Lesson 4

# Treatment of industrial and municipal wastewaters

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desde 1901

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# Contaminated water

Water is contaminated when it contains substances or energy changing its properties and quality, affecting its possible uses or function in the ecosystem

**Contamination types**

- Chemical
- Biological
- Thermal
- Radioactive

**Sources of contaminants**

- Natural processes:

  Disperse sources with minor impact except in specific cases.

  e. g. erosion, fires, volcanic eruptions…

- Anthropogenic

  Major impact, in specific areas

  e.g. waste dumping, sewage, wastewaters, industrial wastes, agriculture additives,…

**Water quality**

Physicochemical and biological characteristics of a water specimen

The required characteristics are different depending on its use: drinking water, industrial water, irrigation…

# Natural Water

**Seawater (97%):**

- seas and oceans.

**Fresh water (3%):**

- 75% Ice, glaciers.
- 24% Aquifers.
- 0,03% Rivers
- 0,06% Soil moisture.
- 0,3% Lakes
- 0,035% Vapor

## Composition of natural water

1. Dissolved gases
   - From atmospheric gases ( $N_2$, $O_2$ y $CO_2$)
   - From organisms metabolic activity ($O_2$ y $CO_2$)
   - From organic matter decomposition ( $N_2$, $SH_2$, $CO_2$ y $CH_4$)
2. Ions
   - From the rain water ($H_3O^+$ y $HCO_3^-$)
   - From organic matter decomposition ($NH_4^+$, $SO_4^{2-}$ , $PO_4^{3-}$, …)
   - From materials in Earth crust ($Ca^{2+}$, $Na^+$, $Mg^{2+}$, $Fe^{2+}$, …)
3. Suspension solids
   - Clays
   - Sands

   From erosion and weathering of materials in the Earth crust
4. Organic matter
   - Amino acids
   - Carbohydrates
   - Fatty acids, …

   Compounds soluble in water. From metabolic activity of organisms

   - Humic substances
   - Fulvic substances
   - Proteins
   - Polysaccharides

   Compounds in suspension in water
   They come from the organic fraction of soils, living organisms,…

# Natural Water: Classification

## Atmospheric water

Contains in solution gases present in the air:

$CO_2$, $SO_2$, NO, $O_2$,…

Low mineralization (10 – 100 ppm) and low content in organic matter

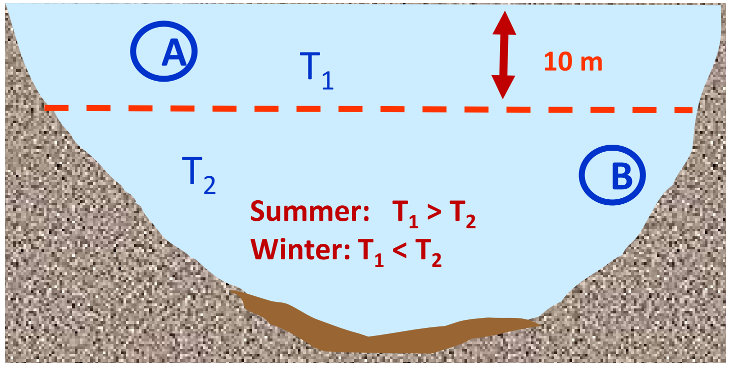
## Lakes and Ponds

Variable composition with depth

Depth > 8 m $\Rightarrow$ thermal stratification

2 zones with different composition (superficial and deep)

*High production of organic matter.*
*High dissolved $O_2$ concentration:*
*Oxidized chemical species: $Fe^{3+}$, $Mn^{4+}$, …*




*Ionic exchange water-sediments*
*Low $O_2$ concentration*
*Reduced chemical species: $Fe^{2+}$…*

## Surface water

Variable composition: it depends on the section of the river course and the soil composition: erosion and dissolution

## Groundwater

No color, no organic mater

Reductive conditions (redox potential < 0) Presence of reduced species: $Fe^{2+}$, $Mn^{2+}$,…

Largely affected by the ionic exchange processes between soil and water

Adsorption in soil of ionic species (metallic cations,…)

## Sea water

Thermal stratification, with different composition in layers: salinity.
High content in salts: 35-40 g/kg
Constant pH, slightly alkaline: pH = 7,8 - 8,2
Dissolved $O_2$ decreases with depth
Organic matter more concentrated in the surface of water
Bionutrientes: N and P; very variable.

## Wastewater Characteristics

Natural water ⇨ { Domestic use, Industry, Agriculture } ⇨ Wastewater Sewage → Solids in solution or suspension

## Composition

Sewage → Sanitary, Commercial, Industrial, Agricultural, Rain water and surface runoff ⇨

- Inorganics
- Nutrients (N and P)
- Oil and grease
- Organics
- Pathogens
- Solids

Industrial ww → Variety of inorganics, organics and heat

Agricultural ww → Nutrients, pesticides, manure

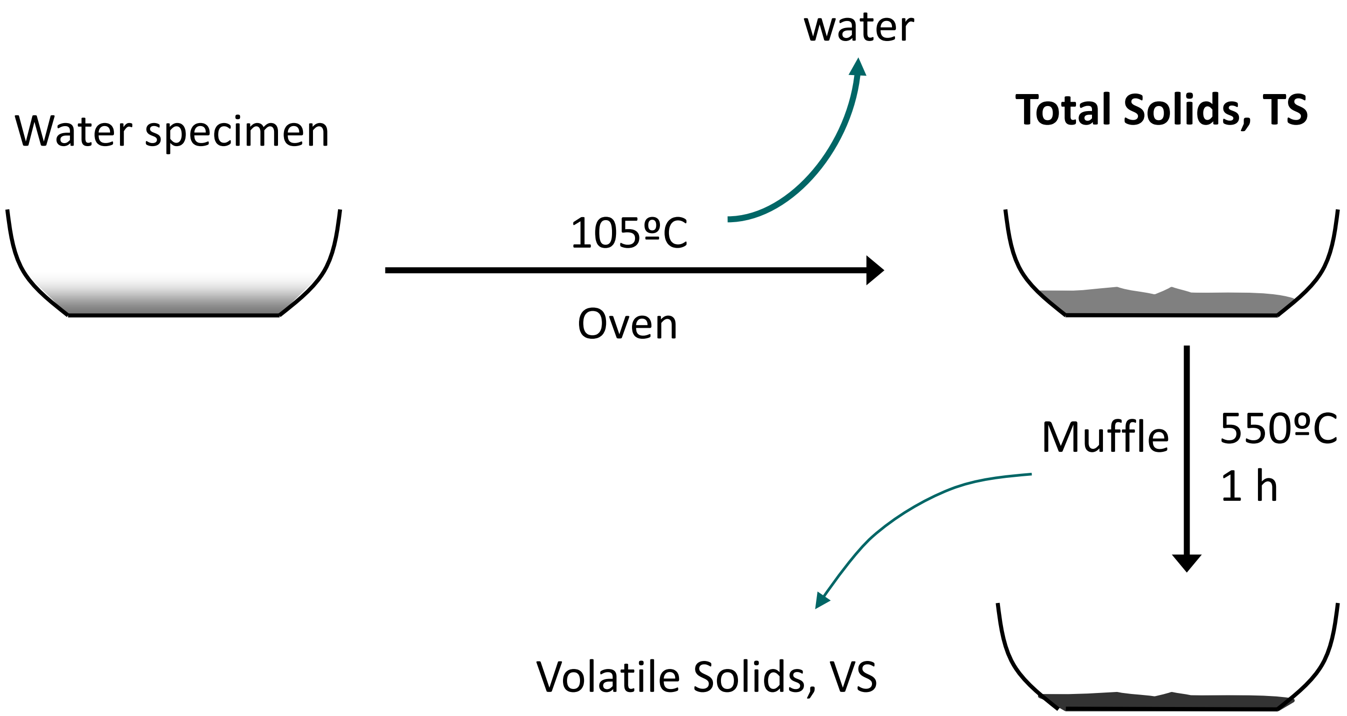
# Wastewater Characteristics

Physical characteristics → 
- Color
- Odor
- Temperature
- **Solid content**

Chemical characteristics → 
- **Organic content: COD, BOD, TOC (TIC)**
- **Elements of special interest: N, P,…**
- Specific compounds

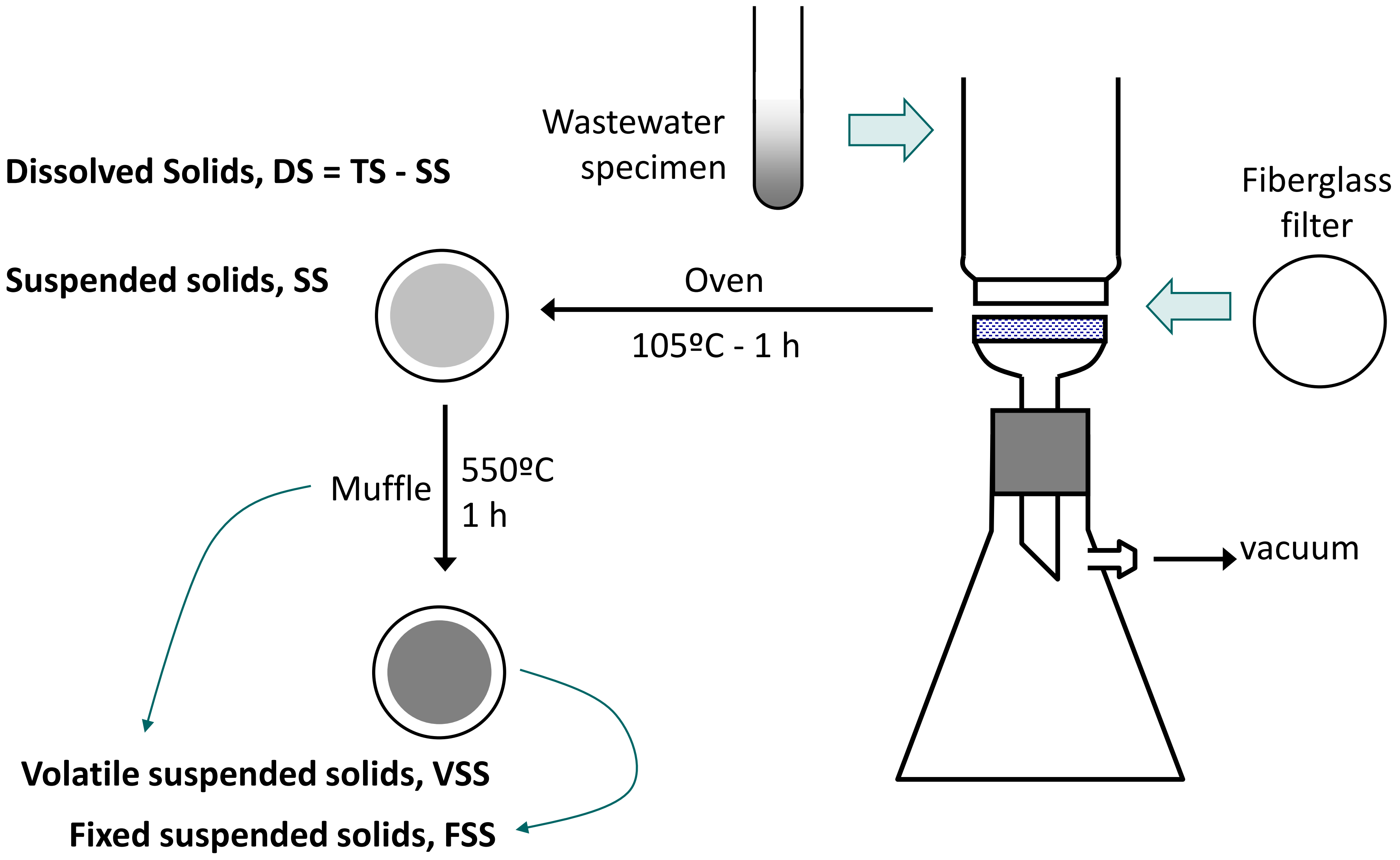
Biological characteristics → 
- Types and concentration of microorganisms
- Pathogens

# Wastewater Characteristics




**Fixed solids = TS - VS**

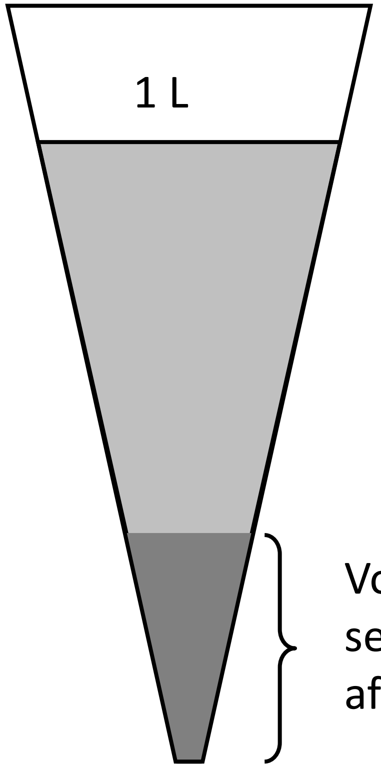
# Wastewater Characteristics



# Wastewater Characteristics

## Settable Solids

Imhoff cone test




sludge volume index (SVI) is the volume in milliliters occupied by 1 g of a suspension after 30 min settling

