ENVE 302

Environmental Engineering Unit Processes

CHAPTER: 1

Principal wastewater constituents

Treatment methods for wastewater

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Wastewater

WASTEWATER
- → Industrial ww
- → Municipal (domestic) ww

Characteristics of industrial ww → vary from industry to industry

Industrial wastewater with characteristics compatible with municipal ww is often discharged to municipal sewers.

However, many industrial ww require pre-treatment to remove non-compatible substances prior to discharge into municipal system

Typical Composition of Domestic Wastewater

Table 3–15
Typical composition of untreated domestic wastewater

Ref: Metcalf & Eddy, 2004

Contaminants	Unit	Concentration[a] Low strength	Medium strength	High strength
Solids, total (TS)	mg/L	390	720	1230
Dissolved, total (TDS)	mg/L	270	500	860
Fixed	mg/L	160	300	520
Volatile	mg/L	110	200	340
Suspended solids, total (TSS)	mg/L	120	210	400
Fixed	mg/L	25	50	85
Volatile	mg/L	95	160	315
Settleable solids	mL/L	5	10	20
Biochemical oxygen demand, 5-d, 20°C (BOD_5, 20°C)	mg/L	110	190	350
Total organic carbon (TOC)	mg/L	80	140	260
Chemical oxygen demand (COD)	mg/L	250	430	800
Nitrogen (total as N)	mg/L	20	40	70
Organic	mg/L	8	15	25
Free ammonia	mg/L	12	25	45
Nitrites	mg/L	0	0	0
Nitrates	mg/L	0	0	0
Phosphorus (total as P)	mg/L	4	7	12
Organic	mg/L	1	2	4
Inorganic	mg/L	3	5	10
Chlorides[b]	mg/L	30	50	90
Sulfate[b]	mg/L	20	30	50
Oil and grease	mg/L	50	90	100
Volatile organic compounds (VOCs)	mg/L	<100	100–400	>400
Total coliform	No./100 mL	10^6–10^8	10^7–10^9	10^7–10^{10}
Fecal coliform	No./100 mL	10^3–10^5	10^4–10^6	10^5–10^8
Cryptosporidum oocysts	No./100 mL	10^{-1}–10^0	10^{-1}–10^1	10^{-1}–10^2
Giardia lamblia cysts	No./100 mL	10^{-1}–10^1	10^{-1}–10^2	10^{-1}–10^3
Alkalinity (as $CaCO_3$)	mg/L	50	100	200
Wastewater flow	Lcd	750	460	240

Constituents of Wastewater

Physical

- Solids
- Turbidity
- Color
- Temperature
- Density
- Conductivity

Chemical

Inorganic

- Nutrients(N,P)
- Metals
- Gases
- pH
- Chloride
- Sulfur
- Alkalinity

Organic

Aggregate organic constituents
(comprising a number of organic constituents with similar characteristics that can not be distinguished separately.

Typical domestic ww 40-60% protein
25-50% carbonhydrate
8-12% oil-fat.

Individual compounds
VOCs, phenols, pesticides.

