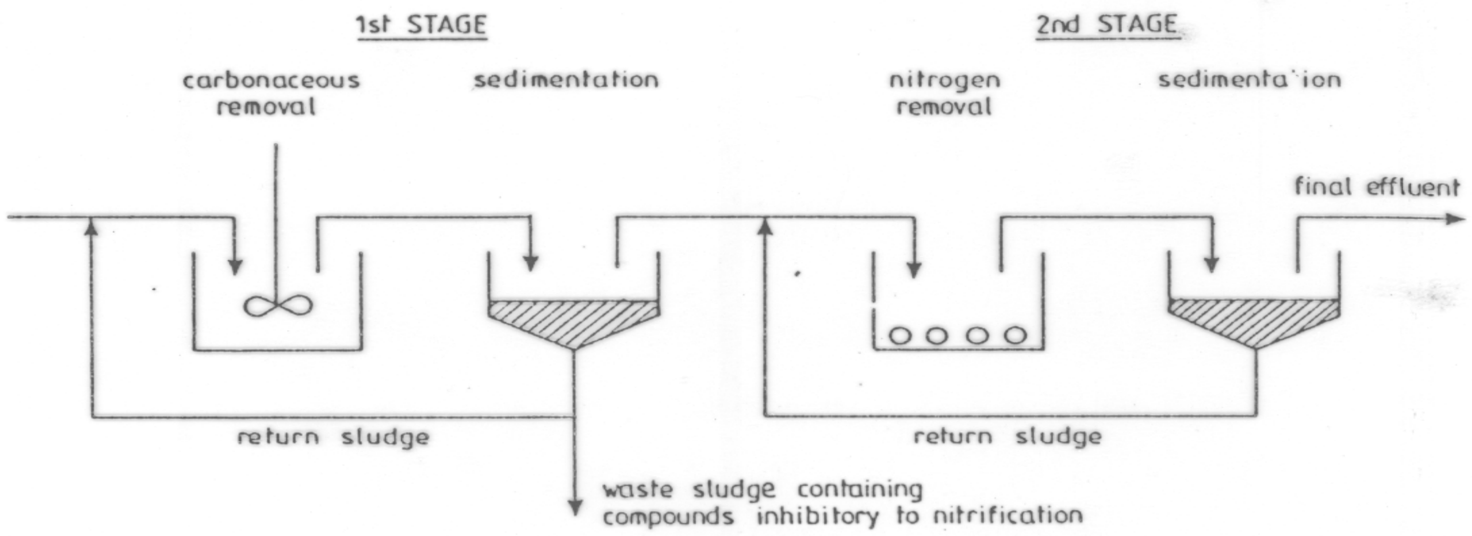
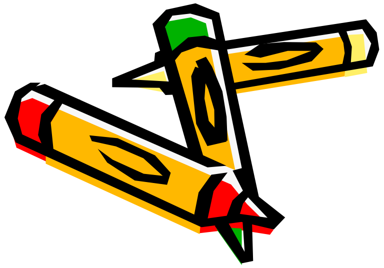


Figure 8.5 Schematic diagram of a two-stage nitrifying activated sludge plant. Stage 1 is a mechanically aerated carbonaceous removal process, whereas stage 2 is a diffused air nitrification process.

Common problems

- Low growth yield of the nitrifies, solids concentration in the second-stage reactor low, which leads to poor sludge settle ability, so, Recirculation solids from the first stage sedimentation tank is needed



Cont== common problems

- Diffused air systems operation at a low solid concentration associated with foaming problems, so , antifoam addition frequently required
- Reduction of wastewater alkalinity enhanced by nitrification in the second-stage, reactor needs pH control.

Nitrification in trickling filter

- Nitrifying bacteria competing with heterotrophic bacteria on oxygen
- Heterotrophic bacteria will outgrow the nitrifiers
- Availability of oxygen within the filter is a function of the BOD concentration
- Limit organic loading rate necessarily to achieve nitrification by trickling filter.

Cont==

Nitrification in trickling filter

- For mineral media 0.16-0.19kg/m^2d is often quoted to achieve an ammonia removal of 75%

At loading rates above 0.4kg/m^3d very little nitrification is obtained.

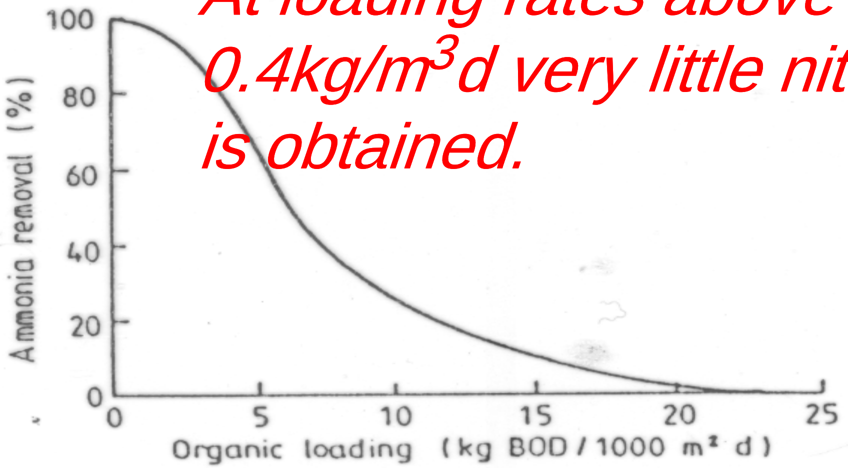


Figure 8.6 The effect of organic loading rate on ammonia removal in trickling filters.

Cont==

Nitrification in trickling filter

- Because of the large reserve of biomass associated with a trickling filter, they are less susceptible to load variations than suspended growth processes, and twofold variations ammonia loading do not affect the effluent quality
- They are, however, very susceptible to flow variations and a flow sufficient to keep the media continuously wet must be provided.

Cont==

Nitrification in trickling filter

- **Nitrification in trickling filters depended on a variety of factors; including temperature, dissolved oxygen, pH, presence of inhibitors, filter depth and media type, loading rate, and wastewater BOD**
- **Low-rate trickling filters allowed development of a high-nitrifying population. For rock media filters, organic loading should not exceed 0.16 kg BOD_5/m^3/day.**
- **Higher loading rates (0.36 kg BOD_5/m^3/day) were allowable in plastic media trickling filters because of the higher surface area of the plastic media.**
- **If two filters were used, heterotrophic growth occurs in the first filter and nitrification in the second filter**
- **Study of tertiary trickling filters recommending a media surface loading rate of 0.4 g NH_3-N/m^2/day for complete nitrification (effluent NH_3-N < 2.0 mg/L) at a water temperature of 10 C.**

De-nitrification

Denitrification is the biological process by which nitrate is converted to nitrogen and other gaseous end products.

- The De-nitrification process occur in absence of dissolved oxygen
- Under absence of O_2, the utilization of oxygen as the terminal electron acceptor for respiration is inhibited

De-nitrification

- Certain chemo-organotrophs (De-nitrification) capable to replace O_2 with NO_3 as the terminal electron acceptor
- This type of respiration reduced nitrate to nitrogen