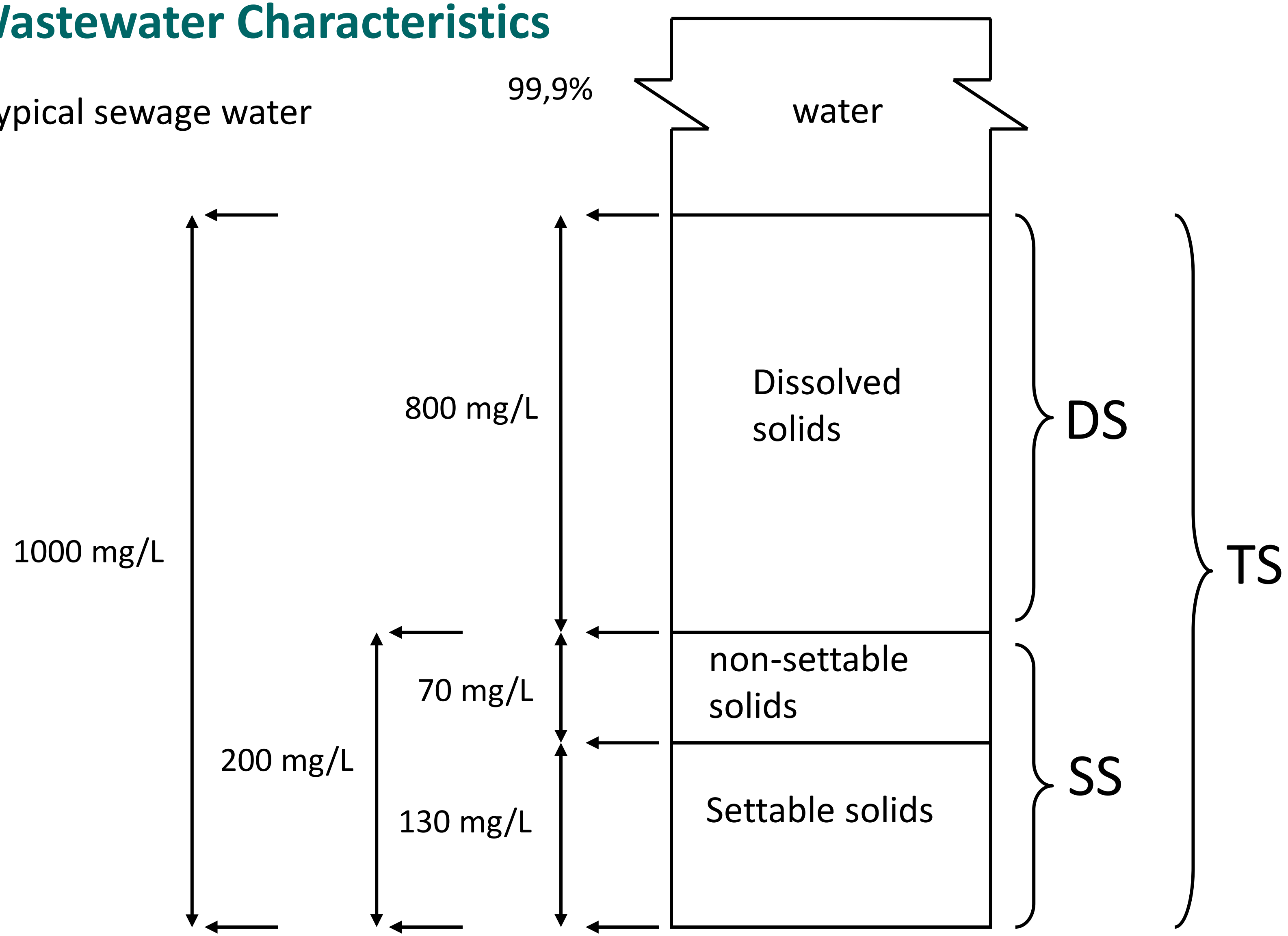
$$\text{SVI} = \frac{\text{settled sludge volume (mL/L)}}{\text{suspended solids (mg/L)}} \cdot 1000\ (\text{mg/g})$$

Volume (in mL) of the settled solids (sludge) after ½ h

| SVI | Value |
|---|---|
| Good | <40 mL/g |
| Fair | 40 a 140 mL/g |
| Poor | >140 mL/g |
| Bulking | >200 mL/g |

## Wastewater Characteristics

Typical sewage water



## Conductivity

Conductivity is the ability of a solution to conduct the electric current. It is the inverse of resistivity (resistance to carry the electric current)

Units: Siemens/cm (S/cm)

| | | | |
|---|---|---|---|
| Ultra pure water: | $0.05 \cdot 10^{-6}$ | S/cm | (Resistivity 18.2 MΩ·cm at 25°C) |
| Boilers: | $10^{-1} - 5 \cdot 10^{-4}$ | S/cm | |
| Drinking water: | 0.005 – 0.01 | S/cm | |
| Sea water: | 5 | S/cm | |

Conductivity is a measure of the ionic concentration in water

# Hardness

The hardness of water is the concentration of ionic calcium and magnesium in solution (**$Ca^{2+}$** & **$Mg^{2+}$**; divalent alkaline earth metals), these are the most abundant divalent ions in natural water. Other polyvalent ions can be included in the definition ($Fe^{2+}$ & $Mn^{2+}$), but they show minor contribution to the hardness of water.

## Total hardness

$$\text{Hardness (M)} = [Ca^{2+}] + [Mg^{2+}]$$

Total hardness is the sum of the **calcium** and **magnesium** concentration (carbonates, bicarbonates,…) in water , expressed as **mg/L** of **$CaCO_3$**

$$\text{Hardness (mg/L) } CaCO_3 = 2.50\,[Ca^{2+}] + 4.16\,[Mg^{2+}]$$

- $2.50 = \frac{100\ g\ CaCO_3}{40\ g\ Ca^{2+}}$
- $[Ca^{2+}]$: mg/L $Ca^{2+}$
- $4.16 = \frac{100\ g\ CaCO_3}{24\ g\ Mg^{2+}}$
- $[Mg^{2+}]$: mg/L $Mg^{2+}$

## Temporary Hardness

It is related to the **calcium** and **magnesium bicarbonates**, $Ca(HCO_3)_2$ & $Mg(HCO_3)_2$

It is eliminated boiling water

$$Ca(HCO_3)_2 + \text{heat} \rightarrow CaCO_3\downarrow + CO_2 + H_2O$$

$$Mg(HCO_3)_2 + \text{heat} \rightarrow MgCO_3\downarrow + CO_2 + H_2O$$

## Permanent Hardness

It is the hardness remaining after boiling water

***Permanent hardness = Total hardness + Temporary Hardness***

## Hardness of water

| | mg/L de $CaCO_3$ | French degrees | German degrees |
|---|---|---|---|
| **classification** | **mg/l** | **ºFR** | **ºDE** |
| **Soft water** | 0 – 75 | ≤ 7,5 | ≤ 0.95 |
| **Moderately hard water** | 75 – 150 | ≤ 15,0 | ≤ 3.35 |
| **Hard water** | 150 - 300 | ≤ 30.0 | ≤ 10.0 |
| **Very hard water** | > 300 | > 30.0 | > 10.0 |

ºFR = $\frac{\text{mg/L } CaCO_3}{10}$

## Hardness of water: analysis

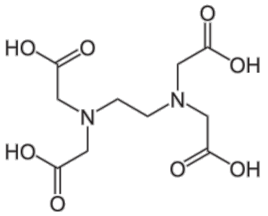
- Chemical analysis of Ca and Mg: Titration with EDTA at pH 10.
- Using conductivity

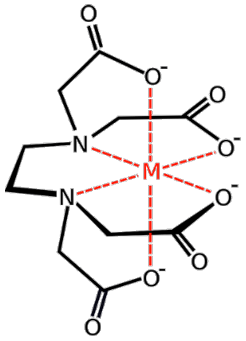
1 **French degree** (ºFR) = **10 mg/L $CaCO_3$**

1 mg/L = 2 µS/cm

1 **French degree** (ºFR) = **20 µS/cm**

EDTA




EDTA-Metal complex

# Hard water: Effects

- formation of limescale (solid deposit of calcium carbonate) in heaters and pipes
- The 2+ ions destroy the surfactant properties of the soap (forming a solid precipitate, the soap scum)
- lack of foam formation with soap
- Limiting the activity of detergents, it is necessary to increase the dose of detergent to achieve the same results in washing

# Softening: removing the hardness of water

## Precipitation with Lime

- Classic method, widely used, and cheap. Commonly used in softening of drinking water
- lime is used to precipitate **Ca** as **$CaCO_3$**, and **Mg** as **$Mg(OH)_2$**

$$Ca^{2+}\text{ (agua dura)} + 2HCO_3^- \text{ (agua dura)} + Ca(OH)_2 \longrightarrow 2\,CaCO_3\downarrow + 2\,H_2O$$

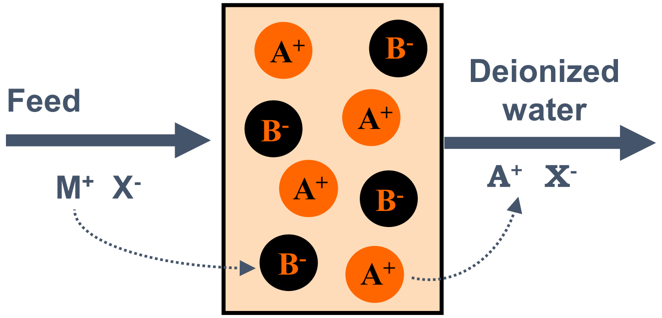
$$Mg^{2+}\text{ (agua dura)} + 2\,HCO_3^- + 2Ca(OH)_2 \longrightarrow Mg(OH)_2\downarrow + 2\,CaCO_3\downarrow + 2\,H_2O$$

# Softening

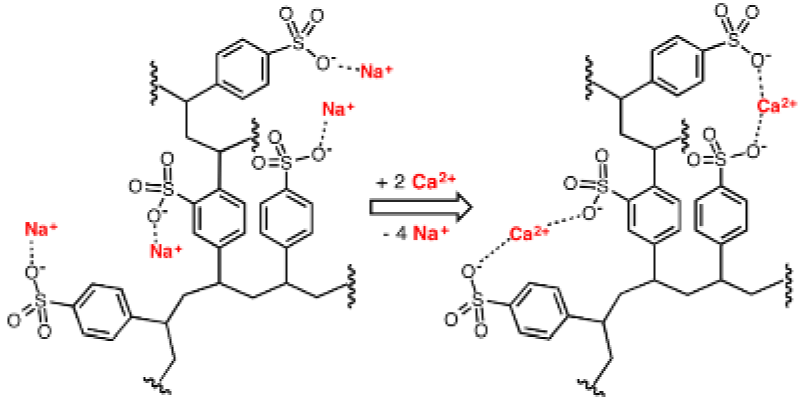
## Ionic exchange

Ionic Exchange Resin:

The resins exchange $Ca^{2+}$ and $Mg^{2+}$ ions by other ions as $H^+$ or $Na^+$ that do not generate hardness.




$$M^+ + B^- \longrightarrow MB$$



# Hardness

The resins used in the softening of water must show the properties:

1. Porous structure
2. Electric nature
3. Capacity to exchange ions in contact with water

**ANIONIC RESINS**
They only Exchange anions

**CATIONIC RESINS**
They only exchange cations

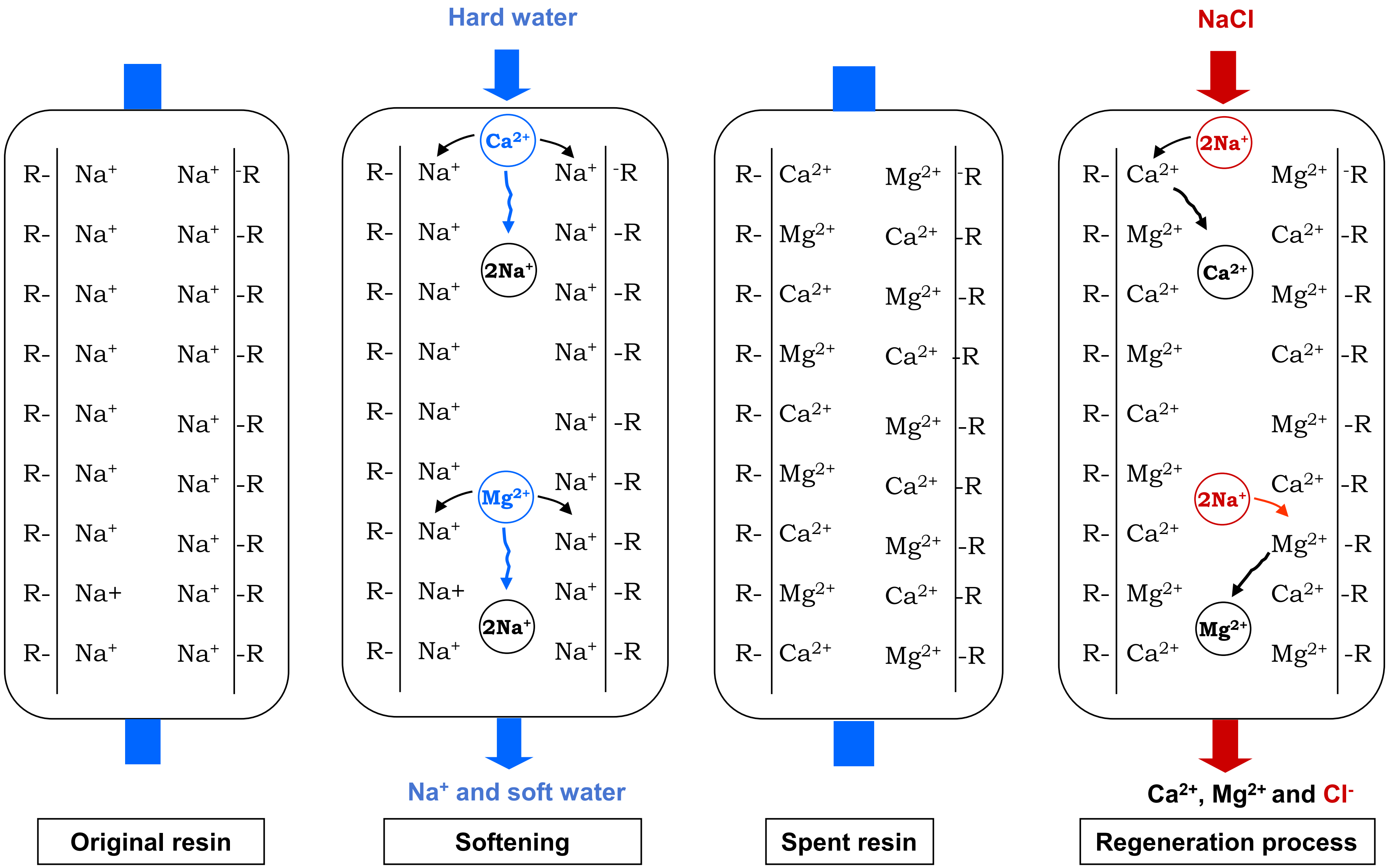
The softening of water uses CATIONIC RESINS (**$R_xNa$** or **$R_xH$**) , composed of an anionic polymeric structure (**$R_x$**) neutralized with the corresponding cations, usually **$Na^+$ or $H^+$**

**e. g.**

$$\underbrace{Na_2Al_2Si_3O_{10}}_{\text{Sodium Aluminosilicate}} + Ca^{2+} \longleftrightarrow Ca(Al_2Si_3O_{10}) + 2\,Na^+$$

- When the resin is saturated with $Ca^{2+}$, they can be regenerated in contact with a solution that release the adsorbed $Ca^{2+}$ and replace the original cations ($Na^+$ or $H^+$). The regeneration solution is concentrated solutions of NaCl or $H_2SO_4$

# Softening by ionic exchange resin



## Exercise. Hard water.

**3.** A natural water contains $4 \cdot 10^{-4}$ M of $Mg^{2+}$, $5 \cdot 10^{-4}$ M of $Ca^{2+}$ and $6 \cdot 10^{-4}$ M of $HCO_3^-$. Determine the amount of $Ca(OH)_2$ and $Na_2CO_3$ per $m^3$ of water in its softening.