Biological

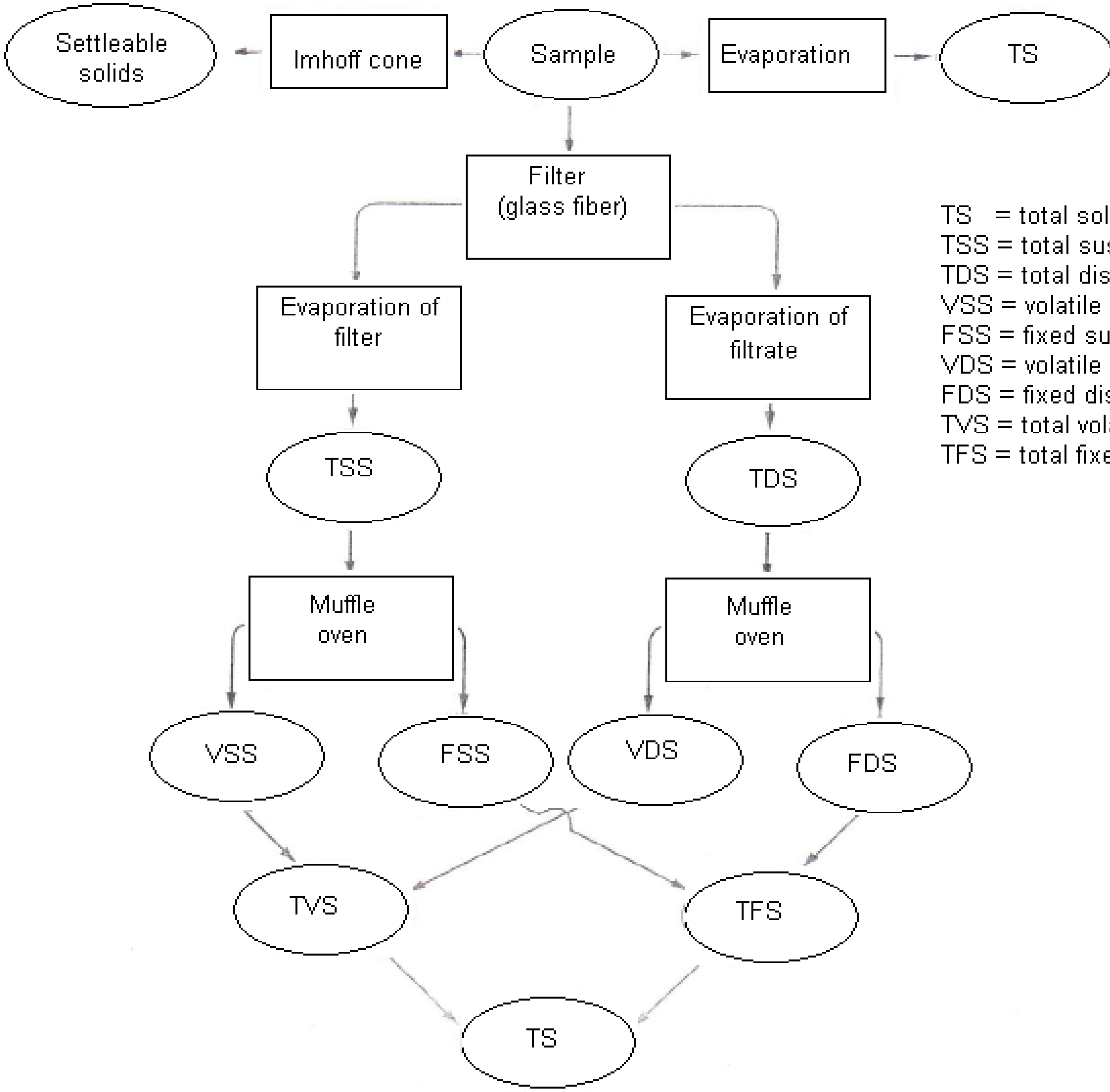
- Microorganisms
- Pathogenic organisms

Classification of Solids

Figure 2-3

Interrelationships of solids found in water and wastewater. In much of the water quality literature, the solids passing through the filter are called dissolved solids. (Tchobanoglous and Schroder, 1985.)

Ref: Metcalf & Eddy, 2004



TS = total solids
TSS = total suspended solids
TDS = total dissolved solids
VSS = volatile suspended solids
FSS = fixed suspended solids
VDS = volatile dissolved solids
FDS = fixed dissolved solids
TVS = total volatile solids
TFS = total fixed solids

Measurement of Solids

Table 2-4

Definitions for solids found in wastewater

Ref: Metcalf & Eddy, 2004

Test[b]	Description
Total solids (TS)	The residue remaining after a wastewater sample has been evaporated and dried at a specified temperature (103 to 105°C)
Total volatile solids (TVS)	Those solids that can be volatilized and burned off when the TS are ignited (500 ± 50°C)
Total fixed solids (TFS)	The residue that remains after TS are ignited (500 ± 50°C)
Total suspended solids (TSS)	Portion of the TS retained on a filter (see Fig. 2-4) with a specified pore size, measured after being dried at a specified temperature (105°C). The filter used most commonly for the determination of TSS is the Whatman glass fiber filter, which has a nominal pore size of about 1.58 μm
Volatile suspended solids (VSS)	Those solids that can be volatilized and burned off when the TSS are ignited (500 ± 50°C)
Fixed suspended solids (FSS)	The residue that remains after TSS are ignited (500 ± 50°C)
Total dissolved solids (TDS) (TS − TSS)	Those solids that pass through the filter, and are then evaporated and dried at specified temperature. It should be noted that what is measured as TDS is comprised of colloidal and dissolved solids. Colloids are typically in the size range from 0.001 to 1 μm
Total volatile dissolved solids (VDS)	Those solids that can be volatilized and burned off when the TDS are ignited (500 ± 50°C)
Fixed dissolved solids (FDS)	The residue that remains after TDS are ignited (500 ± 50°C)
Settleable solids	Suspended solids, expressed as milliliters per liter, that will settle out of suspension within a specified period of time

[a] Adapted from Standard Methods (1998).

[b] With the exception of settleable solids, all solids values are expressed in mg/L.

Characterization of Organic Content

- → BOD (Biochemical Oxygen Demand)
- → COD (Chemical Oxygen Demand)
- → TOC (Total Organic Carbon)
- → ThOD (Theoretical Oxygen Demand)
- → UV absorbing organic constituents

BOD (Biochemical Oxygen Demand)

Measurement of the dissolved oxygen used by microorganisms in the biochemical oxidation of organic matter

→ **CBOD (carbonecous BOD):** oxygen demand exerted by the oxidizable carbon in the sample