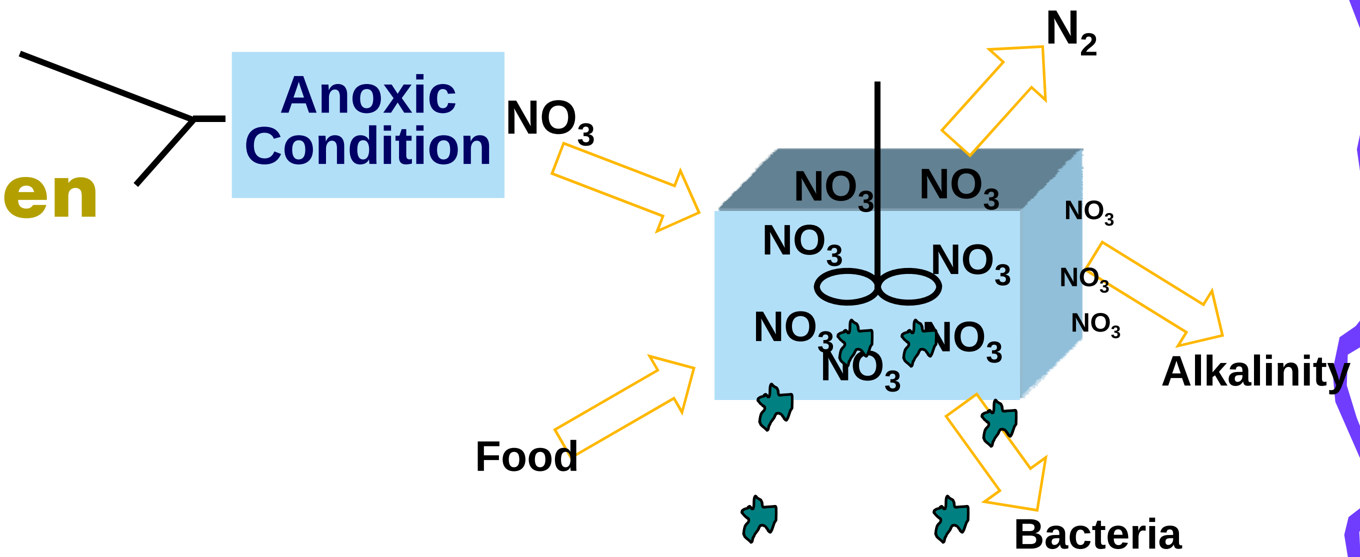
De-nitrification

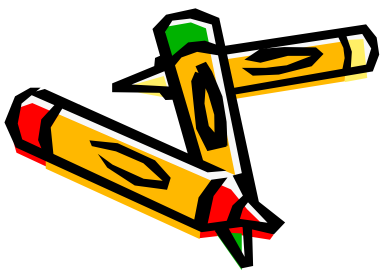
Redox	+5	+3	+2	+1	0
form	NO_3	NO_2	NO	N_2O	N_2
State of nitrogen	Nitrate	nitrite	Nitric* Oxide	Nitrous* Oxide	Nitrogen*

Anaerobic or nitrate respiration

Environmental Conditions For Denitrification must be Created for Nitrogen Removal

- Denitrifying (facultative heterotrophic) bacteria
- Food (BOD or methanol)
- Nitrate
- No oxygen





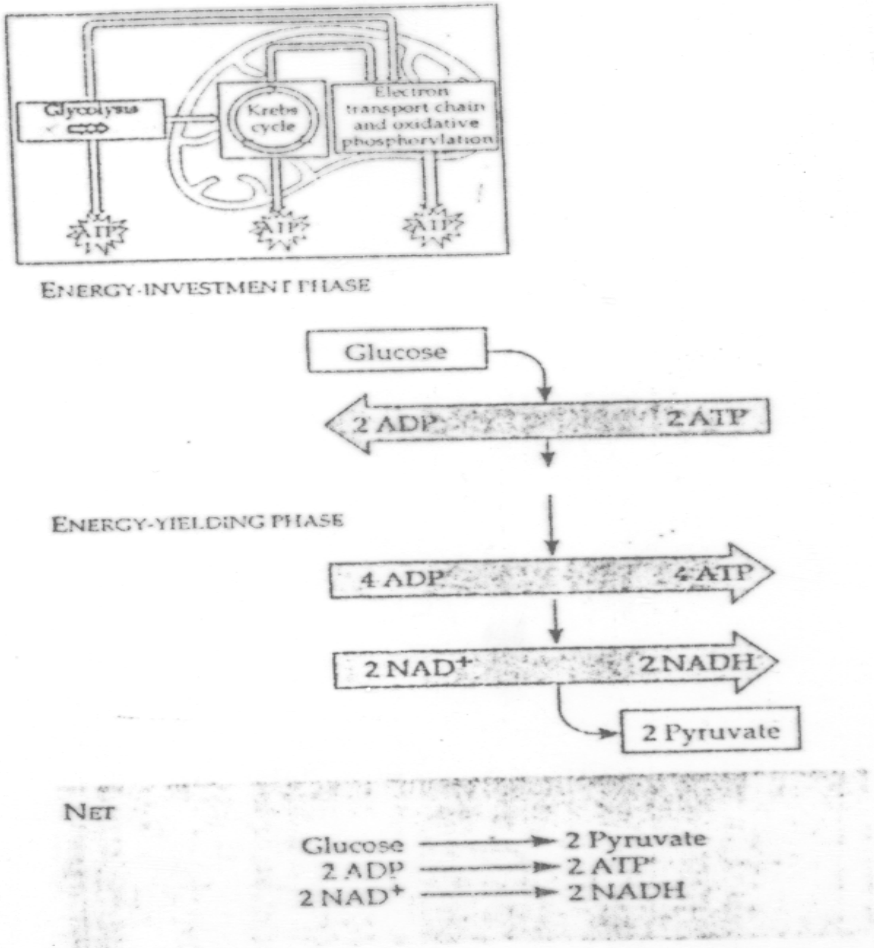
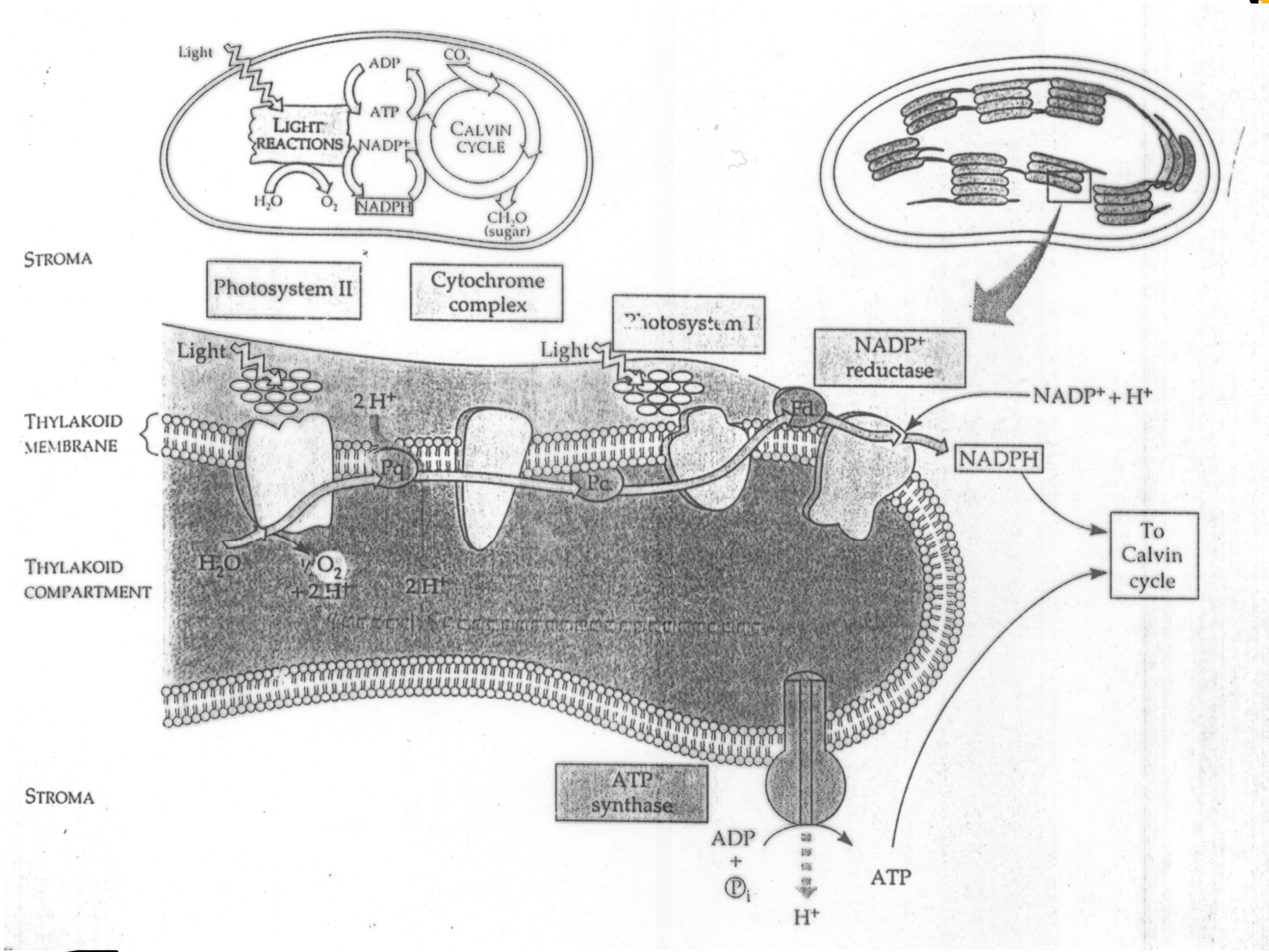


Figure 9.9
A preview of glycolysis. Glycolysis consumes ATP energy during the energy-investment phase, but the energy-yielding phase, which generates ATP and NADH, more than compensates.