*Answer: 51.8 g/m³ Ca(OH)₂, 63.6 g/m³ NaCO₃*

$$Mg^{2+} + Ca(OH)_2 \longrightarrow Mg(OH)_2 \downarrow + \ Ca^{2+}$$

$$Ca^{2+} + 2\,HCO_3^- + Ca(OH)_2 \longrightarrow 2\,CaCO_3 \downarrow + \ 2\,H_2O$$

$$Ca^{2+} + Na_2CO_3 \longrightarrow CaCO_3 \downarrow + \ 2\,Na^+$$

# Content in organic matter

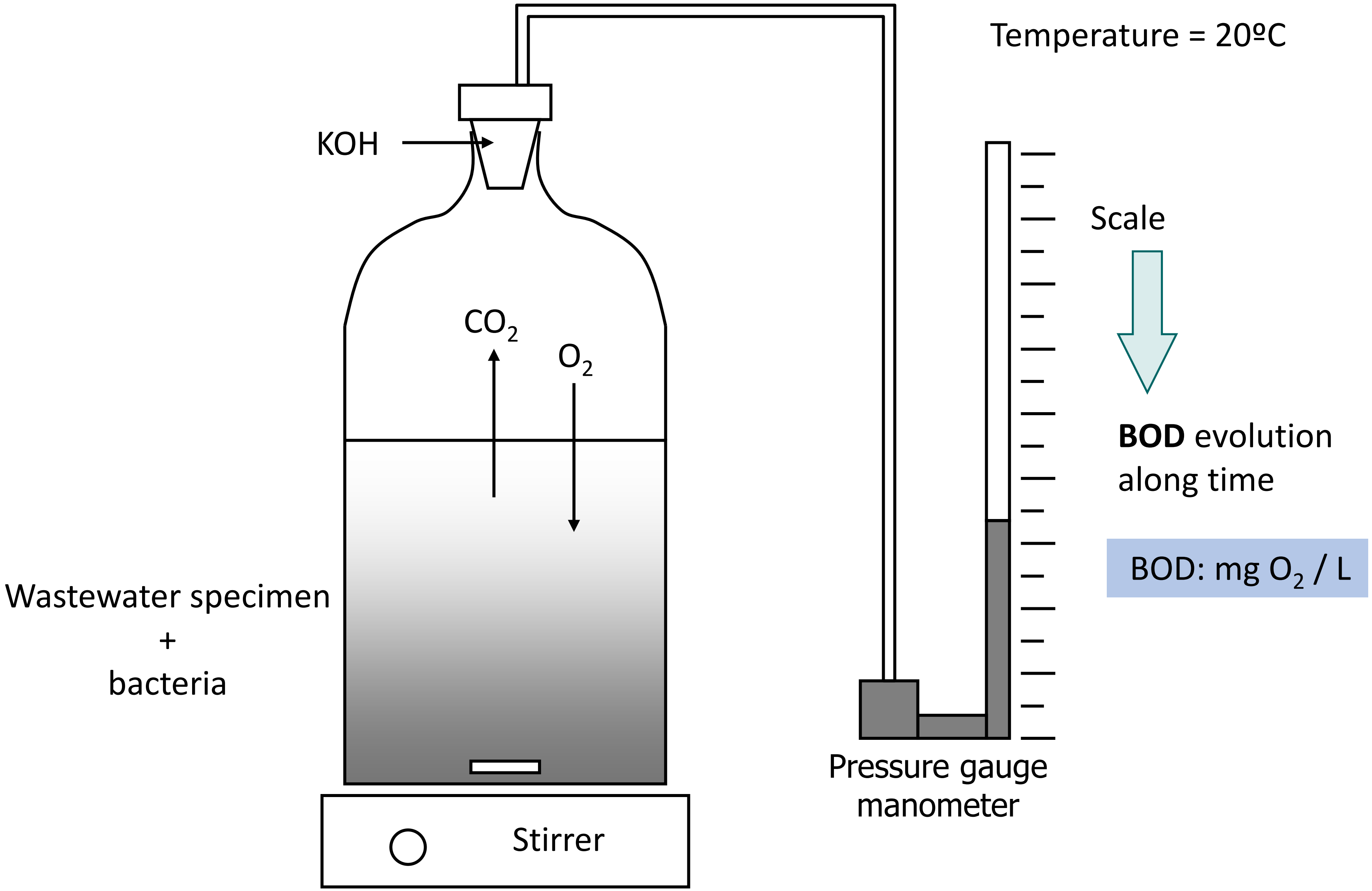
| Parameter | Definition |
|---|---|
| **Theoretical Oxygen Demand (ThOD)** | Stoichiometric amount of oxygen to oxidize an organic compound to $CO_2$ and $H_2O$ (and other oxidized compounds if other elements are present) |
| **Chemical Oxygen Demand (COD)** | Amount of oxygen to oxidize the organic matter in a sample of water.<br>It is determined using an strong oxidizing agent in acid medium at high temperature to assure the complete oxidation of the organic matter.<br>COD includes the biodegradable and non-biodegradable organic matter, it also includes some reduced inorganic compounds in water ($Fe^{+2}$, $NO_2^-$, $S^{-2}$, etc.)<br>Expressed in mg $O_2$/ L |
| **Biochemical Oxygen Demand (BOD)** | Amount of oxygen consumed by the aerobic microorganisms during the oxidation of the biodegradable organic matter in a water specimen.<br>Expressed in mg $O_2$/ L |
| **Total Organic Carbon (TOC)** | Specific analysis to determine the concentration of organic matter measured as C.<br>The method is able to discriminate the organic C from the inorganic C |

## Exercise: Theoretical Oxygen Demand.

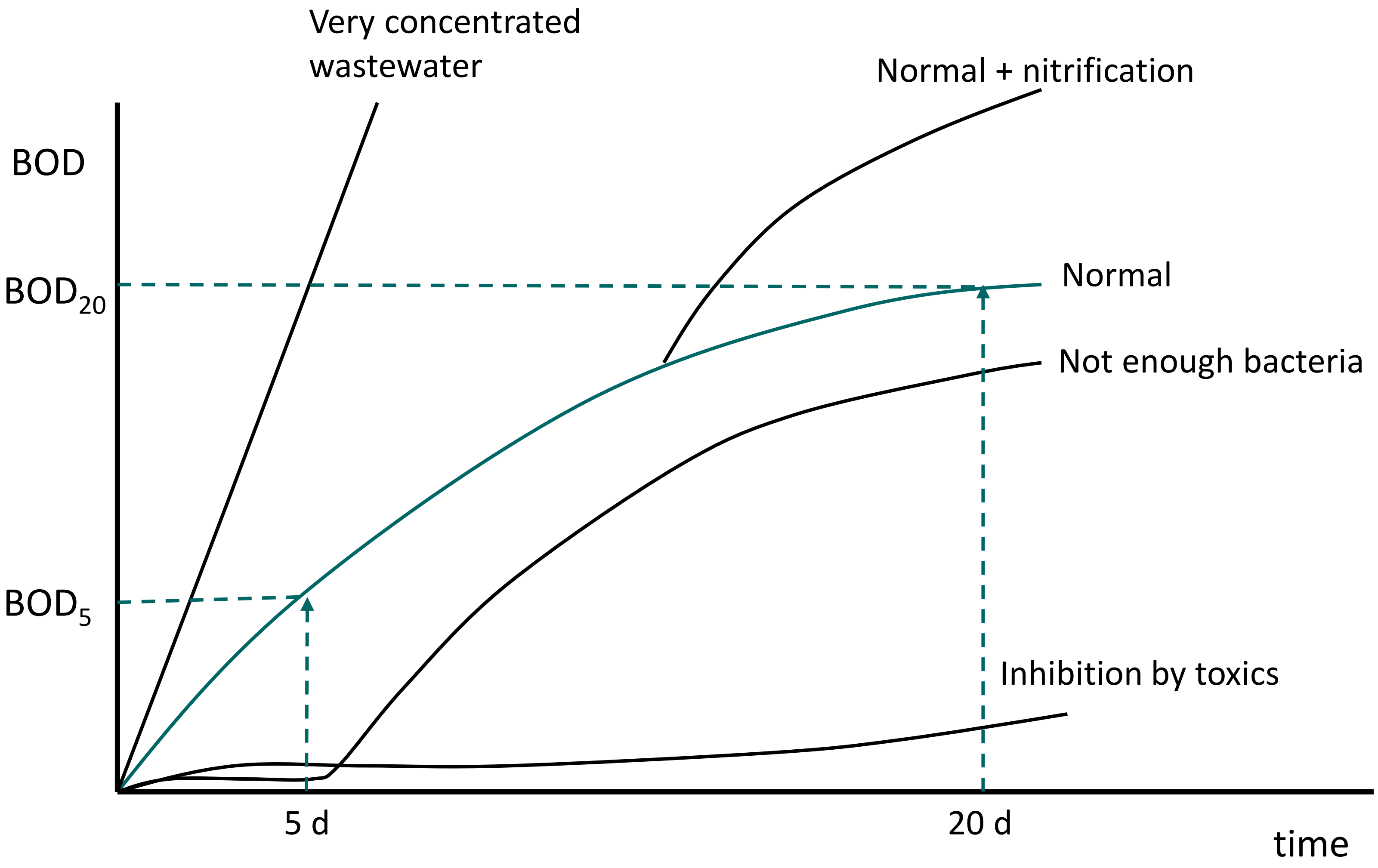
Determine the theoretical oxygen demand (ThOD) of 1 g/L glucose solution.

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

# Wastewater Characteristics



# Wastewater Characteristics



# Biochemical Oxygen Demand

| Classification | DBO (mg $O_2$ /L) |
| --- | --- |
| Pure natural water | < 3 |
| Natural water, intermediate | 3 – 5 |
| Polluted water | > 8 |
| Sewage water | 100 – 400 |
| Wastewater food industry | >1000 |

## BOD limitations

- Long time to get the result of the analysis
- Analysis is affected by toxics or inhibitors in the water that affect the growing of bacteria
- Only determine biodegradable organics, difficult to detect low biodegradable molecules (lignin, oil,…
- Limitations in industrial water with toxics and/or non-biodegradable compounds

# Chemical Oxygen Demand

2.5 mL of sample (<500 mg COD/L)

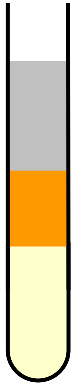
DI water (blank)

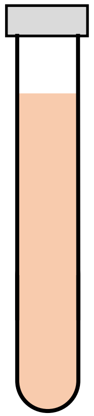
1.5 mL digestion solution

$K_2Cr_2O_7$; $H_2SO_4$; $HgSO_4$

3.5 catalytic solution

$AgSO_4$; $H_2SO_4$





Mix
2 h, 150ºC
Cool down

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

$$6Cl^- + Cr_2O_7^{2-} + 14H^+ \longrightarrow 3Cl_2 + 2Cr^{3+} + 7H_2O$$

$$Ag + Cl^- \longrightarrow AgCl\downarrow$$

$$Hg + Cl^- \longrightarrow HgCl\downarrow$$

Determine the excess of potassium dichromate
Titration with ferrous ammonium sulfate
Indicator: Ferroine (1,10-phenantroline + $Fe^{2+}$)

$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

# Chemical Oxygen Demand

**Ratio BOD / COD**

Inform about the biodegradability of the organic matter in the effluent

| BOD / COD | Comments |
|---|---|
| < 0,2 | Non biodegradable compounds in water |
| > 0,6 | Biodegradable organic matter in water |

**COD, common values**

| COD | Comments |
|---|---|
| < 30 mg/L | Superficial water |
| ≤ 5 mg/L | Drinking water |

**Advantages**

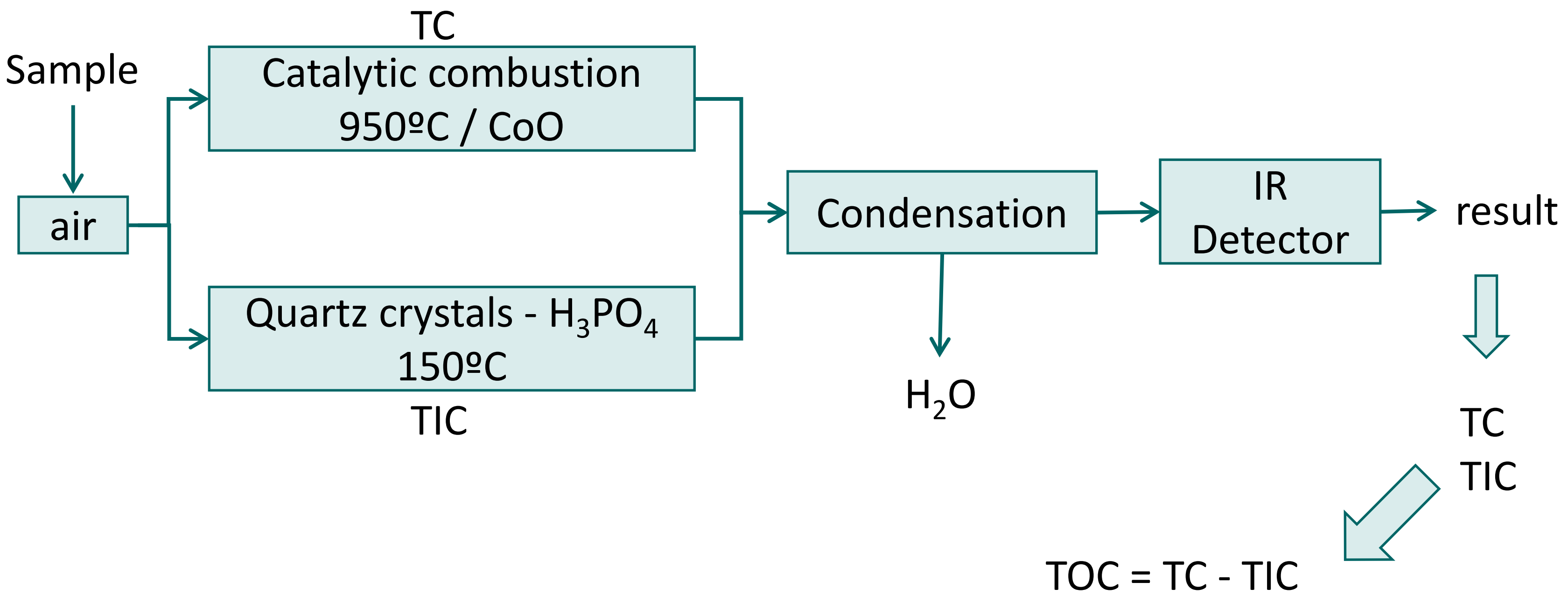
- Fast analysis, <<BOD.
- Determine the non-biodegradable fraction of the organic matter that cannot be detected in BOD

**Drawbacks**

- Does not inform about the biodegradability
- toxic metals in the analysis (Hg and Cr).

# Wastewater Characteristics

**Total organic carbon**



# Biological Characteristics

Biological characteristics of water:

- **Faecal coliforms**: *0/100 mL.*
- **Faecal streptococcus**: *0/100 mL.*
- **Stafilococos aureus***: 0/100 mL.*
- **Pseudomonas aeruginosa***, 0/100 mL.*
- **Other pathogents:** *zero*
- **Parasites, algae, larvae:** *zero*

- Microorganisms in wastewater: bacteria, virus, protozoans, parasites.
- The pathogens in wastewater come from sick people.
- Typical illnesses with origin in water: gastroenteritis, dysentery, hepatitis A, typhoid fever, cholera,…
- It is difficult to determine the concentration of pathogens in wastewaters. Instead of pathogens, total coliforms and total streptococcus are determined, the reduction of these microorganisms assures the reduction of faecal microorganisms and pathogens.