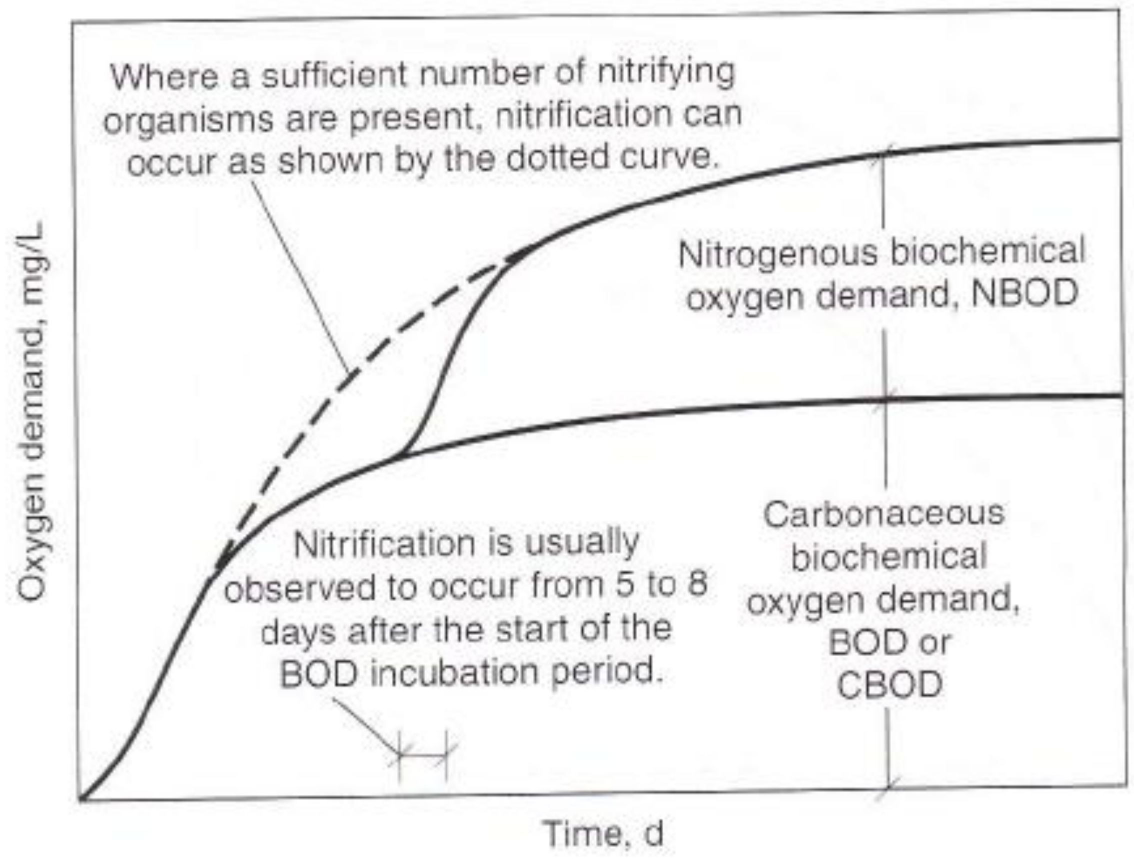
→ **NBOD (nitrogenous BOD):** oxygen demand associated with the oxidation of ammonia to nitrate (nitrification)

cBOD & nBOD

Figure 2–22

Definition sketch for the exertion of the carbonaceous and nitrogenous biochemical oxygen demand in a waste sample.

Ref: Metcalf & Eddy, 2004



Reproductive rate of nitrifiers is slow → it normally takes from 6-10 days for them to reach significant numbers to exert a measurable oxygen demand

However; if a sufficient number of nitrifying bacteria is present initially

interference of cBOD measurement caused by nitrifiers can be significant

To supress nitrification;

- Methylene blue
- ATU (Allythiourea)

COD (Chemical Oxygen Demand)

Measure the oxygen equivalent of the organic material in wastewater that can be oxidized chemically using dichromate in an acid solution

$$C_nH_aO_bN_c + dCr_2O_7^{-2} + (8d+c)H^+ \rightarrow nCO_2 + \frac{a+8d-3c}{2}H_2O + cNH_4^+ + 2dCr^{+3}$$

where $d = \frac{2n}{3} + \frac{a}{6} - \frac{b}{3} - \frac{c}{2}$

Why not cBOD is equal to COD ?

1. Many organic substances which are difficult to oxidize biologically (e.g lignin) can be oxidized chemically.

2. Inorganic substances that are oxidized by dichromate (e.g sulfide,sulfite, ferrous ion)

3. Certain organic substances may be toxic to microorganisms used in the BOD test.

Typical BOD/COD of untreated domestic wastewater: 0.5-0.8

If BOD/COD ratio is 0.5:

→Waste is considered to be easily treatable by biological means

If BOD/COD ratio is 0.3:

→Organics in wastewater may be refractory

→Organics in wastewater are degradable. However, another substance in wastewater leads to inhibition of bacteria that uses organic matter

→Bacteria is not acclimated to wastewater

TOC (Total Organic Carbon)

- → Done instrumentally (5-10 min) to determine total organic carbon in aqueous sample (mg C/L)

- → This test measures all C as CO_2

- → Inorganic C (CO_2, HCO_3) present in wastewater must be removed prior to analysis

by acidification and aeration of sample prior to analysis

Typical BOD/TOC of untreated domestic wastewater 1.2-2mg O_2/mg C

ThOD (Theoretical Oxygen Demand)

→ ThOD of a wastewater is calculated as the oxygen required to oxidize the organics to end products

Example : glycine $CH_2(NH_2)COOH$

→ $CH_2(NH_2)COOH + 3/2\ O_2 \qquad NH_3 + 2\ CO_2 + H_2O$

For nitrogenous oxygen demand :