Light
ADP
CO_2
ATP
LIGHT REACTIONS
NADP+
CALVIN CYCLE
H_2O
O_2
NADPH
CH_2O (sugar)
STROMA
Photosystem II
Cytochrome complex
Photosystem I
NADP+ reductase
Light
Light
2 H+
Fd
NADP+ + H+
THYLAKOID MEMBRANE
Pq
Pc
NADPH
To Calvin cycle
THYLAKOID COMPARTMENT
H_2O
$\frac{1}{2}O_2$ + 2 H+
2 H+
STROMA
ATP synthase
ADP
+
P_i
H+
ATP

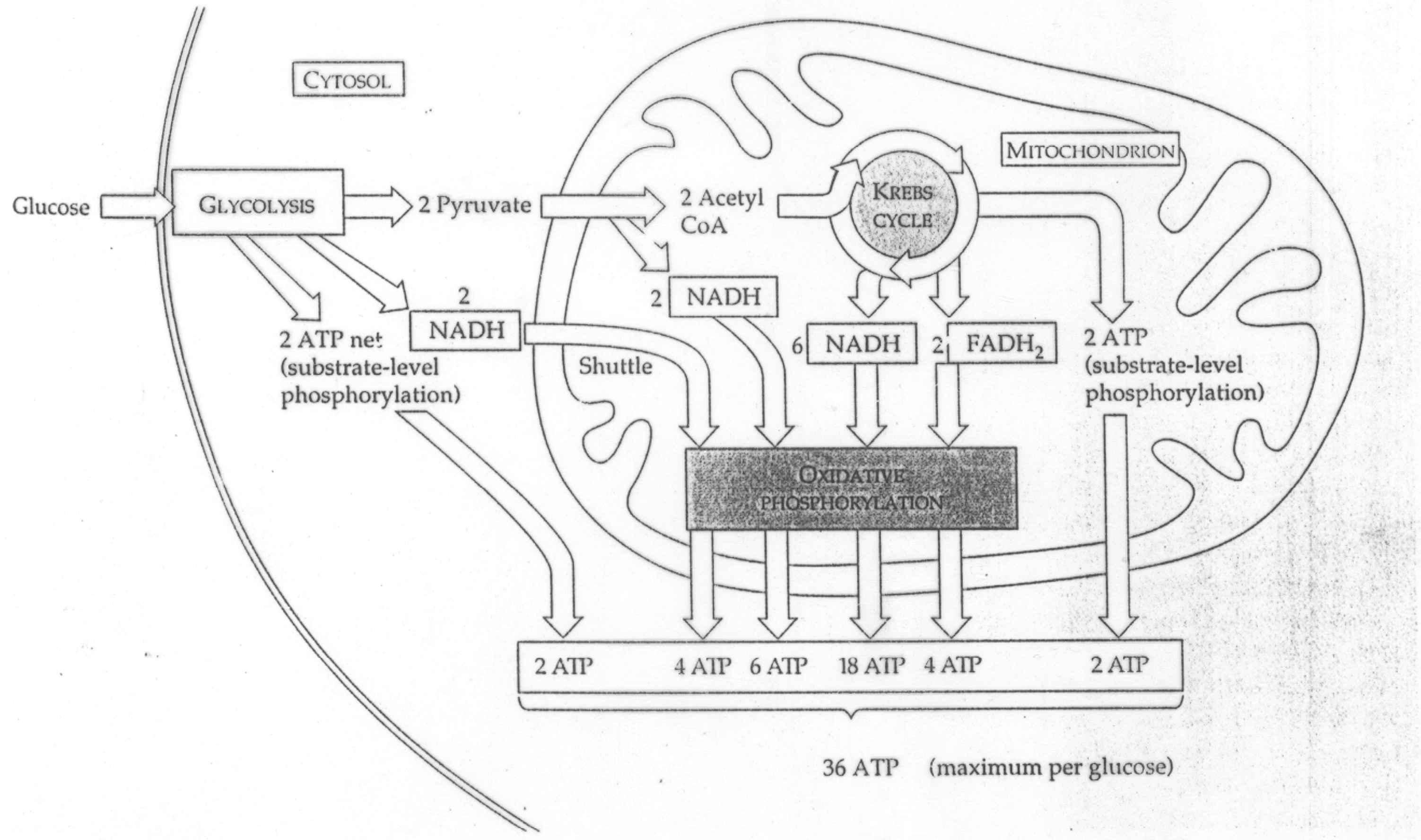

CYTOSOL
MITOCHONDRION
Glucose
GLYCOLYSIS
2 Pyruvate
2 Acetyl CoA
KREBS CYCLE
2 ATP net (substrate-level phosphorylation)
2 NADH
Shuttle
2 NADH
6 NADH
2 $FADH_2$
2 ATP (substrate-level phosphorylation)
OXIDATIVE PHOSPHORYLATION
2 ATP
4 ATP
6 ATP
18 ATP
4 ATP
2 ATP
36 ATP (maximum per glucose)

Figure 9.20

De-nitrification

- Not all De-nitrification capable to complete oxidation to nitrogen
- An electron donor (organic carbon source) required as a source of electrons

De-nitrification Reaction

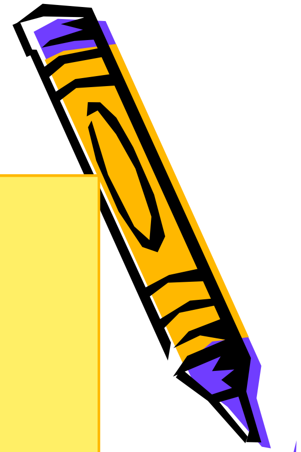
$NO^{-}_3 + 1.08CH_3OH + H^+ \rightarrow$

$0.065C_5H_7O_2N + 0.47N_2 + 0.76CO_2 + 2.44H_2O$

From the reaction

- De-nitrifiers bacteria utilize protons in the reduction of nitrate
- The medium tend to become alkaline compared with the acidity during nitrification
- Denitrifiers yield and growth will be higher than nitrifiers as the first heterotrophic bacteria

De-nitrification



- In sewage treatment by single stage, wastewater itself contains source of organic carbon
- In two-stage systems supplemental source of carbon must be provided

Industrial and agricultural wastes or methanol used commercially as available carbon and energy source

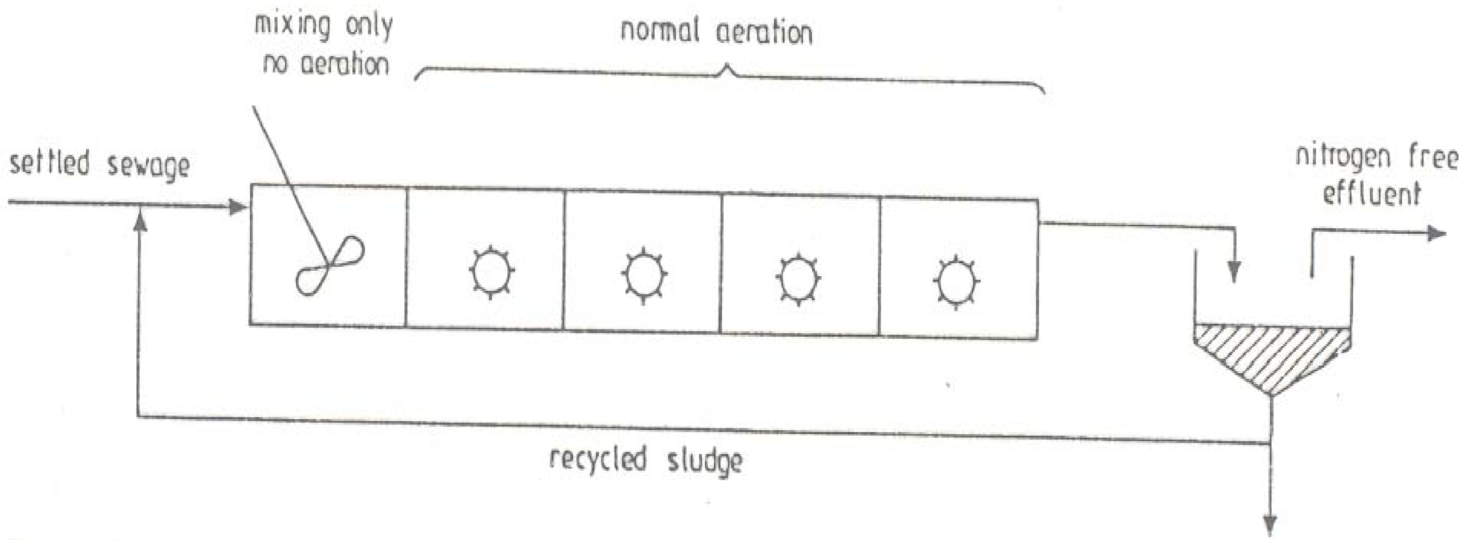


Figure 8.7 Nitrogen removal in a single-sludge activated sludge reactor. The first pocket is anoxic and receives the return sludge and settled sewage. The remaining pockets are aerobic and operated at a long sludge age in order to ensure full nitrification.