# Sewage water, typical composition

| | Concentration (mg/L) | | |
|---|---|---|---|
| | High | Average | Low |
| **Total Solids** | 1200 | 700 | 350 |
| • Dissolved solids | 850 | 500 | 250 |
| Fixed | 525 | 300 | 145 |
| Volatile | 325 | 200 | 105 |
| • Suspension solids | 350 | 200 | 100 |
| Fixed | 75 | 50 | 30 |
| Volatile | 275 | 150 | 70 |
| • Settable solids (mL/L) | 20 | 10 | 5 |
| **$BOD_5$** | 300 | 200 | 100 |
| **COD** | 1000 | 500 | 250 |

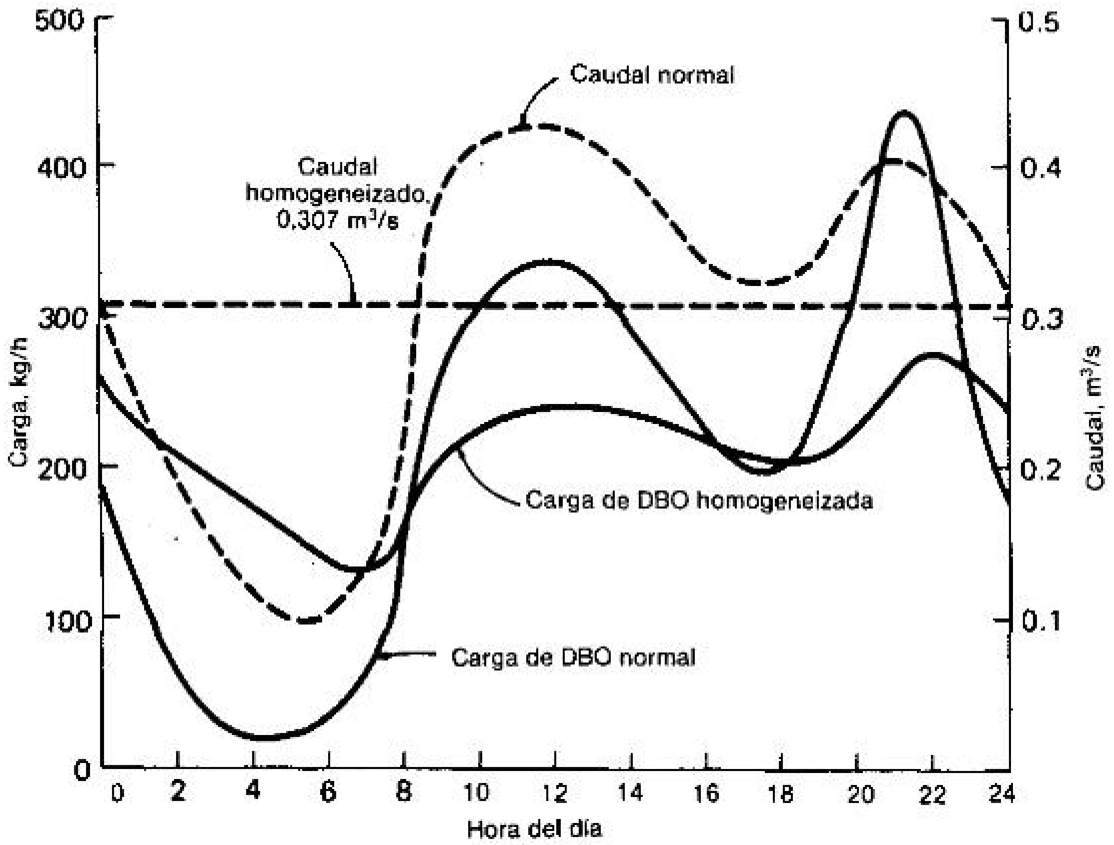
| | Concentration (mg/L) | | |
|---|---|---|---|
| | High | Average | Low |
| **Nitrogen** (N) | 85 | 40 | 20 |
| • Organic | 35 | 15 | 8 |
| • Ammonium | 50 | 25 | 12 |
| • Nitrite & nitrate | 0 | 0 | 0 |
| **Phosphorus** (P) | 20 | 10 | 6 |
| • Organic | 5 | 3 | 2 |
| • Inorganic | 15 | 7 | 4 |
| **Chloride** | 100 | 50 | 30 |
| **Alkalinity ($CO_3Ca$)** | 200 | 100 | 50 |
| **Oil & grease** | 150 | 100 | 50 |

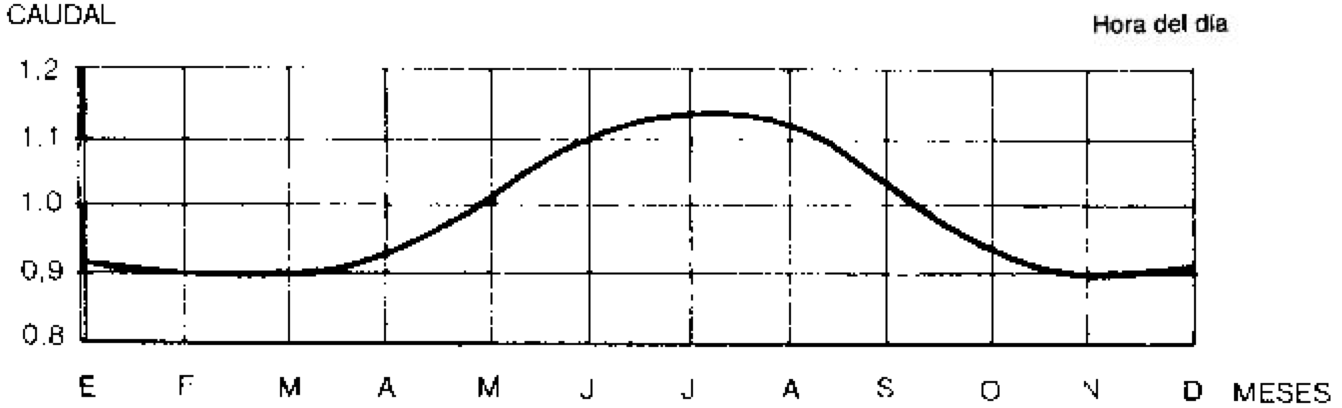
# Drinking water (max. conc. Contaminants)

| Substance | Max. (mg/L) |
|---|---|
| Hydrocarbons | 0.05 |
| Aromatic HC | 0.0002 |
| Surfactants | 0.2 |
| Phenol | 0.001 |
| Pesticides | 0.001 |
| Chloride | 200 |
| Phosphorous ($P_2O_5$) | 0.4 |
| N-$NH_4^+$ | 0.05 |
| Kjeldahl N | 1 |
| Sulfide | 250 |
| Dissolved $O_2$ | 70% |
| Fluoride | 1.5 |

| Substance | Max. (mg/L) |
|---|---|
| Fe | 0.3 |
| Mn | 0.5 |
| Cu | 0.05 |
| Zn | 3 |
| B | 1 |
| As | 0.05 |
| Cd | 0.005 |
| Pb | 0.5 |
| Se | 0.1 |
| Hg | 0.001 |
| Ba | 0.1 |
| CN- | 0.05 |
| Ni | 1 |
| Sb | 0.5 $mg/m^3$ |

# Wastewater Characteristics



## Exercise

**1.** Determine the contaminant load of the discharged effluent of two companies, the activity of the first company is mineral extraction and the other is the production of palm oil. The discharge flow and COD for the mineral extraction company is 20 mg/L and 400 L/s, and that for the palm oil extraction company is 0.1 L/s and 80000 mg/L.

*Answer: 691.2 kg/d, the same value for the two effluents*

## Exercise

**2.** A sewage treatment plant will be designed to serve a city for the next 15-25 years, with a present population of 50000 people. Determine the "population equivalent" or "unit per capita loading, PE", for the design of the sewage treatment plant assuming an annual population growth rate of 1.2 %. Consider the fluctuating population will be 15 %. The fresh water consumption is 300 L/hab day and the $BOD_5$ is 140 mg/L. DATA 1 PE = 60 g/day $BOD_5$.

*Answer: 54235 PE*

## Exercise

**4.** The production of galvanized iron uses zinc cyanide. A spent zinc cyanide bath 0.5 M contains 3 $m^3$ of the solution, which is diluted with water in a tank of $10^3$ $m^3$. Determine the COD of the initial and final $ZnCN_2$ solutions?

$$2\ CN^- + 5\ O_2 + 12\ H^+ \longrightarrow 2\ CO_2 + N_2 + 6\ H_2O$$

*Answer: Initial COD: 40000 mg $O_2$/L, Final COD: 120 mg $O_2$/L*

## Exercise

**5.** The flow of an industrial wastewater effluent is 1200 $m^3/h$ and its characteristics are as follows:

Suspended solids: 600 mg/L

Palmitic acid ($CH_3$-$(CH_2)_{14}$-COOH): 100 mg/L

The effluent must be treated to reach the legal discharged limits:

Suspended solids: 35 mg/L

BOD: 25 mg $O_2$/L

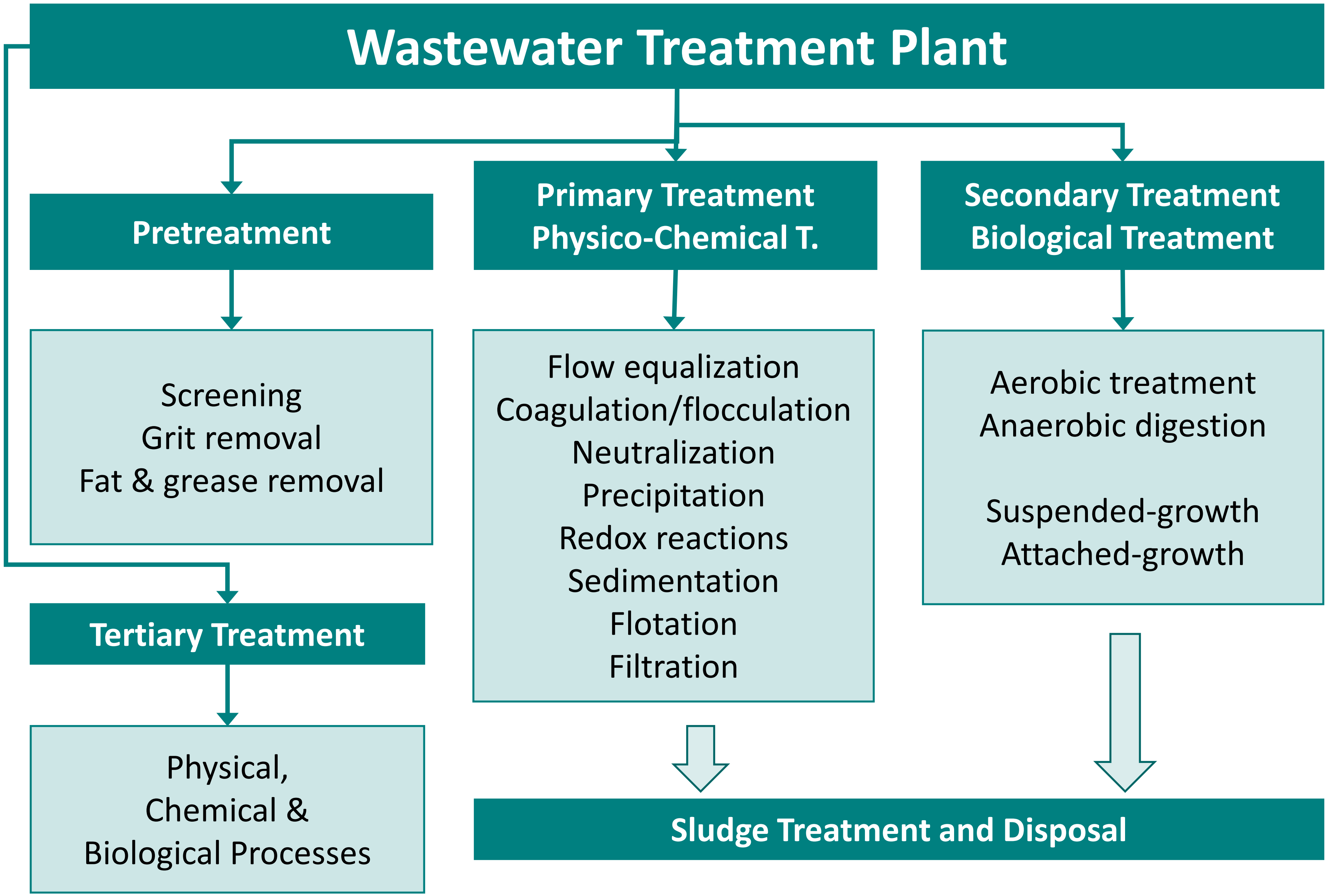
Determine:

a) The sludge production, expressed in t/day, due to the removal of the suspended solids, considering that the moisture content of the sludge is 40 %.

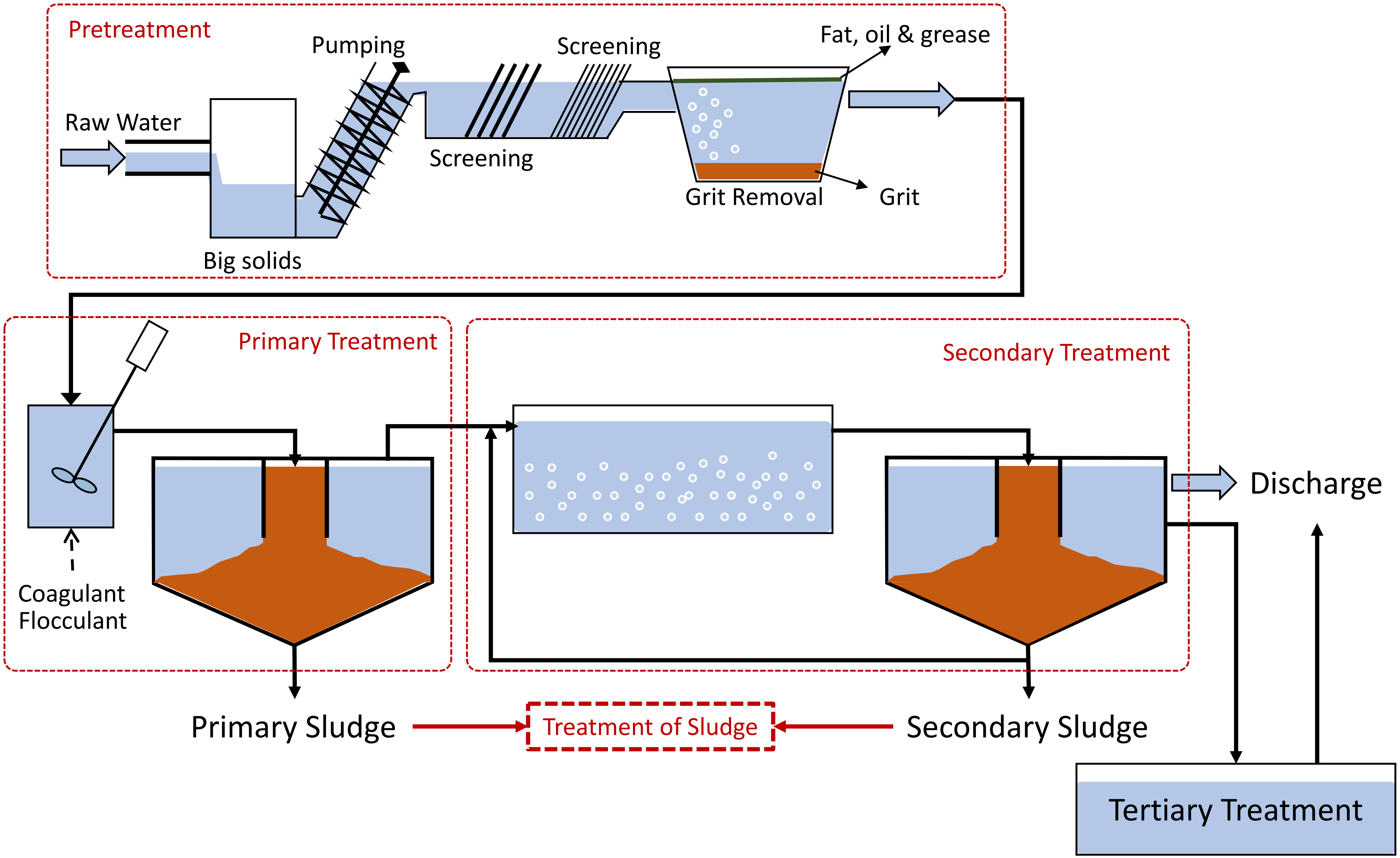
b) The BOD of the wastewater

c) The efficiency to the treatment process to meet the legal DBO discharge limit

*Answer: 27.12 t/day, 287.5 mg $O_2$/L; 91.30 %*


Wastewater Treatment Plant
Pretreatment
Primary Treatment
Physico-Chemical T.
Secondary Treatment
Biological Treatment
Screening
Grit removal
Fat & grease removal
Flow equalization
Coagulation/flocculation
Neutralization
Precipitation
Redox reactions
Sedimentation
Flotation
Filtration
Aerobic treatment
Anaerobic digestion
Suspended-growth
Attached-growth
Tertiary Treatment
Physical,
Chemical &
Biological Processes
Sludge Treatment and Disposal

# Wastewater Treatment Plant



## Pretreatment

Removal of materials and large objects that can be easily collected from the raw sewage.
To avoid damage or clog the pumps and sewage lines and accumulation in other units.