→ $NH_3 + 3/2\ O_2 \qquad HNO_2 + H_2O$

→ $HNO_2 + 1/2\ O_2 \qquad HNO_3 + H_2O$

→ ThOD = (3/2 + 3/2 + 1/2) mol O_2 / mol glycine

UV Absorbing Constituents

- → Humic substances
- → Lignin
- → Tannin
- → Various aromatic compounds

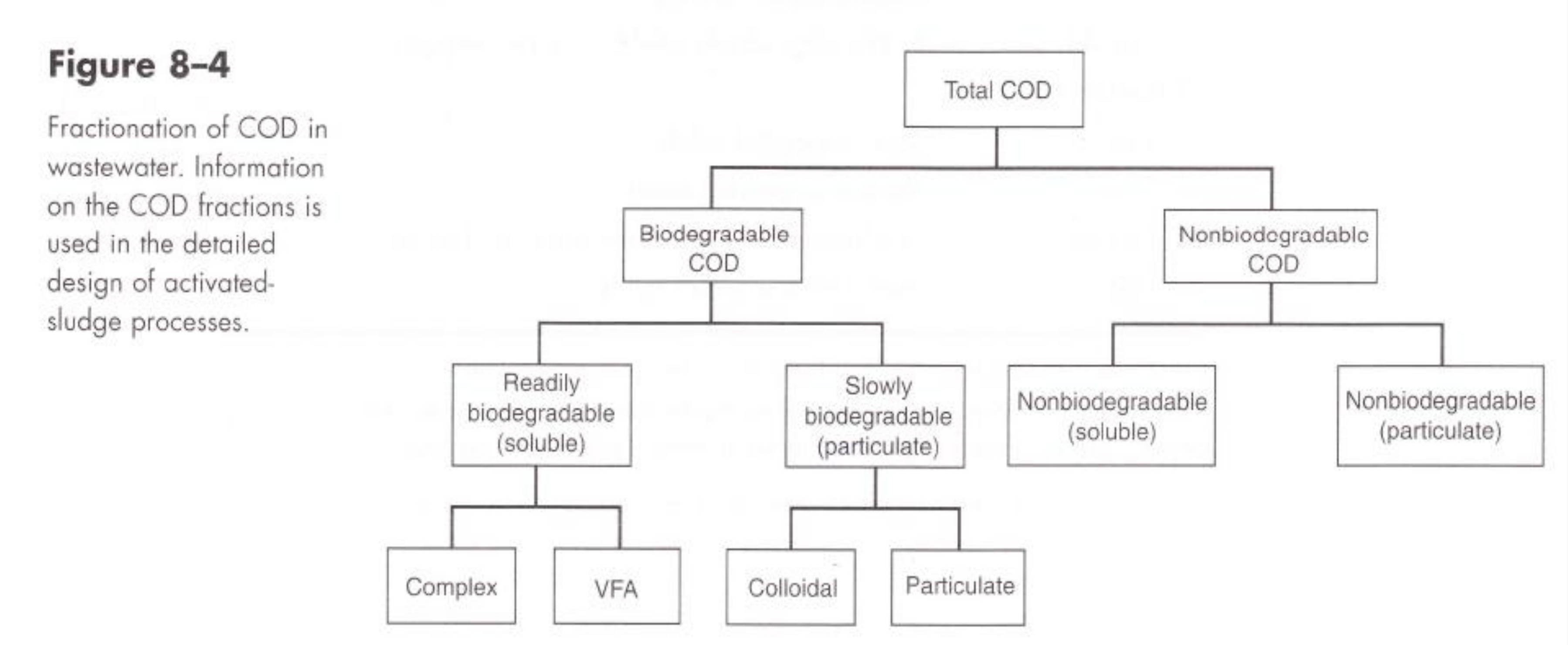
} Strongly absorb UV

UV absorption has been used as a surrogate measure for the organic compounds cited above

UV wavelength = 200 – 400 nm (254 nm most common)

COD Fractionation

Ref: Metcalf & Eddy, 2004



rbsCOD (soluble) : quickly assimilated by biomass

sbCOD (particulate) : must be firts dissolved by extracellular enzymes
assimilated much slower rate

nbVSS – nonbiodegredable particulate (nbpCOD): since it is organic material, it will also contribute VSS.

Influent wastewater will also contain non-voltile suspended solids that add to the MLSS concentration

Inert TSS (iTSS) → $iTSS = TSS_{inf} - VSS_{eff}$

Determination of soluble COD

Filtration through 0.45µm membrane→analysis of the for COD

Determination of bCOD

BOD test data is necessary

bCOD consumed
in BOD test = oxygen consumed (uBOD) + oxygen equivalent of remaining cell debris

bCOD = uBOD + 1.42 fd Yh bCOD

fd: Fraction of cell mass remainig as cell debris (g/g)

Yh: Yield coeff. g VSS/g COD used

bCOD/BOD= (uBOD/BOD) / (1-1.42 fd Yh)

For typical domestic ww:

fd=0.15, Yh=0.4, uBOD/BOD=1.5 → bCOD/BOD=1.64

Not all of the bCOD is oxidized in the BOD test

Some of the bCOD is converted into biomass

→ uBOD < bCOD

Determination of rbCOD

Biological Response Test for rbCOD

→ Pre-aerated wastewater mixed with acclimated sludge

→ DO concentrations with respect to time is measured

→ Slope of DO vs time graph

(mg/L DO) / time = OUR (Oxygen Uptake Rate)