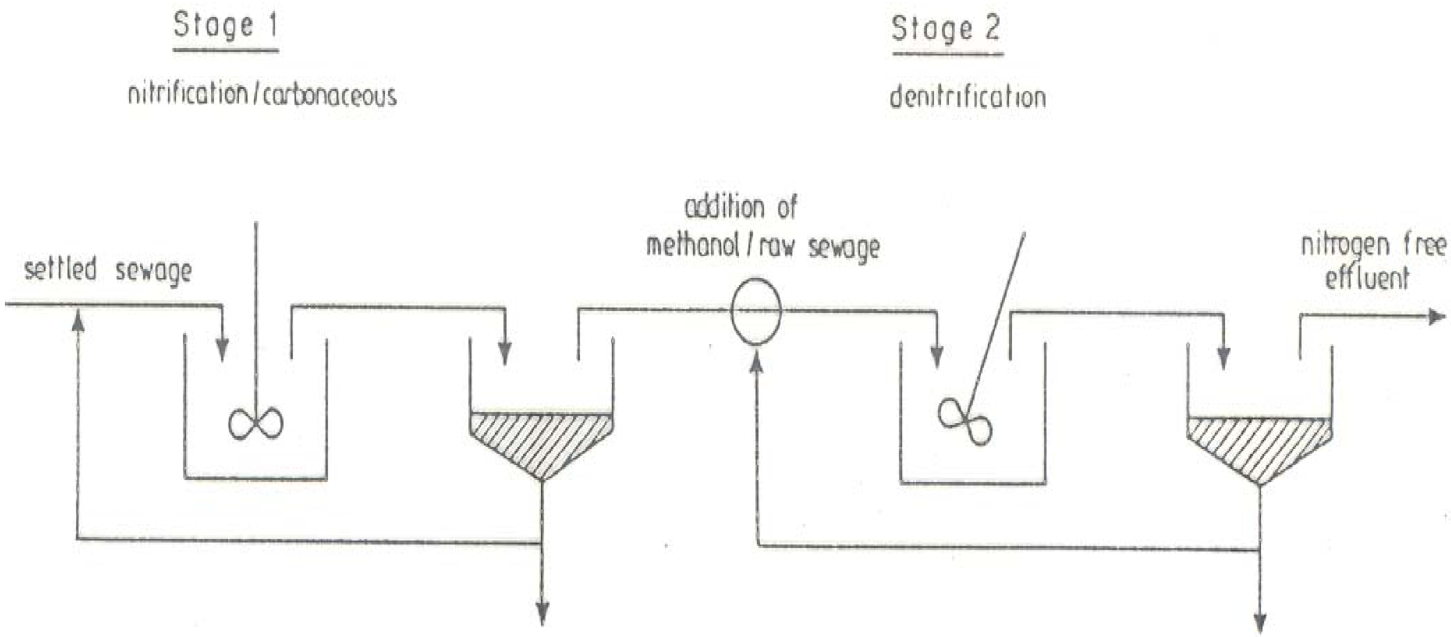
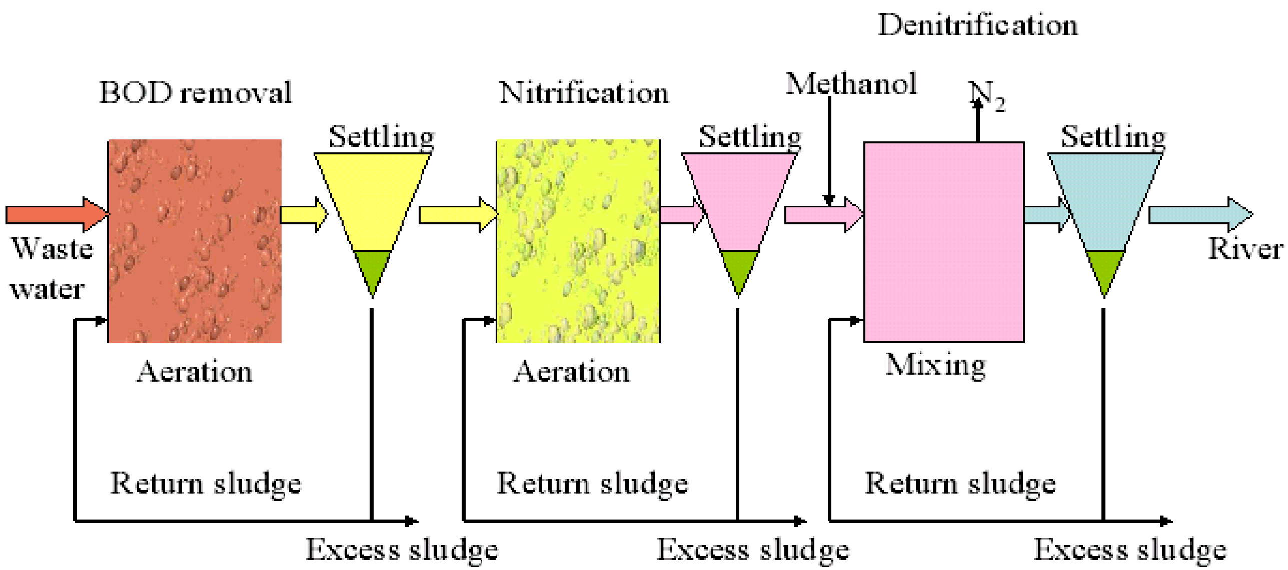


Figure 8.8 Two-stage system for nitrogen removal. Stage 1 is an aerobic reactor operated with a long sludge age to ensure nitrification. Stage 2 is anoxic and incorporates addition of a carbon source to ensure denitrification.



Advanced waste water treatment by three activated sludge system (Nitrogen removal)

Phosphorus Removal

- Phosphorus as nutrient , is rate limiting factor of growth of algae in receiving water
- Concentration of 10ug/1 required for algal growth

Cont==

Phosphorus Removal

- **Phosphorus control is one of effective ways of man-made eutrophication**
- **Apply phosphorus standard for sewage effluent discharges (1mg/1dissolved ortho-phosphate as phosphorus)**

Cont==

Phosphorus Removal

- **Typical concentration in sewage 10-30mg/1 as phosphorus**

- **Source of phosphorus: Human excreta (50-60%) and synthetic detergents (30-50%)**

Phosphorus Removal

Biological in AS system

Special system (stripper)

Enhanced biological phosphorus removed in activated sludge

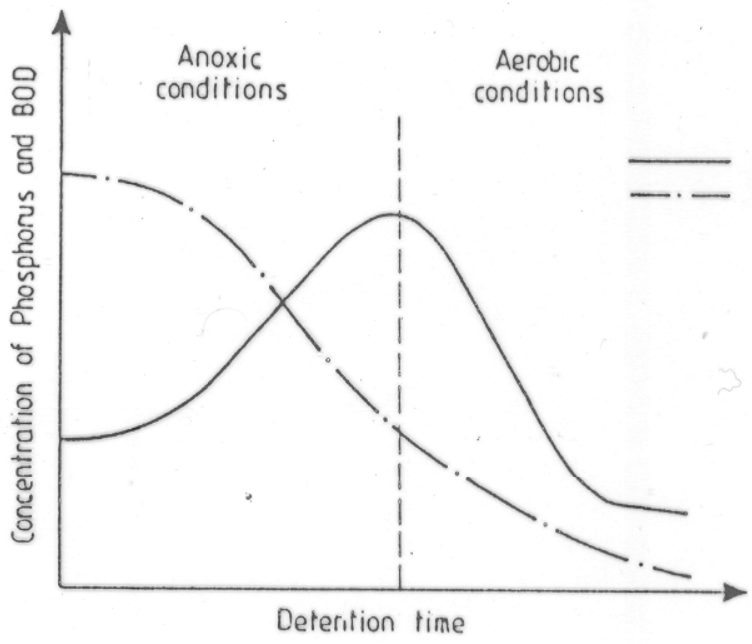


Figure 8.9 Enhanced phosphorus uptake observed in activated sludges when transferred from anoxic to aerobic conditions.