**Screening**

Removal of large objects while sewage water passes through a bar screen

# Pretreatment

## Grit removal

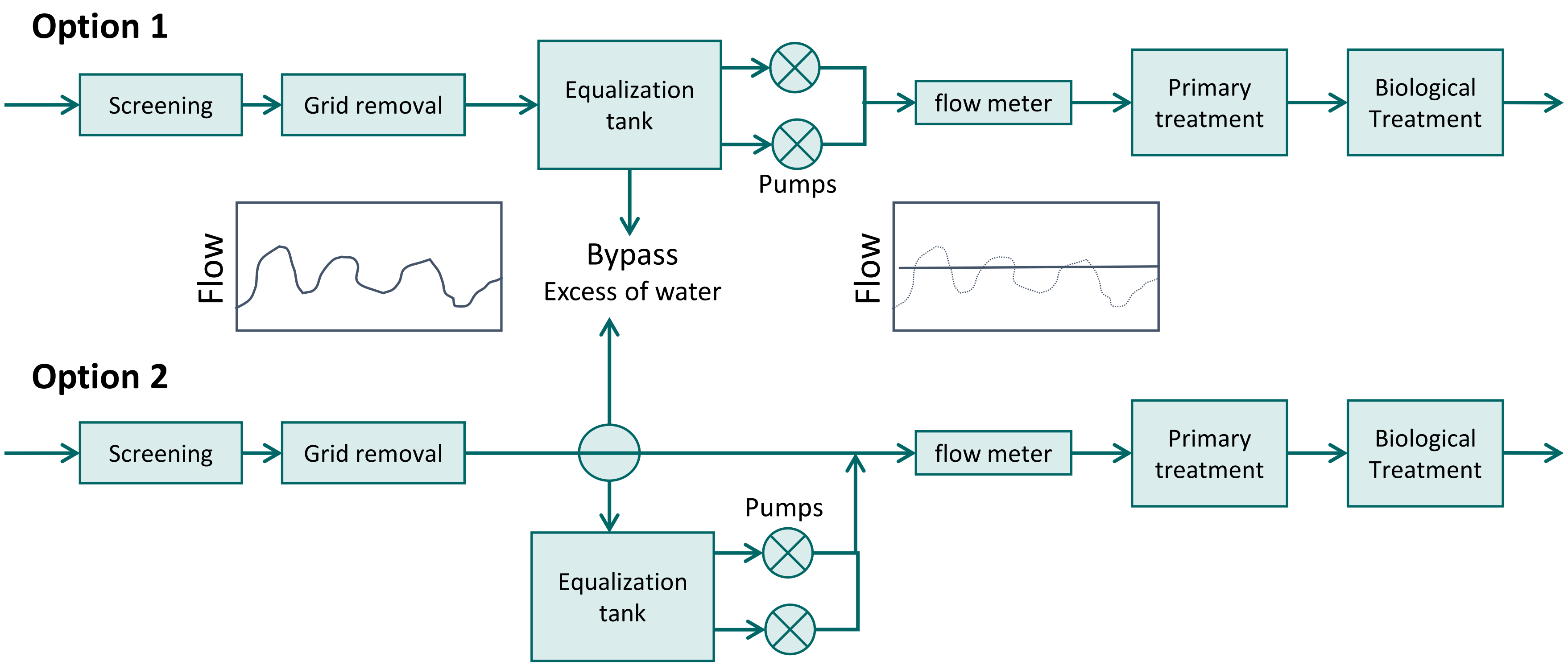
Sewage water enter to a tank where the water velocity is adjusted to allow the settling of sands and grits (inorganic solids) avoiding the settling of organic material.
0.4-0.6 m/s < V < 1 m/s

## Fat and grease removal

Fat and grease is removed in the grit removal system or in skimmers floating on the surface. Air blowers favor the separation.

## Flow equalization

WWTP (wastewater treatment plant) is like a processing plant. It operates better at constant feed (constant flow and constant concentration). Physico-chemical treatment it reported to be more effective, easier controllable and require less chemicals when operated at constant flow.
Biological treatment is claim to be more stable and effective when fed at constant flow.



# Primary Treatment

Removal of settable solids, especially flocculating organic matter.

1. Chemical treatment: coagulation-flocculation
2. Physical separation: settling

| Solid/liquid system | Particle (cm) | |
|---|---|---|
| Suspension | $> 10^{-5}$ | Possible separation by settling |
| Colloidal suspension | $10^{-5} > dp > 10^{-7}$ | Charged particles |
| Solution | $< 10^{-7}$ | Homogeneous system |

# Primary Treatment

**$1^{st}$ Coagulation**

Addition of coagulants to brake down the electrostatic stability of the colloidal particles. The particles aggregate to each other and settle down.

Very fast process, < 1 s

Coagulants : $Fe^{3+}$ and $Al^{3+}$ salts

1 mole $Al^{3+}$, $Fe^{3+}$ ≈ 1000 moles $Ca^{2+}$ ≈ 10,000 mole $Na^{+}$, $K^{+}$

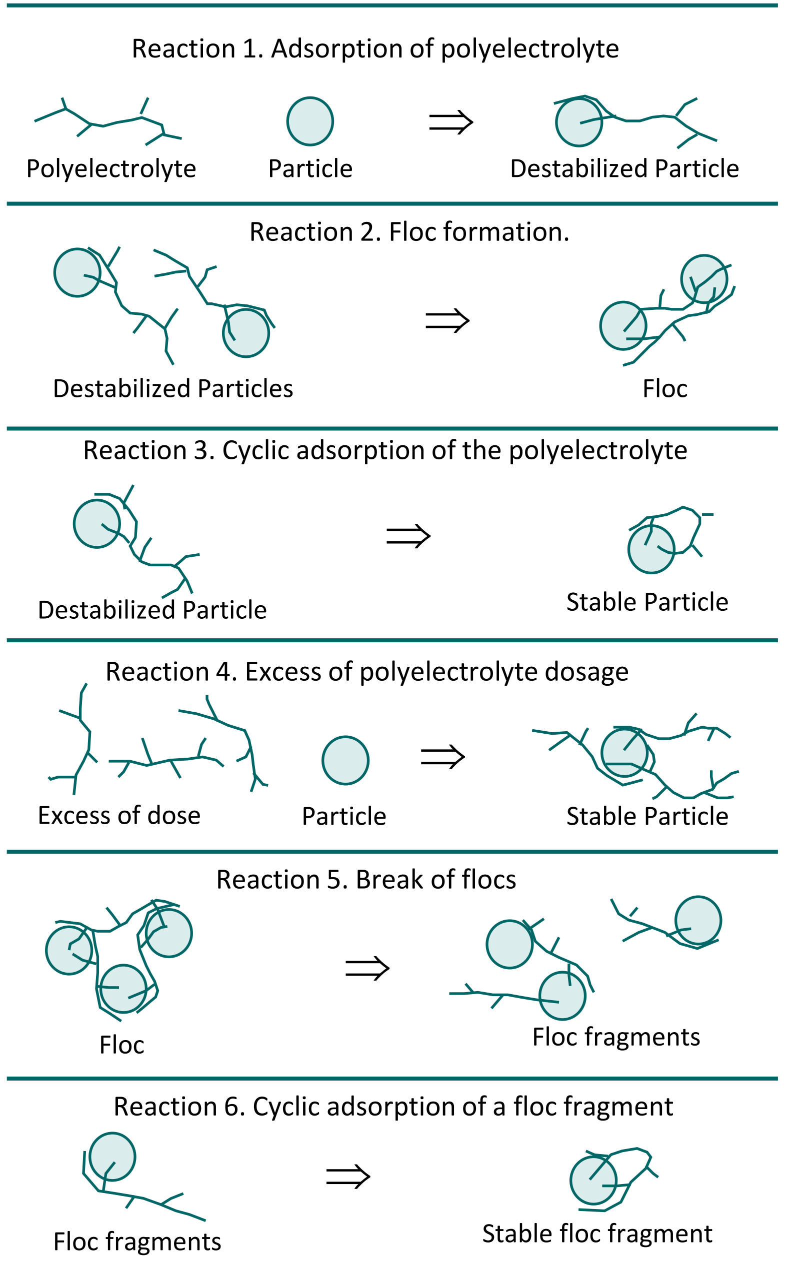
**$2^{nd}$ Flocculation**

Addition of a polyelectrolyte that forms bridges inter-particles creating a bigger particles.

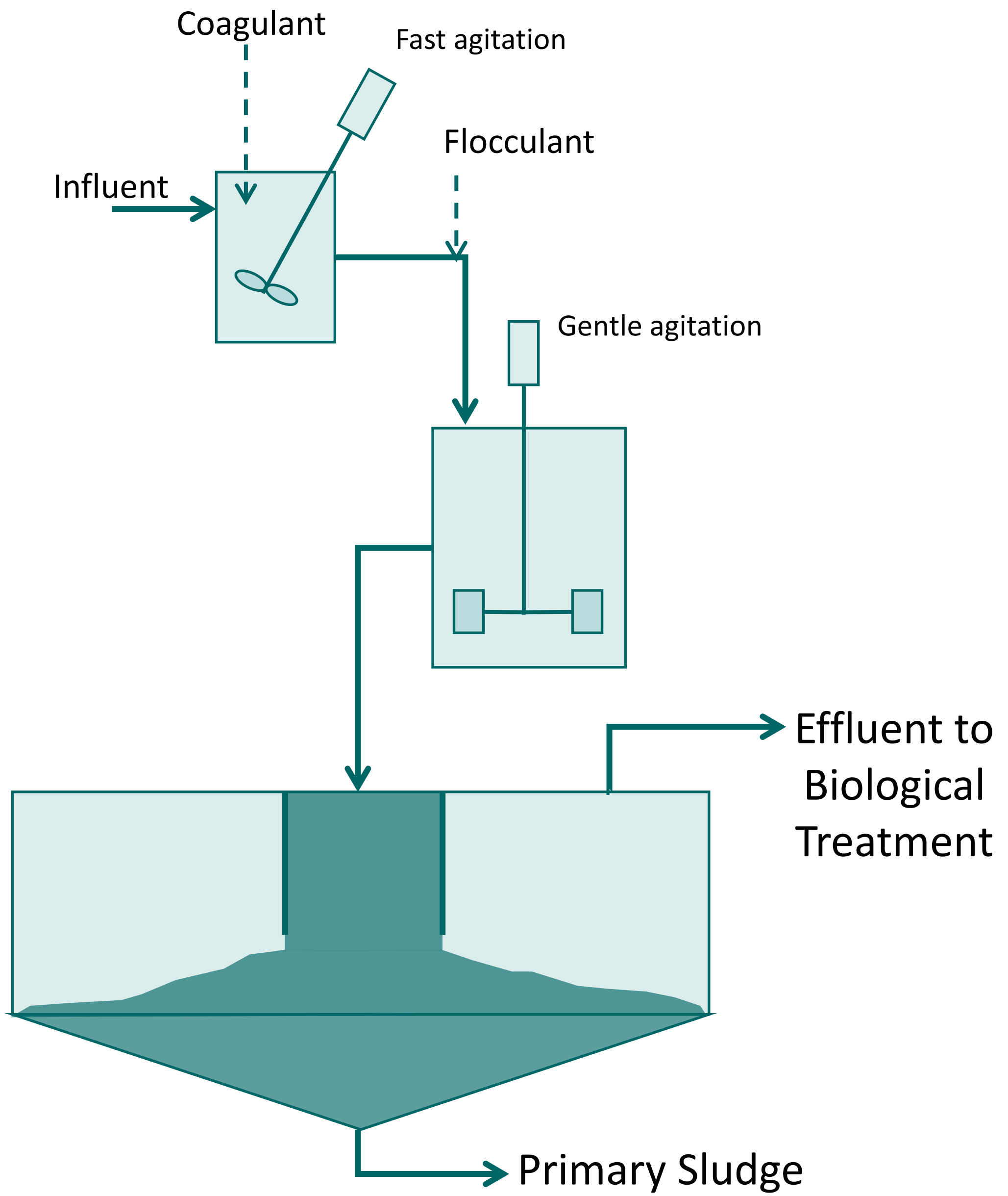
Labile bonds particle-polyelectrolyte-particle. Easily breakable.

Agitation is necessary to form the bonds and make the particles grow (flocs)

High shear stress will brake the bonds resulting in smaller particles (flocs)



Reaction 1. Adsorption of polyelectrolyte
Polyelectrolyte
Particle
Destabilized Particle
Reaction 2. Floc formation.
Destabilized Particles
Floc
Reaction 3. Cyclic adsorption of the polyelectrolyte
Destabilized Particle
Stable Particle
Reaction 4. Excess of polyelectrolyte dosage
Excess of dose
Particle
Stable Particle
Reaction 5. Break of flocs
Floc
Floc fragments
Reaction 6. Cyclic adsorption of a floc fragment
Floc fragments
Stable floc fragment

Coagulant
Fast agitation
Flocculant
Influent
Gentle agitation
Effluent to Biological Treatment
Primary Sludge

# Secondary Treatment (Biological Treatment)

It is designed to degrade the biodegradable organic matter in the sewage water.
The organic matter, soluble or colloidal, comes from food, washing products, human waste, etc.
Biological treatment is based in the metabolic activity of bacteria and protozoa. Biota needs a source of carbon (organic matter in water), nutrients and oxygen to live.
The environmental conditions in the biological reactor are designed to favor the fast growth of biota.
Most of the organic matter consumed is transformed in new microorganisms (it is called biomass)
Microorganisms tend to aggregate forming dense flocs that can be separated form the treated water by settling or flotation.