→ When DO decreases to about 3mg/L , vigorous aeration is applied to elevate DO conc. to 5 to 6 mg/L. So another OUR measurement can begin

Biological Response Test for rbCOD (continue)

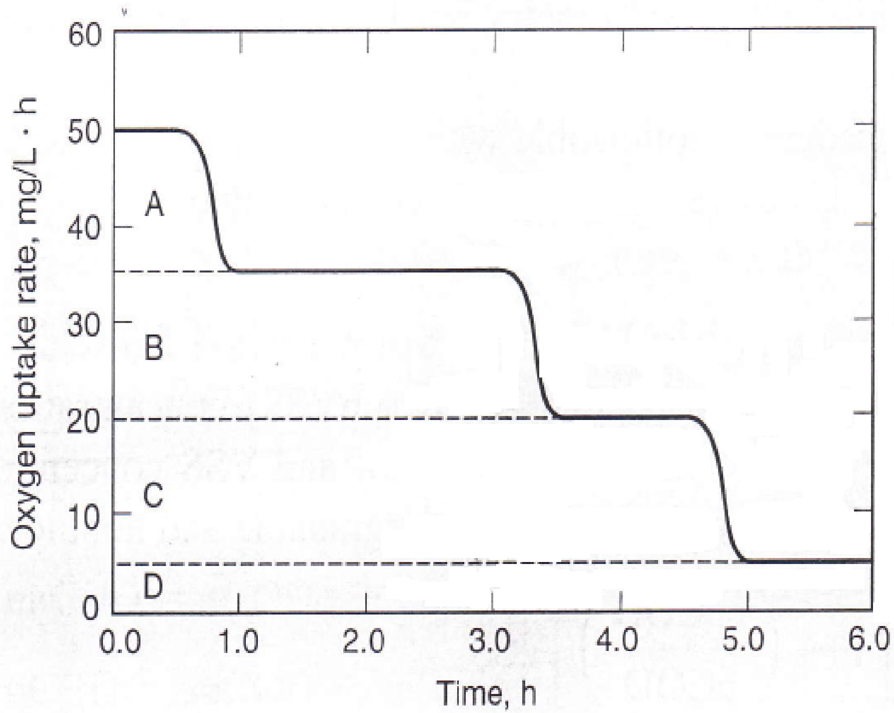


Figure 8.6
Idealized OUR in aerobic batch test for a mixture of influent wastewater and activated sludge mixed liquor. Area A represents rbCOD oxygen demand (Barker and Dold, 1997)

$$rbCOD = \frac{O_A}{1 - Y_{H,COD}} \left(\frac{V_{AS} + V_{WW}}{V_{WW}} \right)$$

V_{AS}=volume of activated sludge used in the test (mL)

V_{ww}=volume of ww (mL)

O_A=oxygen consumed in area A (mg/L)

$Y_{H,COD}$=synthesis yield coeff for heterotrophic becteria

(g cell COD/g COD used)

b) Physical seperation technique for rbCOD (Mammais et al, 1993)

- → may not give the exact results as the rbCOD concentration determination by respirometry, but it provides a reasonable estimate
- → used widely because of its simplicity
- → The procedure is based on the assumption that suspended solids and colloidal material can be captured effectively and removed by flocculation with a zinc hydroxide precipitate to leave only truly dissolved organic material after filtration

Physical seperation technique for rbCOD (continue)

Procedure:

- → 1 ml of a 100 g/L $ZnSO_4$ solution is added to 100 ml of sample with vigorous mixing for 1 min
- → The pH is raised to about 10.5 using 6 M NaOH with 5-10 min of gentle mixing for floc formation
- → The sample is settled for 10-20 min and the supernatant is withdrawn and filtered using a 0.45 µm membrane filter
- → The filtrate is analyzed for COD conc. → rbCOD
- → rbCOD = COD_{ww} – COD act. sludge treated sample

sCOD= soluble COD
sBOD= soluble BOD

} Filtration through 0.45μm membrane filter

Non – biodegradable VSS

$$nbVSS = \left[1 - \left(\frac{bpCOD}{pCOD}\right)\right] VSS$$

$$\frac{bpCOD}{pCOD} = \frac{(bCOD/BOD)(BOD - sBOD)}{COD - sCOD}$$

Summary

COD= bCOD+nbCOD

bCOD= 1.6 BOD (for domestic wastewater)

nbCOD= $sCOD_e$+nbpCOD

bCOD= sbCOD+rbCOD

Nitrogen Forms in Wastewater

- Ammonia (NH_3)
- Ammonium (NH_4)
- Nitrite (NO_2^-)
- Nitrate (NO_3^-)
- Organic nitrogen