- **In anaerobic condition phosphorus transferred to ortho-phosphate, $PO^{-}4$, in the supernatant (soluble phosphorus)**

- **In aerobic condition, rapid uptake of phosphate by the sludge occur (insoluble phosphorus)**

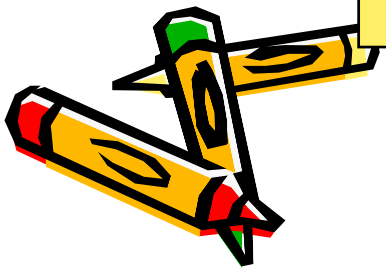
Mechanism of phosphorus stored and released in AS plants

- Phosphorus dynamic within the system connected with bacteria known as <u>Acinetobacter</u> <u>spp</u>
- Under aerobic condition , Acinetobacter spp, able to utilize sugars (normal pathway – high energy production
- Under aerobic condition , Acinetobacter spp, able to utilize sugars (normal pathway – high energy production
- Under anaerobic conditions , they degraded volatile fatty acids (acetate) with low energy yield

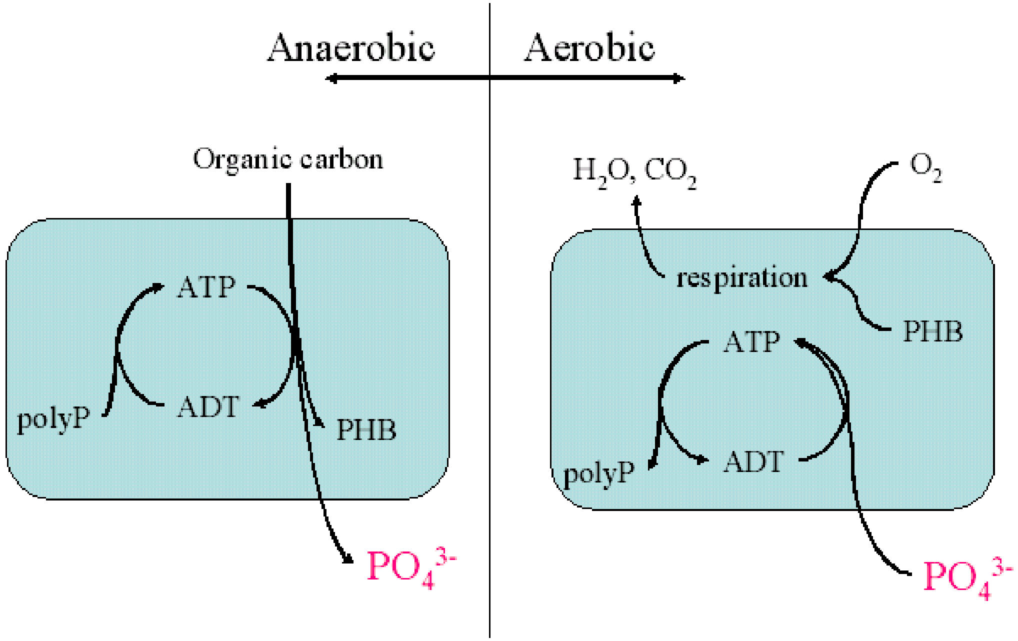
Organic matter

Acinetobacter SSP

Fatty acids
(poly 2-hydroxy butyrate)



Biochemical model of enhanced phosphorus uptake and release



PHB : poly-β-3 hydroxy butyric acid
polyP : poly phosphate

- **They storage the polymers ; Polly 2-hydoxy butyrate (phb) as an electron sink for the storage of excess organic carbon and volution (metachromate) granules as polyphosphate**

➢Polyphosphate formation from phosphate

synthesis

$$ATP + (PO_4)n \rightleftharpoons ADP + (PO_4)n+1$$

Degradation

Or by hydrolysis:

$$H_2O + (PO_4)n \rightarrow (PO_4)n-1 + HPO^{2-}_4 + H$$

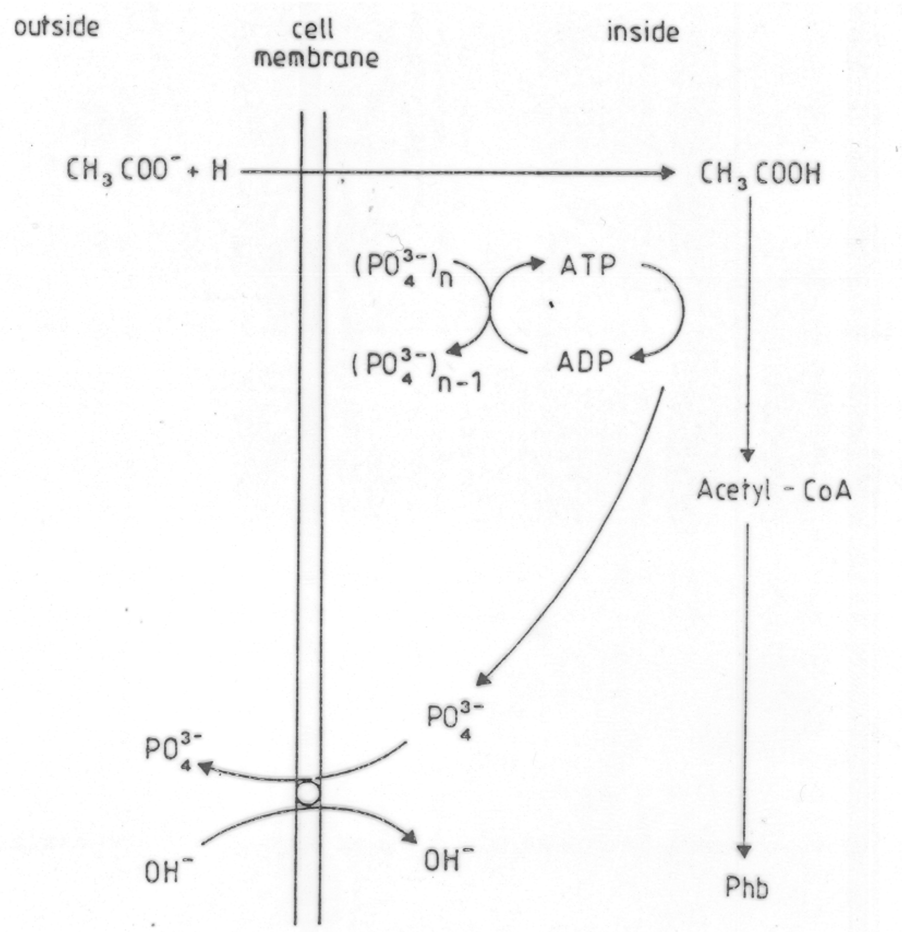


Figure 8.10 The uptake of acetate by *Acinetobacter* under anaerobic conditions and the synthesis of phb, concomitant with polyphosphate degradation and the release of phosphate across the cell wall.