1. Biological reactor
2. Clarifier-settling tank
3. Sludge recirculation system

**Biological reactor**

**Suspended-growth**

Activated sludge

**Fixed-film** or **attached growth**

Filter beds (oxidizing beds)

Rotating biological contactors

## Tertiary treatment

Tertiary treatment is the final treatment stage to further improve the effluent quality before it is discharged to the receiving water body or is reused.

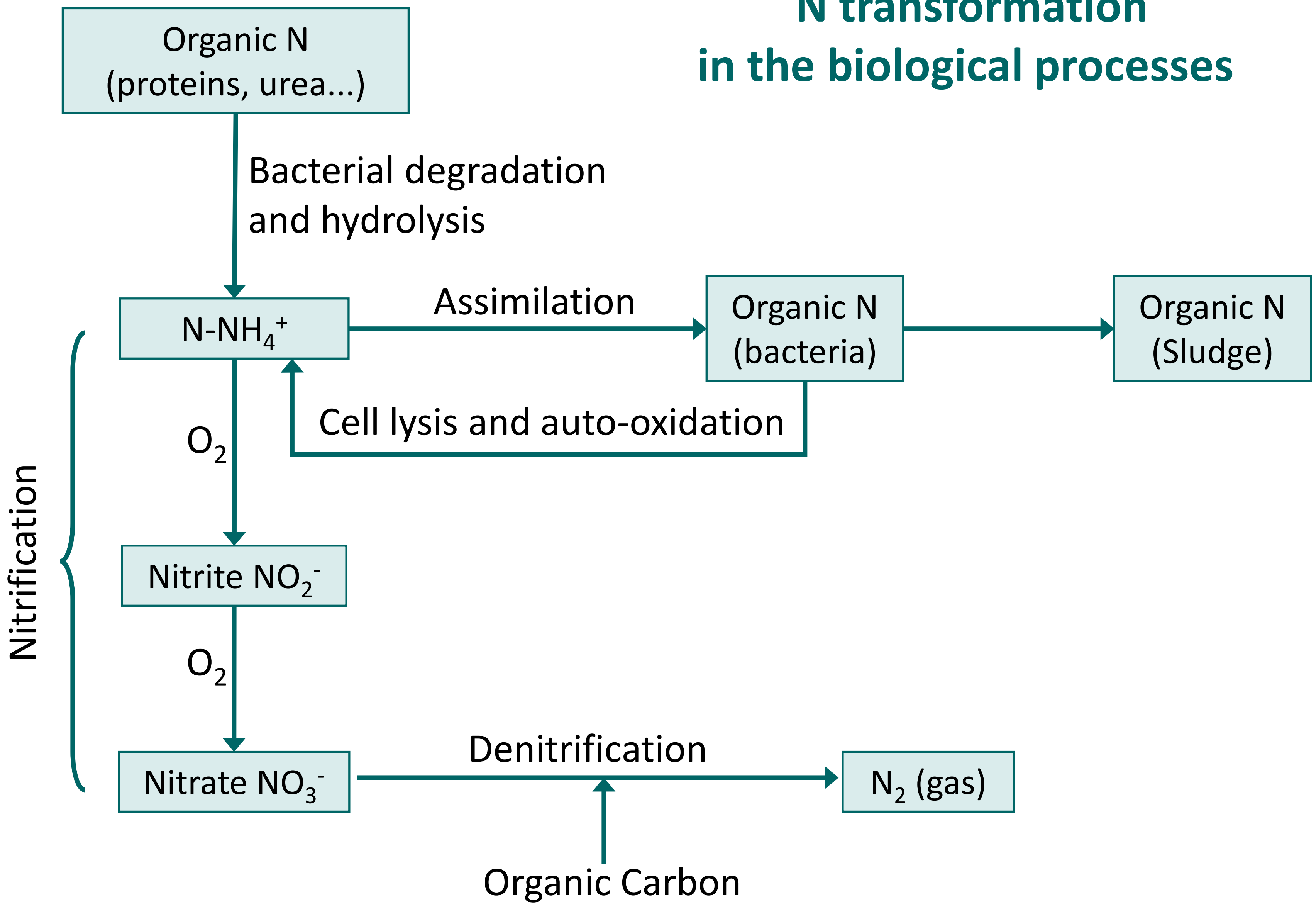
Tertiary treatment is any physical, chemical or biological process or a combination of them to remove the remaining contaminants in water.

Remaining contaminants in water:

- Recalcitrant organic matter (non-biodegradable organic matter)
- Nutrients: N, P
- Particles
- Microorganisms (pathogens and others)
- Soluble compounds: heavy metals…

> ➢ Filtration in sand beds: removal of particles
>
> ➢ Microfiltration
> ➢ Ultrafiltration
> ➢ Nanofiltration
> ➢ Reverse osmosis
>
> → Removal of large molecules
> Removal of soluble substances
> Removal of soluble ions

# N transformation in the biological processes



## Nitrogen removal (Nitrification-Denitrification)

**Nitrification** is a two-step aerobic biological process. The involved bacteria do not require org-C, but $CO_2$, and oxygen. The are chemo-autotrophic bacteria.

| | |
|---|---|
| $NH_3 + 3/2\ O_2 \longrightarrow HNO_2 + H_2O$ | oxidation to nitrite, nitrosomonas sp. |
| $HNO_2 + ½O_2 \longrightarrow HNO_3$ | oxidation to nitrate, nitrobacter sp. |
| $NH_3 + 2\ O_2 \longrightarrow HNO_3 + H_2O$ | Global reaction |

$$55\ NH_4^+ + 76\ O_2 + 109\ HCO_3^- \longrightarrow C_5H_7O_2N + 54\ NO_2^- + 57\ H_2O + 104\ H_2CO_3$$

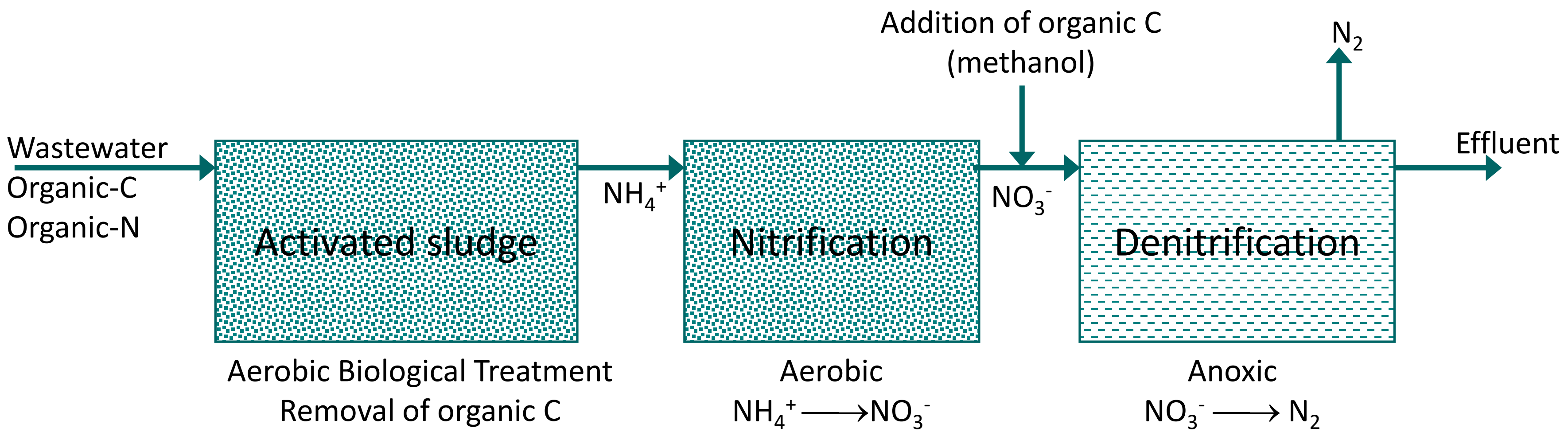
$$400\ NO_2^- + NH_4^+ + 4\ H_2CO_3 + HCO_3^- + 195\ O_2 \longrightarrow C_5H_7O_2N + 3\ H_2O + 400\ NO_3^-$$

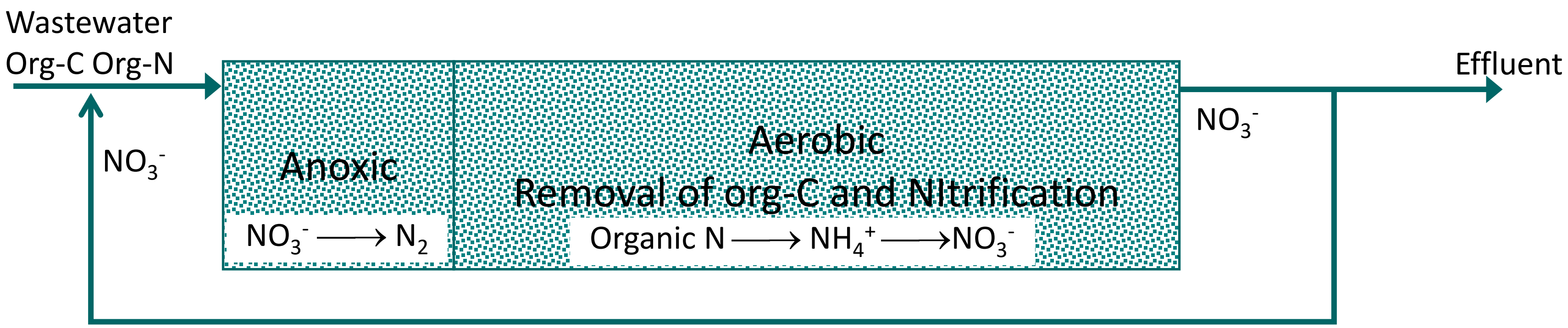
Oxygen: 4.3 mg $O_2$/mg N-$NH_4^-$ oxidized to $NO_3^-$
Alkalinity consumption: 8.64 mg de $HCO_3^-$/mg N-$NH_4^-$

**Denitrification** is the reduction of Nitrate to $N_2$ in an anoxic process. The bacteria involved in the process is heterotrophic bacteria with a respiratory metabolism. So, they require org-C as a source of C and an external e- acceptor, which is $NO_3^-$.

$$NO_3^- \longrightarrow NO_2^- \longrightarrow NO \longrightarrow N_2O \longrightarrow N_2$$

## Nitrogen removal (Nitrification-Denitrification)



## Phosphorus removal

P-org (proteins...)
$PO_4^{-3}$ (Phosphate)
$P_2O_7^{-4}$ (polyphosphate)

The alternating use of anaerobic / anoxic /aerobic stages induces in the biota the accumulation of P.
P is removed in the sludge.

PhoStrip Process

Bardenpho Process

# Disinfection

Elimination of microorganisms from the treated water to avoid the microbiological contamination of the water bodies

Disinfection uses chemical agents (oxidizing chemicals) or UV radiation

- Chlorine and derivatives
- Ozone ($O_3$)
- UV radiation

# Disinfection with Chlorine

Common Cl compounds used in disinfection of water

- ✓Chlorine (**$Cl_2$**)
- ✓Na Hypochlorite **NaClO**
- ✓Ca Hypochlorite **$Ca(ClO)_2$** → small WWTP
- ✓Chlorine dioxide (**$ClO_2$**)

Chlorine is the most common compound used: efficiency, economy

## Chlorine reactions ($Cl_2$)

$Cl_2 + H_2O \rightarrow$ **HClO** $+ H^+ + Cl^-$ Hydrolysis

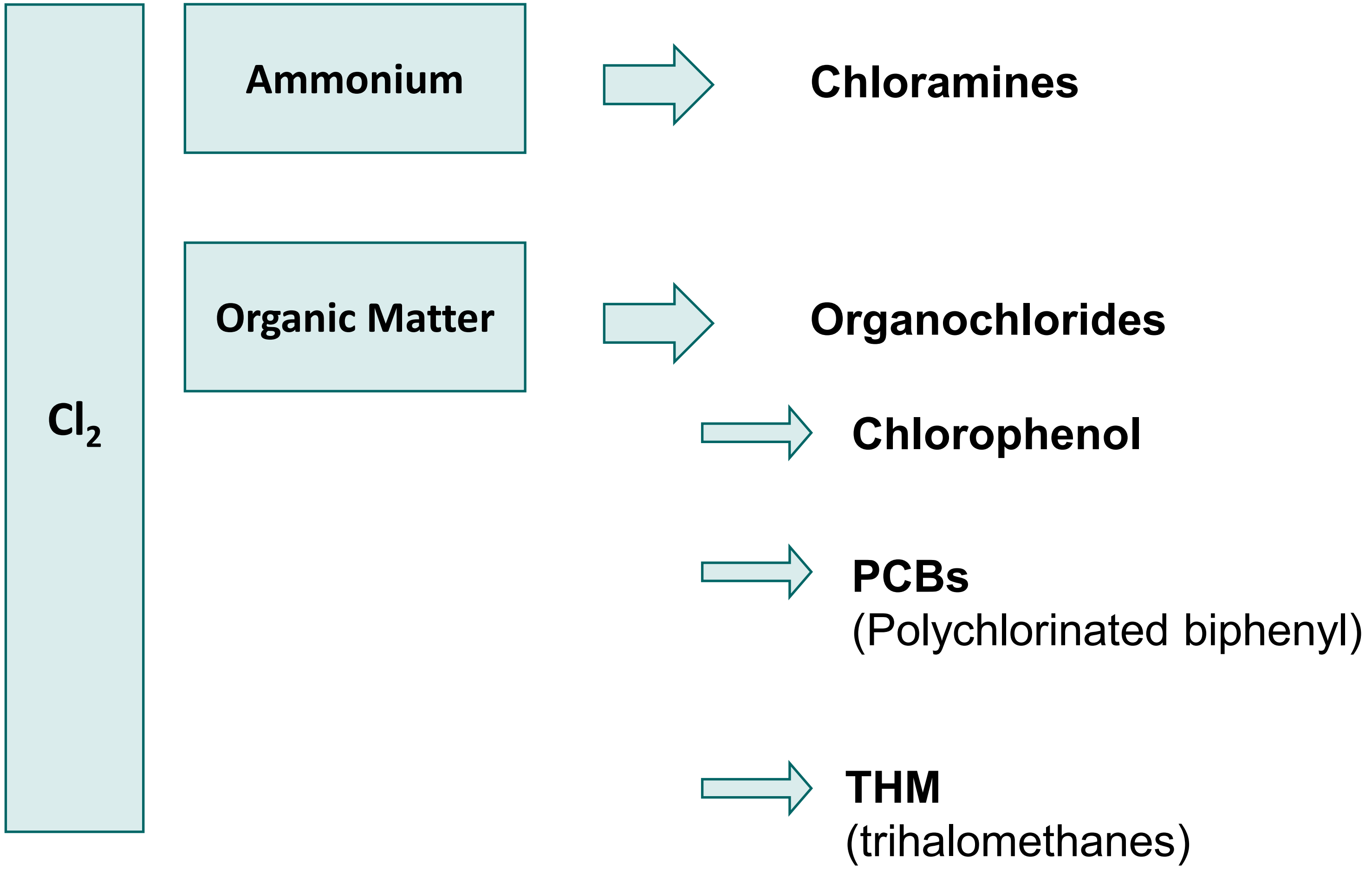
Hypochlorous acid

HClO → $H^+$ + **$ClO^-$** Ionization

Hypochlorite

The amount of HClO / $ClO^-$ in water is called **Free chlorine**

# Undesirable Products with Chlorine ($Cl_2$)



# Dechlorination

Removal/elimination of residual chlorine

- ✓ **Sulfur dioxide ($SO_2$)**

Reaction with chlorine:

$\mathbf{SO_2} + H_2O \rightarrow HSO_3^- + H^+$

$HSO_3^- + \mathbf{HClO} \rightarrow Cl^- + SO_4^{-2} + 2\,H^+$

Reaction with chloramines:

$HSO_3^- + \mathbf{NH_2Cl} + H_2O \rightarrow Cl^- + SO_4^{-2} + NH_4^+ + H^+$

- ✓ **Activated Carbon**

With Chlorine: $\mathbf{C} + 2\,\mathbf{Cl_2} + 2\,H_2O \rightarrow 4\,HCl + CO_2$

With Chloramines: $\mathbf{C} + 2\,\mathbf{NH_2Cl} + 2\,H_2O \rightarrow 2\,NH_4^+ + 2Cl^- + CO_2$

# Disinfection: Chlorine dioxide ($ClO_2$)

## Benefits

Chlorine dioxide shows better bactericidal capacity than chlorine
The bactericidal capacity is almost independent of the pH (4-10)
It is more effective with spores
It is more reactive, It is faster, It requires lower treatment time
It is very soluble in water
No corrosion at high concentrations (compared to $Cl_2$)
Does not produce undesirable compounds as chloramines or organochlorides
Oxidizes phenol and remove odors
It is able to remove Fe and Mg more effectively than $Cl_2$

## Drawbacks

It is not stable, it cannot be stored or transported, It must be produced in situ
It is more expensive than $Cl_2$

# Disinfection: Ozone ($O_3$)

**Ozone production:**

It is not stable an it has to be generated in situ , when it is necessary.
The production is expensive and that limits its use

I can be used in disinfection and in the removal of substances associated to color, odor or taste.
It is used in the potabilization of water

***Ozone is very reactive.***

- ✓ $O_3 + H_2O \rightarrow HO_3^+ + OH^-$
- ✓ $HO_3^+ + OH \rightarrow 2\, HO_2\cdot$
- ✓ $O_3 + HO_2\cdot \rightarrow HO\cdot + 2\, O_2$
- ✓ $HO + HO_2 \rightarrow H_2O + O_2$

Free radicals: $HO^{\cdot}_2$ / $HO\cdot$
They are very active, very oxidizing
They are the responsible of the disinfection capacity

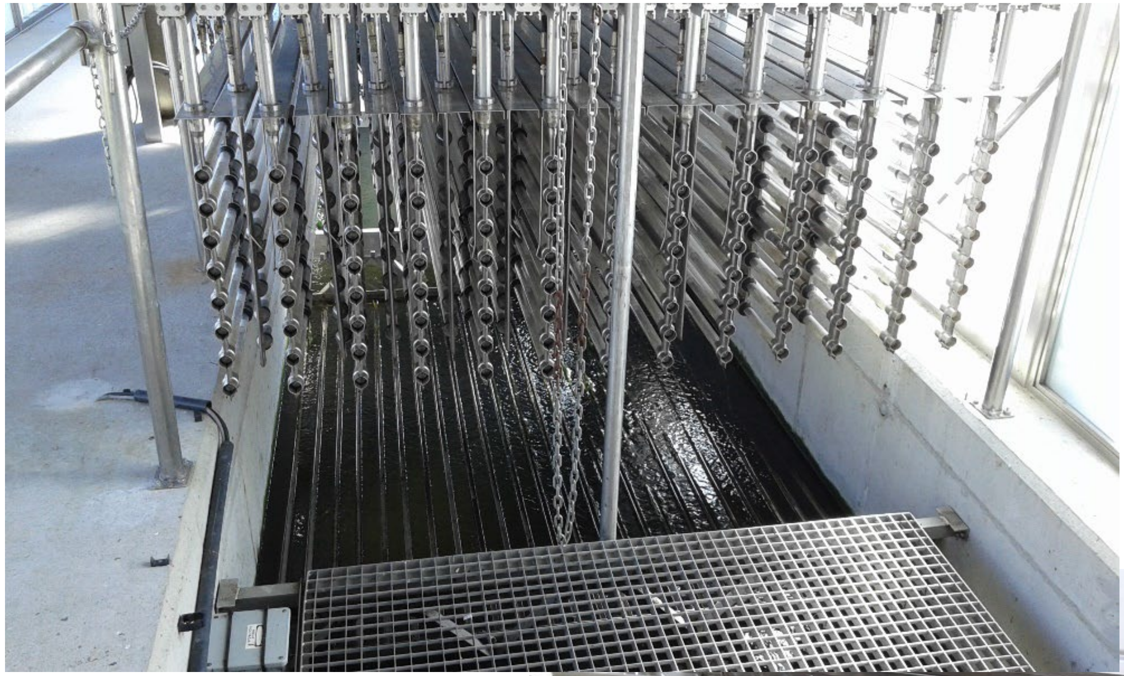
# Disinfection: Ozone ($O_3$)

## Advantages

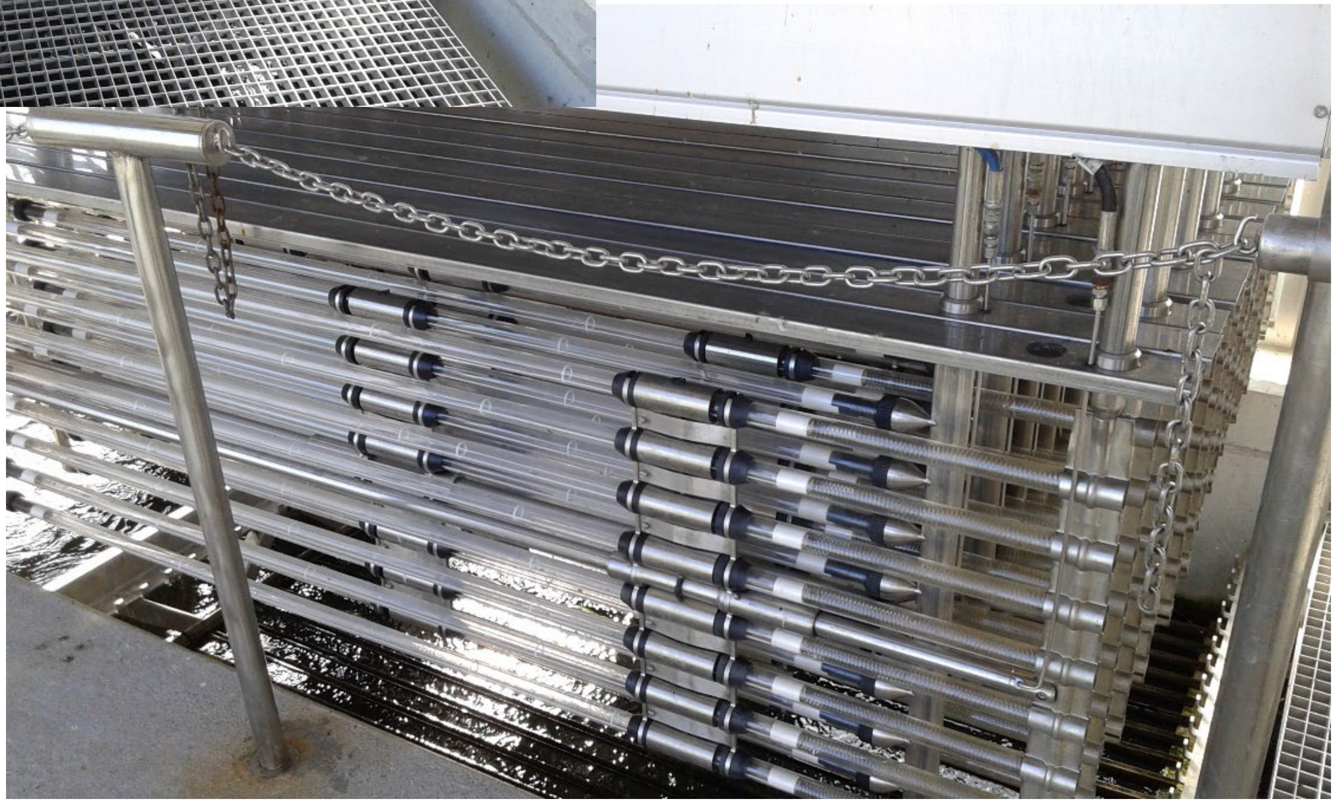
- ✓ Remove dissolved solids, and suspended solids: reduce turbidity
- ✓ Soluble in water
- ✓ Do not let undesirable products
- ✓ Does not react with ammonia
- ✓ Oxygenates the effluents
- ✓ Decreases BOD and COD
- ✓ Minor influence of the pH
- ✓ It is an effective disinfectant, more effective than Cl2 with virus, spores and others microorganisms.
- ✓ Remove flavor, odor, color
- ✓ Does not increase the concentration of dissolved solids

## Disinfection: UV Radiation

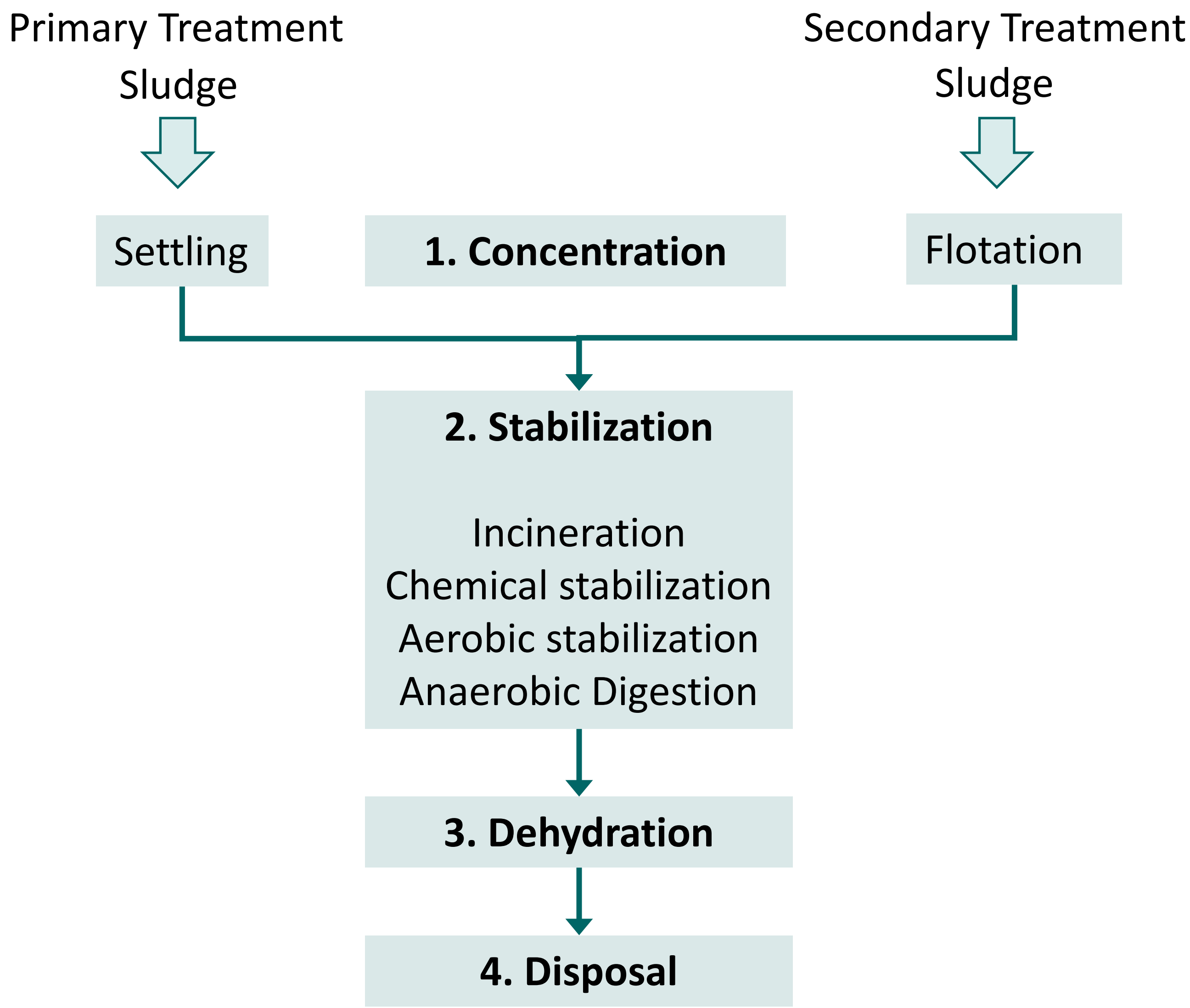
| FACTOR | EFECT |
|---|---|
| Suspended solids | Block the penetration of the UV radiation |
| Iron / Magnesium | Scale formation on the surface of the lamp blocking the radiation |
| Calcium / Magnesium | Hardness: limescale |
| Absorbents | Some substances (humic and fulvic acid) absorb the UV radiation reducing its disinfection capacity. |
| Temperature | Optimum T = 40 ºC |



## Disinfection
## With UV Radiation



# Sludge treatment



# Water treatment and reuse

| Suggested Water Recycling Treatment and Uses | | | |
|---|---|---|---|
| Increasing Levels of Treatment;<br>Increasing Acceptable Levels of Human Exposure | | | |
| Primary Treatment: Sedimentation | Secondary Treatment: Biological Oxidation, Disinfection | Tertiary / Advanced Treatment: Chemical Coagulation, Filtration, Disinfection | |
| No uses Recommended at this level | Surface irrigation of orchards and vineyards<br>Non-food crop irrigation<br>Restricted landscape impoundments<br>Groundwater recharge of non potable aquifer<br>Wetlands, wildlife habitat, stream augmentation<br>Industrial cooling processes | Landscape and golf course irrigation<br>Toilet flushing<br>Vehicle washing<br>Food crop irrigation<br>Unrestricted recreational impoundment | Indirect potable reuse: Groundwater recharge of potable aquifer and surface water reservoir augmentation |

## Discharge Tax

Tax (CCV) is determined by the formula:

$$CCV = V \cdot P \cdot k1 \cdot k2 \cdot k3$$

- V = volume, flow ($m^3$/year)
- P = unit price 0,01653 €/$m^3$ (updated every year, 2012)
- k1 = Coefficient, effluent characteristics
- k2 = Coefficient, contaminant concentration, treatment
- k3 = Coefficient, environmental quality of the discharge point (waterbody)

e.g. k2 is 0.5 if the effluent is properly managed and treated, and k2 is 2.5 if it is not treated or not properly treated.
So, the tax increases 5 times when the effluent is not properly managed.