$NH_4 \longleftrightarrow NH_3 + H^+$

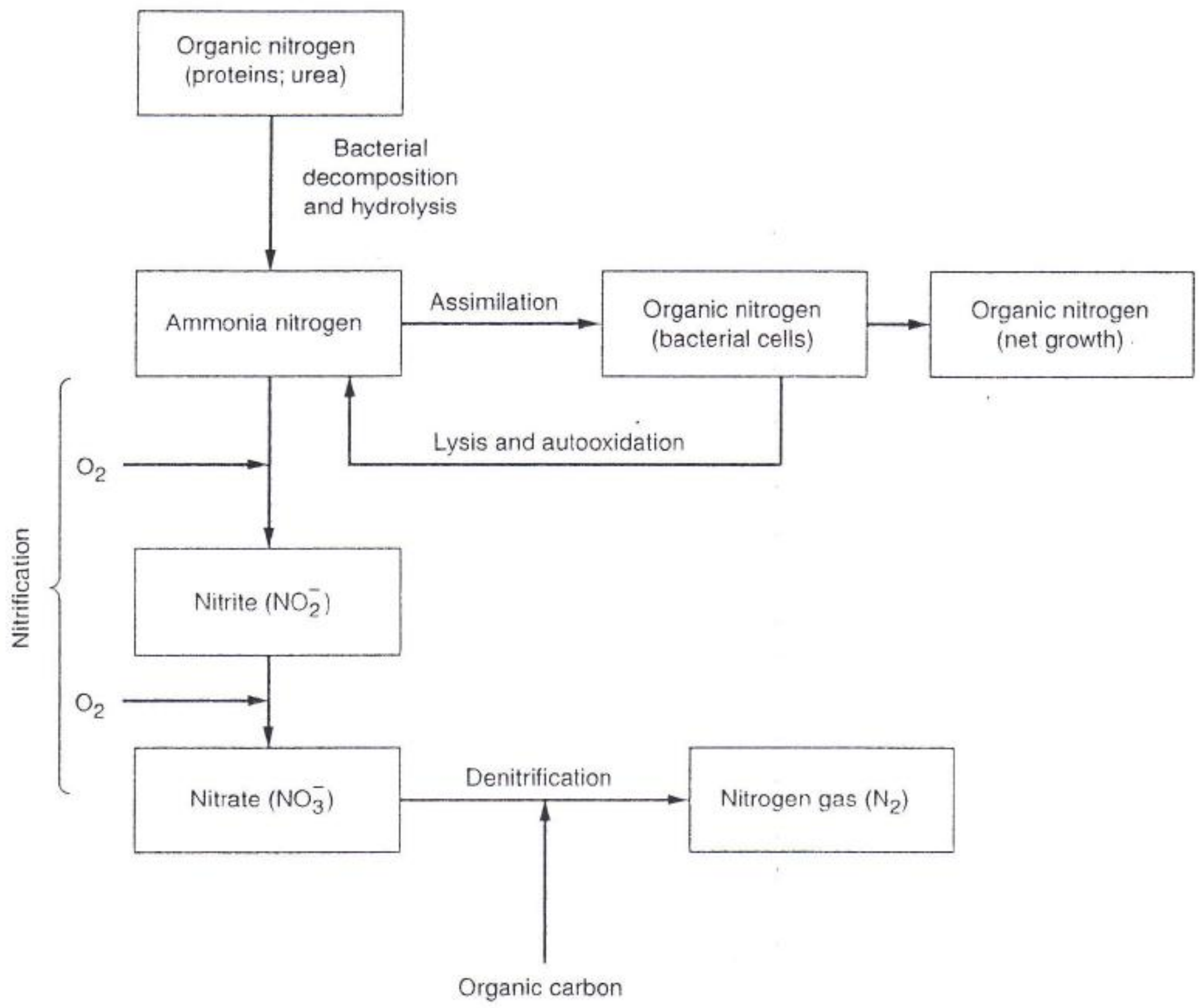
pH>7 rxn. shifts right

pH<7 rxn. shifts left

Total Nitrogen = Organic N+NH_3+NH_4+NO_2^-+NO_3^-

Total Kjeldahl Nitrogen (TKN) = Organic N+NH_3+NH_4

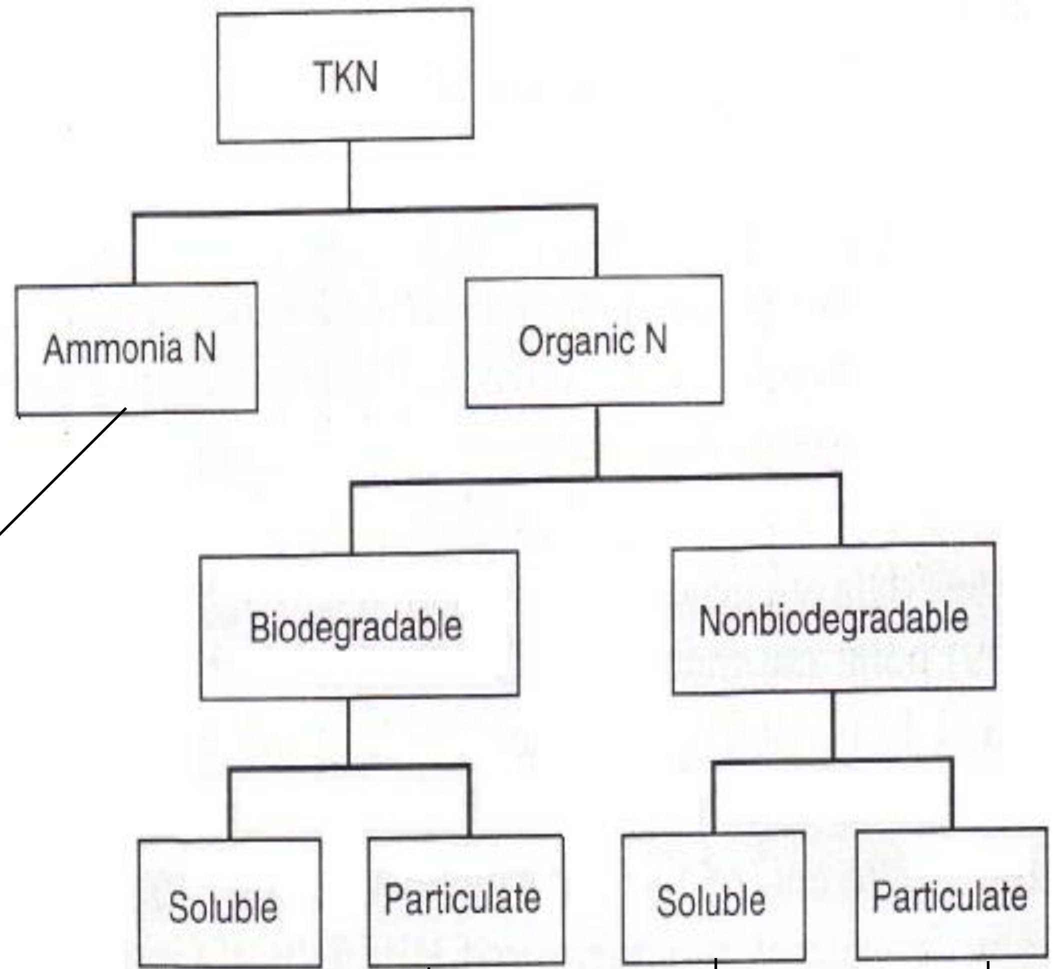
Nitrogen Transformations in Biological Treatment Processes



Ref: Metcalf & Eddy, 2004

Figure 8-5

Fractionation of nitrogen in wastewater. Information on the nitrogen fractions is used in the detailed design of nitrification and denitrification processes.



Ammonia N: about 60-70% of the influent TKN

readily available for bacterial synthesis and nitrification.

Biodegradable particulate: will be removed more slowly than soluble degradable organic nitrogen because a **hydrolysis** reaction is necessary first

Nonbiodegradable soluble: will be found in the secondary clarifier effluent (<3% of influent TKN)

Nonbiodegradable particulate: will be captured in the activated sludge floc and exit in waste sludge

Ref: Metcalf & Eddy, 2004

Table 8.2
Definition of terms used to characterize important wastewater constituents used for the analysis an design of biological wastewater processes

Constituent[a,b]	Definition
BOD	
BOD	Total 5-d biochemical oxygen demand
sBOD	Soluble 5-d biochemical oxygen demand
UBOD	Ultimate biochemical oxygen demand
COD	
COD	Total chemical oxygen demand
bCOD	Biodegradable chemical oxygen demand
pCOD	Particulate chemical oxygen demand
sCOD	Soluble chemical oxygen demand
nbCOD	Nonbiodegradable chemical oxygen demand
rbCOD	Readily biodegradable chemical oxygen demand
rbsCOD	Readily biodegradable soluble chemical oxygen demand
sbCOD	Slowly biodegradable chemical oxygen demand
bpCOD	Biodegradable particulate chemical oxygen demand