Degradation of polyphosphate associated with energy release

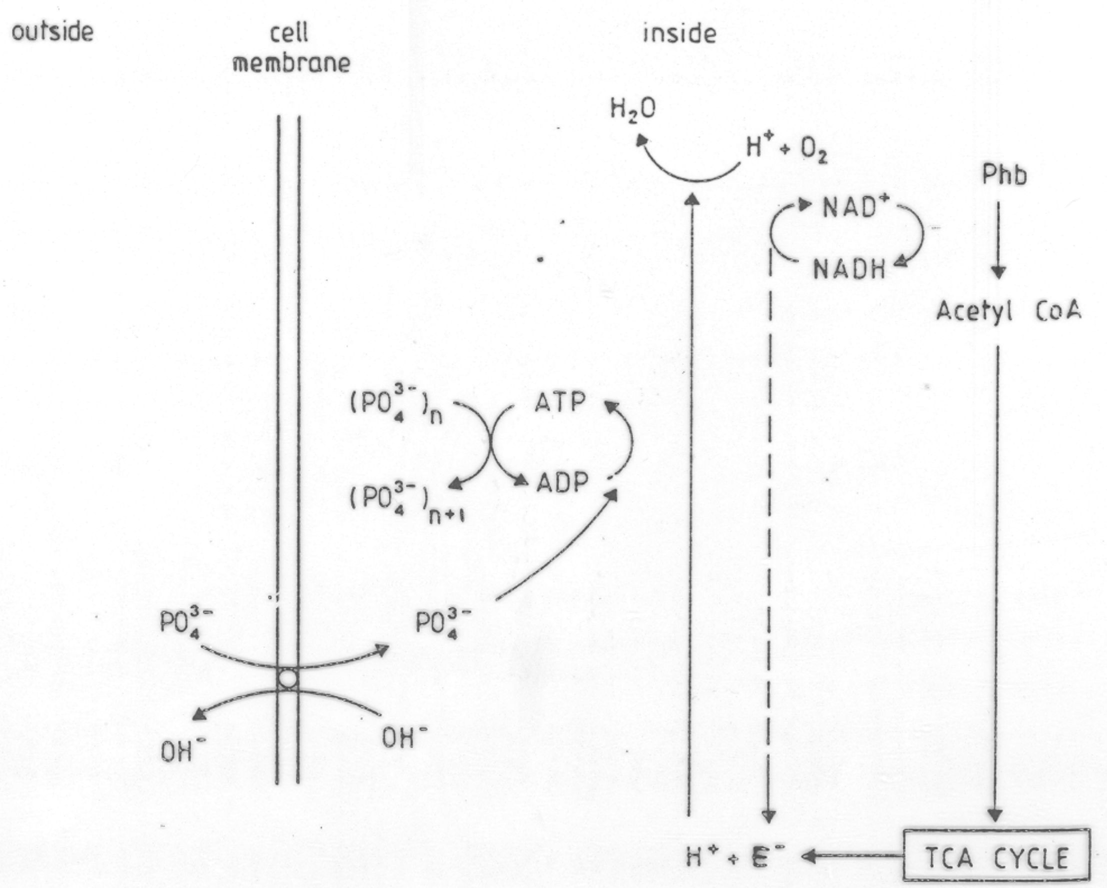
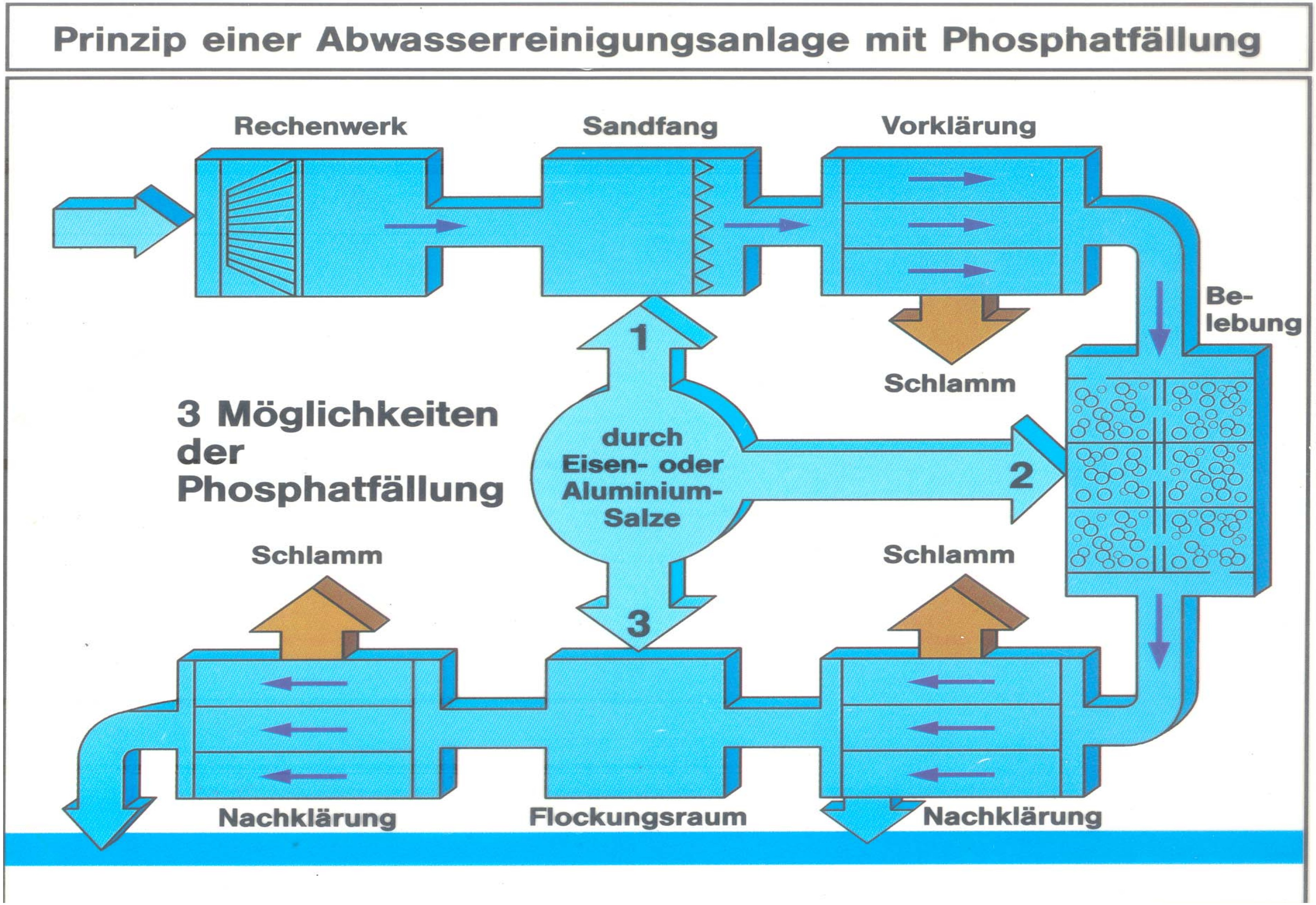


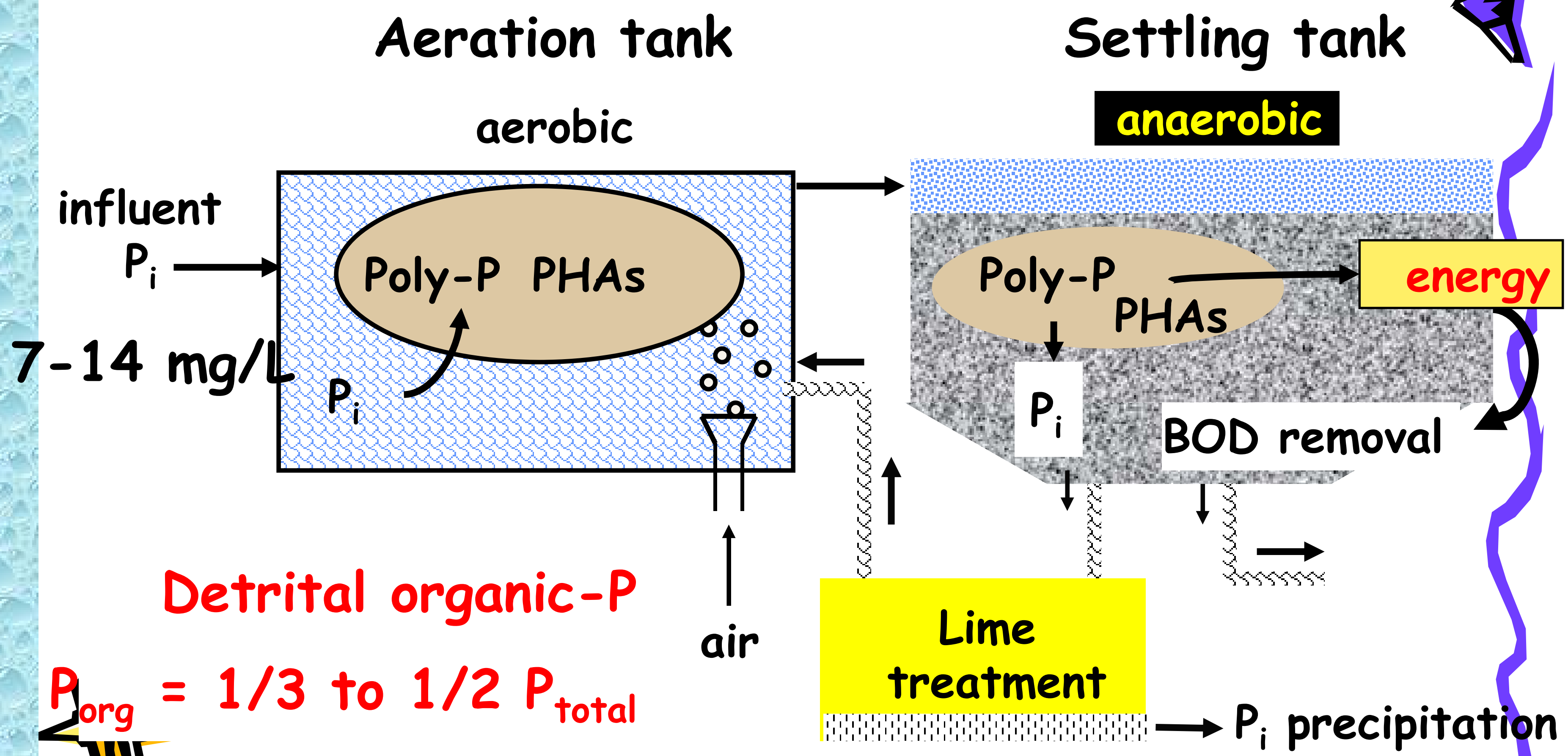
Figure 8.11 Phosphate uptake by *Acinetobacter* under aerobic conditions which is used in the synthesis of ATP and polyphosphate, using the energy from phb degradation.