nbpCOD	Nonbiodegradable particulate chemical oxygen demand
nbsCOD	Nonbiodegradable soluble chemical oxygen demand
Nitrogen	
TKN	Total Kjeldahl nitrogen
bTKN	Biodegradable total Kjeldahl nitrogen
sTKN	Soluble (filtered) total Kjeldahl nitrogen
ON	Organic nitrogen
bON	Biodegradable organic nitrogen
nbON	Nonbiodegradable organic nitrogen
pON	Particulate organic nitrogen
nbpON	Nonbiodegradable particulate organic nitrogen
sON	Soluble organic nitrogen
nbsON	Nonbiodegradable soluble organic nitrogen
Suspended Solids	
TSS	Total suspended solids
VSS	Volatile suspended solids
nbVSS	Nonbiodegradable volatile suspended solids
iTSS	Inert total suspended solids

[a] *Note:* b = biodegradable; i = inert; n = non; p = particulate; s = soluble.

[b] Measured constituent values, based on the terminology given in this table, will vary depending on the technique used to fractionate a particular constituent.

Phosphorus

- Orthophosphate (PO_4^{-3} , HPO_4^{-2} , H2PO_4^{-} , H_3PO_4)

  available for biological metabolism without further breakdown

- Polyphosphate

  Undergo hydrolysis (quite slow) and convert to orthophosphate form

- Organic phosphate

  minor importance in most domestic wastes

Chloride

Human excreta contains ≈ 6g chloride /person /day

Conventional methods of waste treatment → do not remove Cl^-

Higher tan usual Cl^- conc. → indication that a body water is being used for waste disposal

Infiltration of grounwater into sewers adjacent to ea water

Sulfate

Occurs naturally in most water supplies and is present in wastewater as well

<u>Crown corrosion problem in sewers:</u>

Org. Matter + $SO_4^{-2} \rightarrow S^{-2} + H_2O + CO_2$

$S^{-2} + 2H^{+} \rightarrow H_2S$ (under anaerobic conditions)

H_2S collected at the crown of sewer not flowing full $\rightarrow H_2SO_4$

(seriously threaten structural integrity of pipe

Color

Give rough information about age of wastewater

Fresh wastewater → light brownish gray color

As the travel time in the collection system increases

more anaerobic conditions develop

color of wastewater sequentially changes

gray→dark gray →black (SEPTIC)

Odor

Gases found in untreated wastewater

N_2, O_2, CO_2 (from in all waters exposed atmosphere)

H_2S, NH_3, CH_4 (from the decomposition of organic matter)

H_2S:

from the anaerobic decomposition of organic matter

Org. Matter + $SO_4^{-2} \rightarrow S^{-2} + H_2O + CO_2$

$S^{-2} + 2H^+ \rightarrow H_2S$

Odor :rotten egg

Colorless

Inflammable

H_2S poisoning is one of the leading cause of accidents in WWTP

5ppm→ moderate odor

10ppm→ eye irritation begins

30ppm→strong,unpleasent odor of rotten egg

100 ppm→ loss of smell

>300ppm →unconsciousness, death

Mercaptan

formed during anaerobic decomposition of organic matter

may cause odor more offensive than that of H_2S

Methane(CH_4)

principal by-product from the anaerobic decombosition of organic matter

Large quantities are not encountered in untreated ww

Colorless, odorless, combustible hydrocarbon with high flue value

Explosion risk

PLANT EMPLOYEES SHOULD BE INSTRUCTED IN SAFETY

MEASURES WHILE WORKING IN AND ABOUT STRUCTURES

WHERE H_2S AND CH_4 MAY BE PRESENT

VENTILATION, GAS SENSORS, ALARM SYSTEMS

Temperature

Temperature of domestic wastewater is commonly higher than that of local water supply, because of the addition of warm water from households

Alkalinity

Domestic wastewater is normally alkaline receiving its alkalinity from the water supply, the groundwater, the materials added during domestic use

Metals

Discharged from residental dwellings, groundwater infiltration, commercial and industrial discharge

Oil and Grease

term used for fats, oils, waxes

Surfactants

Surface active agents

Large organic molecules that are slightly soluble in water

Cause foaming in ww treatment plants

During aeration of ww → these compounds collect on the surface of the air bubble and thus create a very stable foam

Cause foaming in the surface water into which ww is discharged

Surfactants (continue)

Before 1965 → ABS (Alkly-benzene-sulfonate)
resistant to breakdown by biological means

After 1965 → LAS (linear –alkly-sulfonate
biodegradable

Come primarily from synthetic detergents

PRINCIPAL CONSTITUENTS OF CONCERN IN MUNICIPAL WASTEWATER TREATMENT

Constituent	Reason of Importance	Unit operation and process used to remove
Suspended Solids	Can lead to development of sludge deposits and anaerobic conditions when untreated wastewater is discharged	Screening Grit Removal Sedimentation Flotation Chemical precipitation Filtration
Biodegradable organics	If discharged untreated to the environment their biological stabilization can lead to the depletion of natural oxygen resources and to the development of septic conditions	Aerobic suspended growth variations Aerobic attached growth variations Anaerobic suspended growth variations Lagoon variations Chemical oxidation Advanced oxidation Membrane filtration

PRINCIPAL CONSTITUENTS OF CONCERN IN MUNICIPAL WASTEWATER TREATMENT

Constituent	**Reason of Importance**	**Unit operation and process used to remove**
Nutrients (Nutrient and phosphorus)	Both nitrogen and phosphorus, along with carbon are essential nutriens for growth. When discharged to aquatic environment these nutrients can lead to the growth of undesirable aquatic life. may cause eutrophication NO_2:extremely toxic to fish NO_3:fatal effects on infants (blue baby sendrome)	For Nitrogen; suspended growth nitrification-denitrification variations attached growth nitrification-denitrification variations air stripping ion exchange breakpoint chlorination For phosphorus; biological phosphorus removal chemical precipitation
Pathogens	Communicable diseases can be transmitted by the pathogenic organisms that may be present in wastewater	Chlorine compounds Chlorine dioxide ozonation Ultraviolet (UV) radiation

Classification Of Biological Treatment Processes

SUSPENDED-GROWTH PROCESSES

Biological treatment processes in which the microorganisms responsible for the conversion of the organic matter or other constituents in the wastewater to gases and cell tissue are maintained in suspension within the liquid.

ATTACHED-GROWTH PROCESSES

Biological treatment processes in which the microorganisms responsible for the conversion of the organic matter or other constituents in the wastewater to gases and cell tissue are attached to some inert medium, sucj as rocks,slag or especially designed ceramic or plastic materials. Attached film processes are also known as fixed film processes.

LAGOON PROCESSES

A generic term applied to treatment processes that take place in ponds or lagoons with various aspect ratios and depths.

OBJECTIVES OF BIOLOGICAL TREATMENT OF DOMESTIC WASTEWATER

1. Transform (i.e. oxidize) dissolved and particulate biodegradable constituents into acceptable end products.

2. Capture and incorporate suspended and non-settleable colloidal solids into a biological floc or biofilm

3. Transform or remove nutrients (nitrogen and phosphorus)

4. In some cases, remove specific trace organic constituents and compounds