Synthesis of polyphosphate associated with using energy release from phb degradation

Treatment system with phosphorus Removal



Luxury Phosphorus Uptake

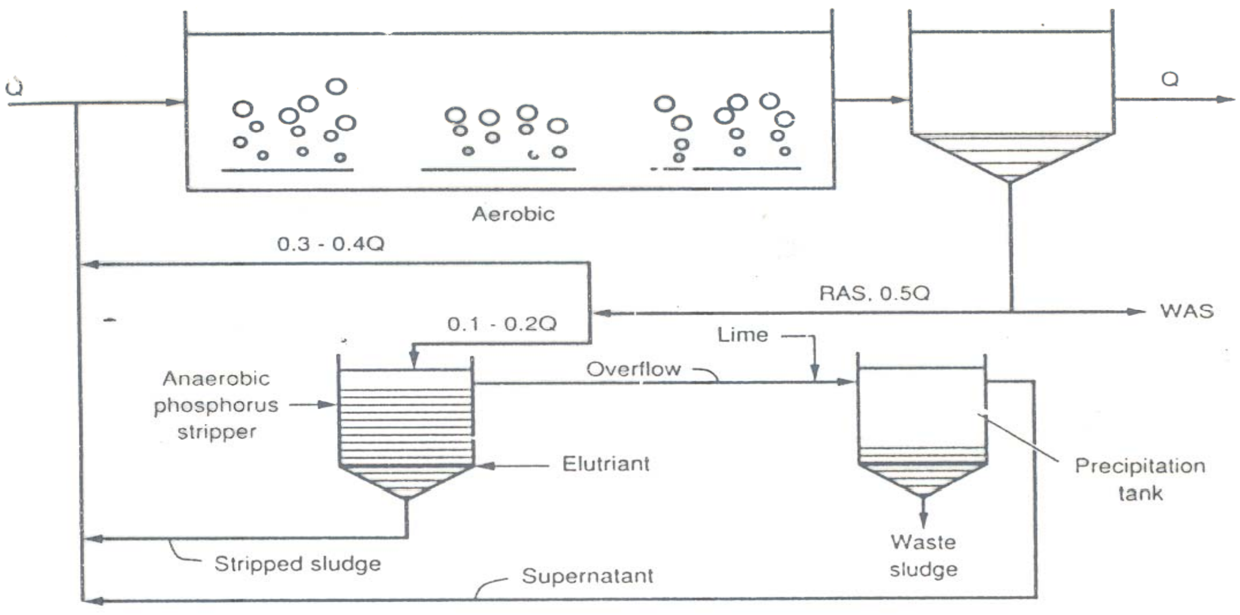


Detrital organic-P

P_{org} = 1/3 to 1/2 P_{total}

The phostrip process:

- **Under typical activated sludge system, sludge being wasted from the clarifies.**
- **The sludge retained for several hours in anaerobic tank**
- **Under anaerobic condition, phosphate released from the sludge in the supernatant**
- **The supernatant fed to tank dosed with lime and removed as calcium phosphate slurry {phosphate precipitated as Ca3(PO4)2}**



(a)

Bardenpho process

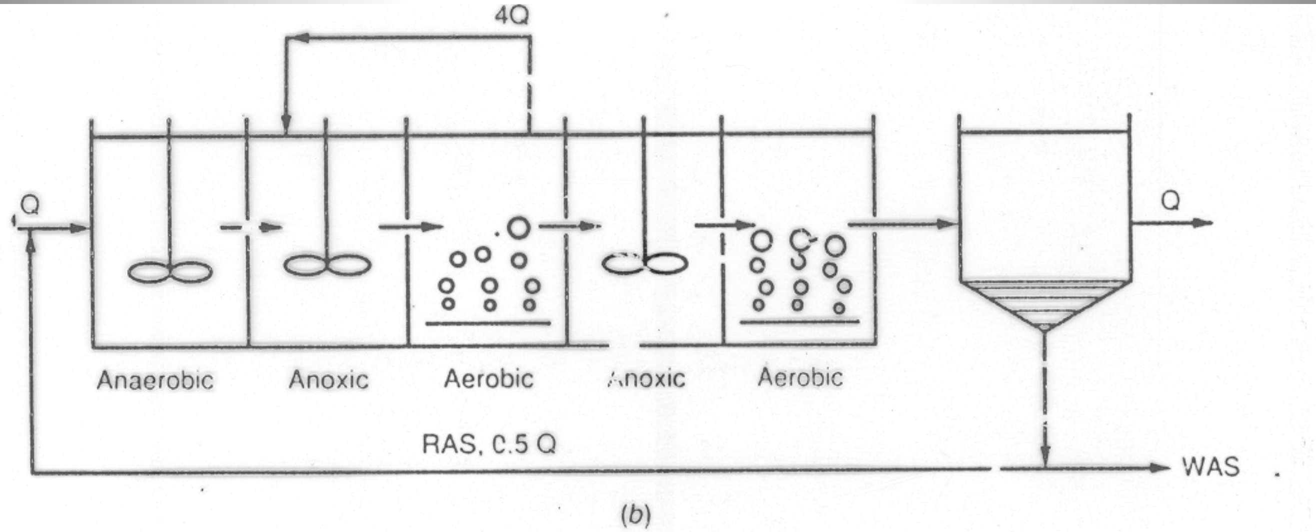
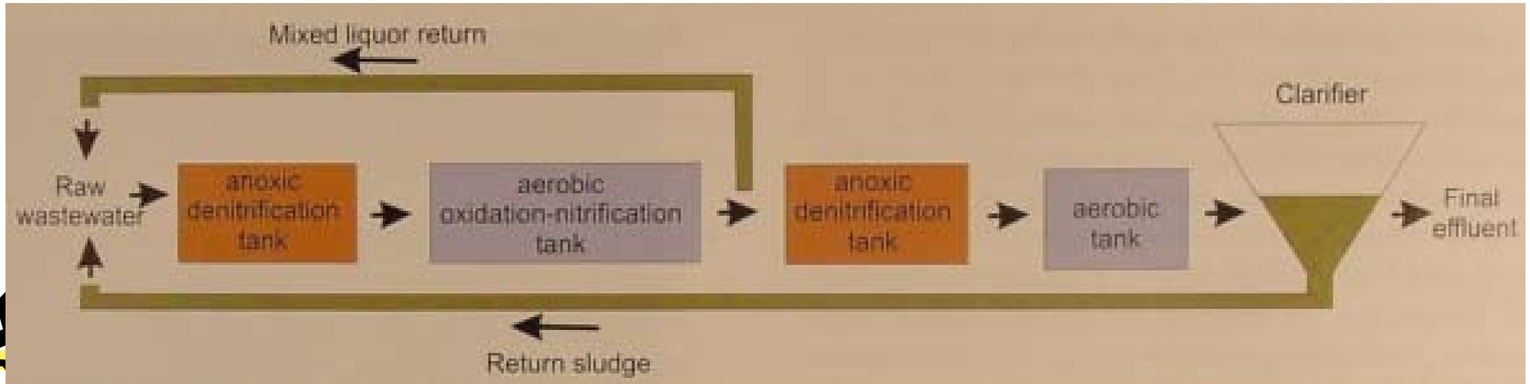
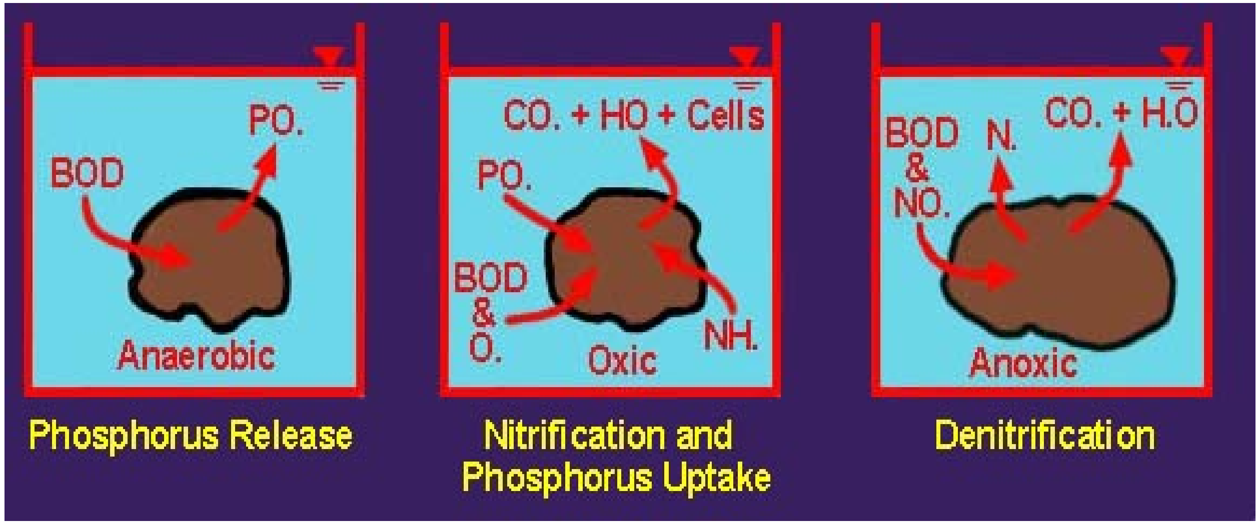
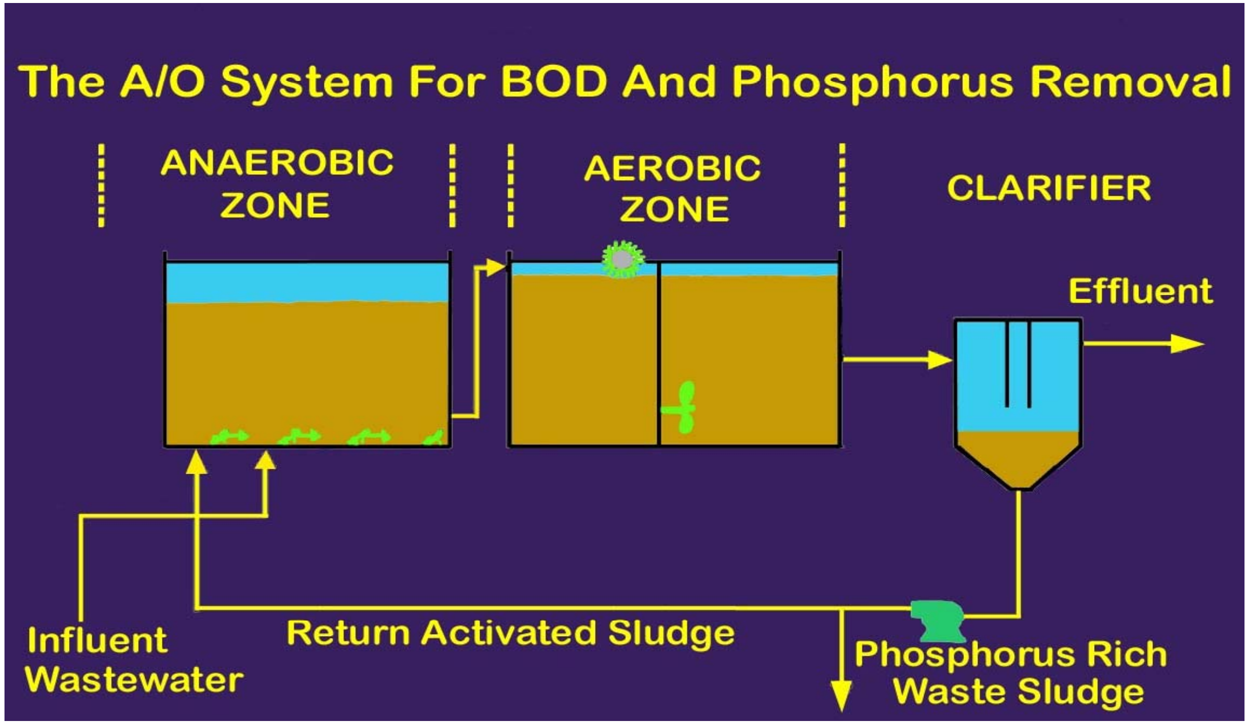


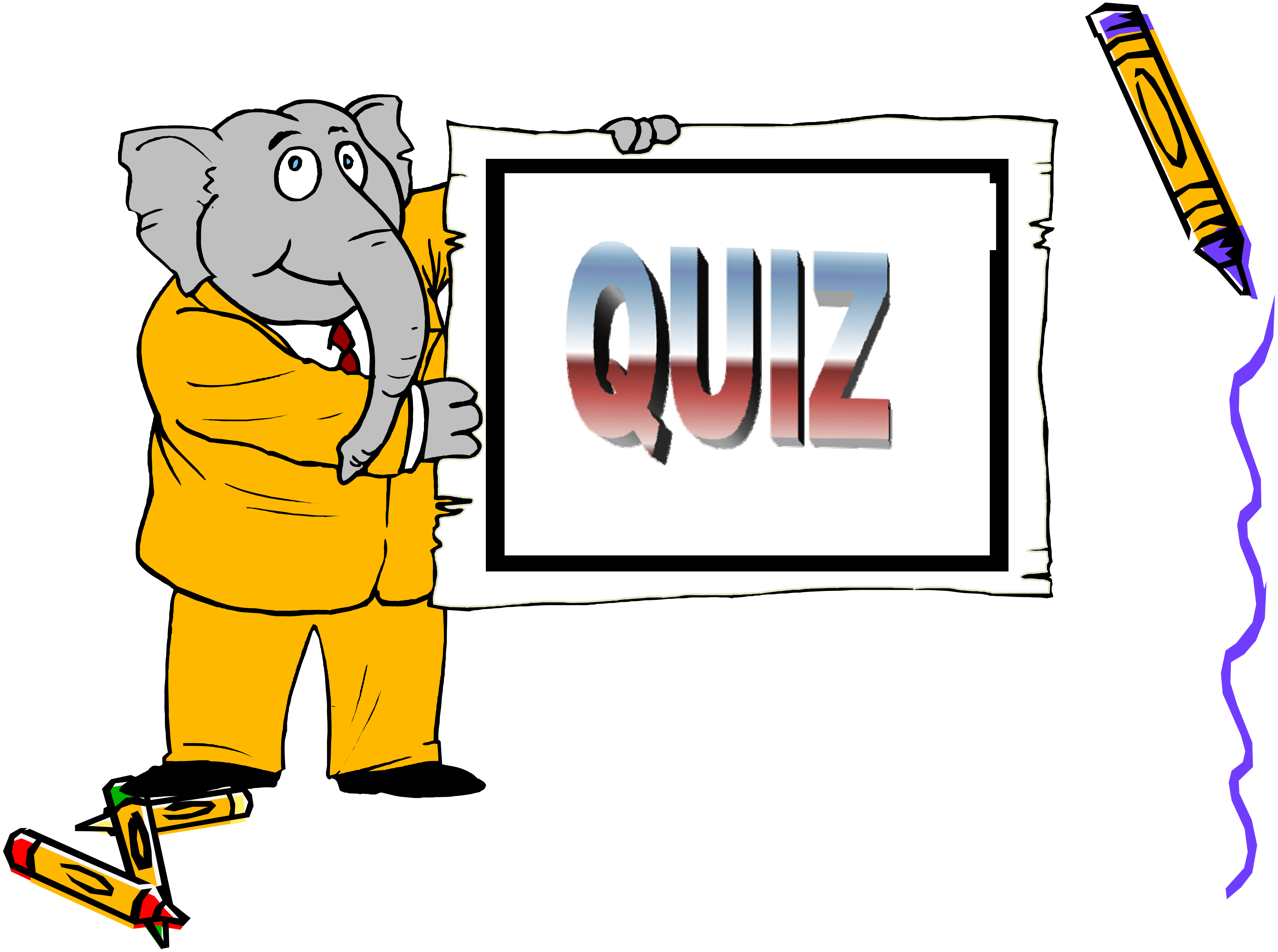
FIGURE 8-33
Typical treatment processes used for the biological removal of phosphorus: (a) PhoStrip process and (b) five-stage Bardenpho (adapted from Ref. 28).



Biological phosphorus removal reactions




The A/O System For BOD And Phosphorus Removal
ANAEROBIC ZONE
AEROBIC ZONE
CLARIFIER
Effluent
Influent Wastewater
Return Activated Sludge
Phosphorus Rich Waste Sludge


QUIZ

True or false:

1. Phosphorus is limiting factor of growth of algae in receiving water
2. In aerobic condition, slow uptake of phosphate by the sludge occur

3. The sludge retained for several hours in anaerobic tank in phostrip process

4. Concentration of 10Mg/1 required for algal growth

5. Under anaerobic condition , Acinetobacter spp, able to utilize sugars