## 1. Effluent origin.

- Urban wastewater (Sewage water) (Industrial waterwater content below 30%)
- Industrial wastewater

## K1: Effluent characteristics.

- Urban wastewater up to 1999 PE = 1
- Municipal wastewater, 2000 - 9999 PE = 1.14
- Urban wastewater, >10000 PE = 1.28
- Industrial wastewater, class 1 = 1
- Industrial wastewater, class 2 = 1.09
- Industrial wastewater, class 3 = 1.18
- Class 1, 2 or 3 with hazardous substances = 1.28

Population equivalent or unit per capita loading, (PE), in waste-water treatment is the number expressing the ratio of the sum of the pollution load produced during 24 hours by industrial facilities and services to the individual pollution load in household sewage produced by one person in the same time.

1 PE = 60 g $DBO_5$/day

| Class | Group | Activity |
|---|---|---|
| 1 | 0 | Services |
| | 1 | Energy and Water |
| | 2 | Metalurgy |
| | 3 | Food |
| | 4 | Canned Food |
| | 5 | Confectionery |
| | 6 | Wood |
| | 7 | Manufacturing industry (various) |
| | 7 | Agriculture, hunting, fishing |
| | 7 | Waste management |
| 2 | 8 | Mining |
| | 9 | Chemistry |
| | 10 | Construction |
| | 11 | Drinks and tobacco |
| | 12 | Meat and diary |
| | 13 | Textile |
| | 14 | Paper |
| 3 | 15 | Tanning |
| | 16 | Surface treatment |
| | 17 | zootechnics |

### 3. Effluent contaminant concentration: k2

- Urban effluents, proper treatment = 0.5
- Urban effluents, no proper treatment = 2.5
- Industrial effluents, proper treatment = 0.5
- Industrial effluents, no proper treatment = 2.5

Proper treatment
RD Ley 11/1995.

Proper treatment: The treatment of urban wastewater by any process or system of elimination, so the receiving waterbody meets after the discharge, the quality objectives foreseen in the applicable legal system

### 4. Environmental quality of the waterbody: k3

- Category I = 1.25
- Category II = 1.12
- Category III = 1

**Extract of the regulation**

- Category I:collection of water for human consumption; recreational use and bathing waters; areas vulnerable to contamination by nitrates from agriculture; areas sensitive to urban water discharges; perimeters of mineral and thermal waters; species habitat protection zones; hydrological reserves; groundwater.
- Category II: protection zones for aquatic species of economic interest; areas in the register of protected areas.
- Category III: other areas not included before.

**Example:** Calculate the discharge fee of the extraction of anthracite and coal industry that discharges water after treatment, in an area intended for the collection of drinking water. The discharge flow is 400 L/s. Calculate the fee in 2 scenarios: water subjected to adequate treatment and water not subjected to adequate treatment.

Data:

Fee of urban water discharge: 0.01683 €/m$^3$

Fee of industrial water discharge 0.04207 €/m$^3$

**a) Discharged volume per year:**

$$\frac{400\ \mathrm{L}}{\mathrm{s}} \cdot \frac{60\ \mathrm{s}}{\mathrm{min}} \cdot \frac{60\ \mathrm{min}}{\mathrm{h}} \cdot \frac{24\ \mathrm{h}}{\mathrm{day}} \cdot \frac{365\ \mathrm{days}}{\mathrm{año}} \cdot \frac{1\ \mathrm{m}^3}{10^3\mathrm{L}} = 12614400\ \mathrm{m}^3/\mathrm{year}$$

**b) Type of discharged effluente** — Industrial water

**c) Class of industrial activity** — Class II: coeficient k1 = 1.09

**d) Water treatment** — Discharged effluent after proper treatment, coeficient k2: 0.5
Non proper treatment, coeficient k2 = 2.5

**e) Discharge point** — Category I, coeficient k3 = 1.25

1. Proper treatment: CCV = V · P · k1 · k2 · k3 = 0.04207 €/m$^3$ · 12614400 m$^3$/año · 1.09 · 0.5 · 1.25 = 361531 €/año

2. Non- proper treatment: CCV = V · P · k1 · k2 · k3 = 0.04207 €/m$^3$ · 12614400 m$^3$/año · 1.09 · 2.5 · 1.25 = 1807655 €/año

**Exercise**: Calculate the discharge fee for a wastewater with a flow rate of 400 L/s in an area that belongs to category II. This water has a suspended solid (SS) content of 5 mg/L.

Data: 1 Population equivalent (PE) = 60 g $O_2$ $BOD_5$/day or 90 g SS/day
Fee of urban water discharge: 0.01683 €/$m^3$
Fee of industrial water discharge 0.04207 €/$m^3$

Exercise

# LESSON 4. TREATMENT OF INDUSTRIAL AND MUNICIPAL WASTEWATERS

**1.** Determine the contaminant load of the discharged effluent of two companies, the activity of the first company is mineral extraction and the other is the production of palm oil. The discharge flow and COD for the mineral extraction company is 20 mg/L and 400 L/s, and that for the palm oil extraction company is 0.1 L/s and 80000 mg/L.

*Answer: 691.2 kg/d, the same value for the two effluents.*

**2.** A sewage treatment plant will be designed to serve a city for the next 15-25 years, with a present population of 50000 people. Determine the "population equivalent" or "unit per capita loading, PE", for the design of the sewage treatment plant assuming an annual population growth rate of 1.2 %. Consider the fluctuating population will be 15 %. The fresh water consumption is 300 L/hab day and the $BOD_5$ is 140 mg/L. DATA 1 PE = 60 g/day $DBO_5$.

*Answer: 54235 PE.*

**3.** A natural water contains $4 \cdot 10^{-4}$ M of $Mg^{2+}$, $5 \cdot 10^{-4}$ M of $Ca^{2+}$ and $6 \cdot 10^{-4}$ M of $HCO_3^-$. Determine the amount of $Ca(OH)_2$ and $Na_2CO_3$ per $m^3$ of water in its softening.

*Answer: 51.8 g/$m^3$ $Ca(OH)_2$; 63.6 g/$m^3$ $NaCO_3$*

**4.** The production of galvanized iron uses zinc cyanide. A spent zinc cyanide bath 0.5 M contains 3 $m^3$ of the solution, which is diluted with water in a tank of $10^3$ $m^3$. Determine the COD of the initial and final $ZnCN_2$ solutions?

$2\ CN^- + 5\ O_2 + 12\ H^+ \longrightarrow 2\ CO_2 + N_2 + 12\ H_2O$

*Answer: Initial COD: 40000 mg $O_2$/L; Final COD: 120 mg $O_2$/L.*

**5.** The flow of an industrial wastewater effluent is 1200 $m^3$/h and its characteristics are as follows:

Suspended solids: 600 mg/L

Palmitic acid ($CH_3$-$(CH_2)_{14}$-COOH): 100 mg/L

The effluent must be treated to reach the legal discharged limits:

Suspended solids: 35 mg/L

COD: 25 mg $O_2$/L

Determine:

a) The sludge production, expressed in t/day, due to the removal of the suspended solids, considering that the moisture content of the sludge is 40 %.

b) The BOD of the wastewater

c) The efficiency to the treatment process to meet the legal DBO discharge limit

*Answer: a) 27.12 t/day; b) 287.5 mg $O_2$/L; c) 91.30%*

**6.** A metallurgical industry generates a liquid effluent that is discharged at 3 L/s. The effluent has a COD of 864 mg $O_2$/L due to the content in toluene ($C_6H_5$-$CH_3$), the suspended solids content is 500 mg/L, and chromium (III) concentration is 30 mg/L. Determine:

a) The toluene concentration in the discharge, expressed in mg/L.

b) If the suspended solids are removed by settling, with a yield of 90%, generating a sludge with a density of 1.2 g/$cm^3$ and moisture content of 65%, determine the volume of sludge, expressed in m3, generated per year.

c) If the chromium is removed by precipitation with calcium hydroxide, determine the amount of the precipitating reagent per day to completely remove the chromium from the effluent.

d) The population equivalent of the discharged effluent. 1 population equivalent = 60 g BOD/day (assume that COD = BOD, biodegradable effluent)

*Answer: a) 276 mg/L; b) 101.37 $m^3$/year; c) 16.60 kg/day; d) 3733 PE.*

**7.** A wastewater treatment plant treats various residual effluents from different sources: flushing waters, runoff streams, dehydration of sludge, etc. The WWTP receives 12 $m^3$/h from the different sources. The effluents are mixed and treated together in the WWTP. The plant is composed of a primary treatment (settling tank) and a secondary treatment (biological reactor and a secondary settling tank). The primary treatment removes 35% of $BOD_5$ and decreases the suspended solids (SS) content to 30 mg/L. The separation of suspended solids generates a sludge with 93% of moisture content. The raw water

has 600 mg/L of SS and 850 mg $O_2$/L of $BOD_5$. The final treated effluent is discharged in a nearby watercourse meeting the following legal limits: SS ≤ 35 mg/L; $BOD_5$ = 25 mg $O_2$/L.
a) Plot a flowchart of the process.
b) Determine de daily production of primary sludge (only consider the removal of suspended solids)
c) Determine the efficiency of the biological reactor to meet the legal discharge limit for $BOD_5$
d) Using the $BOD_5$ for the raw water, determine the population equivalent for the WWTP.
Assume that the flow of water is 12 $m^3$/h throughout the plant.

*Answer: b) 2.35 t/day; c) 95.5%; d) 4080 h-eq.*

## ADDITIONAL EXERCISES (LESSON 4)

**1.** A pulp and paper factory consumes 1400 $m^3$/day. The average $Ca^{2+}$ and bicarbonate content in the water are $6\cdot10^{-3}$ M and $8\cdot10^{-3}$ M respectively. What is the weekly cost of the water softening using lime? Cost of reagents: 0.25 €/kg of $Na_2CO_3$ and 0.30 €/kg of $Ca(OH)_2$

*Answer: 1389.64 €/week*

**2.** The removal of chlorine in water using activated carbon follows the reaction:

$$2\ Cl_{2(ac)} + C_{(s)} + 2\ H_2O \longrightarrow CO_{2(g)} + 4\ H^+_{(ac)} + 4\ Cl^-_{(ac)}$$

Determine the amount of a commercial activated carbon (purity 92% of carbon) to treat 1 $m^3$ of water with 0.58 ppm of chlorine. A column filled with 200 g of the commercial activated carbon is used to dechlorinate water with 0.9 mg/L of $Cl_2$. How many $m^3$ of water can be treated?

*Answer: $5.33\cdot10^{-2}$ g; 2419.26 $m^3$*

**3.** The wastewater effluent from a chemical company shows the following characteristics:
Flow = 20 L/s
Suspended solids: 400 mg/L
Butanol ($CH_3$-$(CH_2)_2$-$CH_2OH$): 100 mg/L
Propanoic acid ($CH_3$-$CH_2$-COOH): 140 mg/L
Determine:
a) The BOD due to butanol and propanoic acid.
b) Assuming a selective oxidation of the palmitic acid with gas chlorine yielding $CO_2$, what is the daily volume of chlorine, measured in normal conditions?
c) The residual concentration of suspended solids after the treatment is 25 mg/L, what is the annual amount of sludge with 80 % of moisture produced due to the removal of solids from the wastewater?

*Answer: a) 471.35 mg $O_2$/L; b) 512.61 $m^3$/day; c) 1182.6 t/year.*

**4.** Sugar cane processing industry produces 2000 t/month of sugar. The residual effluent contains 2000 mg/L of sucrose ($C_{12}H_{22}O_{11}$) and 12 g/L of suspended solids (SS). The treatment of the effluent uses an anaerobic process, transforming 70 % of the sucrose in methane and $CO_2$. The flow of the residual effluent is 0.6 $m^3$/t of sugar. The heating power of the methane is 39747 kJ/$m^3$. Determine:
a) The amount of sludge per month if the SS content decreased to 30 mg/L, the moisture content of the sludge is 65 %
b) The energy produced per month (expressed as kWh/month)

*Answer: a) 41.04 t/year; b) 7289.28 kWh/month.*

5. A wastewater treatment plant receives 15 $m^3$/h of wastewater. In the primary treatment, the water enters with a BOD of 1500 mg/L (this is the maximum treatment capacity of the plant) and the water exits after a reduction of 40% in the BOD.
In the secondary treatment, the water, 15 $m^3$/h, enters an activated sludge reactor to remove the organic matter in the water. Then, the wastewater flows into the secondary settling tank with a suspended solid concentration of 2% (vol/vol). The solids are concentrated in the sludge stream (10% vol/vol) and the clarified effluent (with only 0.2% of solids) is discharged in the nearby watercourse.
a) Determine the population equivalent (h-eq) for the raw water that enters the plant.

b) The legal limit for BOD is the final discharged effluent is 25 mg/L. Determine the efficiency of the biological reactor to meet the legal limit in the final effluent.
c) Determine the flow of the clarified effluent and the sludge stream in the secondary settling tank.
d) Determine the dimensions (height) of a cylindrical tank (10 m diameter) to store the sludge stream for 1 month.

*Answer: a) 9000 PE; b) 99.22%; c) 12.24 $m^3/h$; 2.76 $m^3/h$; d) 25.26 m.*

**6.** The wastewater from electroplating and electronic industries are commonly contaminated with cyanide. This compound is highly pollutant ant it needs to be removed from the effluents. One possible process for the removal of cyanide is the adsorption with activated carbon. The saturated activated carbon with cyanide must be stored in a safe deposit. The adsorption capacity of $CN^-$ on activated carbon is 200 mg of $CN^-$/g of activated carbon. The flow of the $CN^-$ contaminated effluent is 1000 $m^3$/day and the concentration is 50 000 mg $CN^-$/L. Determine:
a) The annual consumption of activated carbon to treat the CN- contaminated wastewater (assume that the wastewater is produced 365 days per year).
b) The amount of sludge generated per year, in $m^3$, with a moisture content of 55% (vol/vol), assuming a complete removal of cyanide.
c) Number of rectangular basins to store the sludge generated in a year. The maximum dimensions of the basins are 890 $m^2$ of area and 10 m of height.
DATA: Density (spent activated carbon) = 0.7 kg/L; Density (water) = 1 kg/L.

*Answer: a) 91250 t; b) 260714 $m^3$/year; c) 30 basins.*

## Exercise

**1.** Determine the contaminant load of the discharged effluent of two companies, the activity of the first company is mineral extraction and the other is the production of palm oil. The discharge flow and COD for the mineral extraction company is 20 mg/L and 400 L/s, and that for the palm oil extraction company is 0.1 L/s and 80000 mg/L.

*Answer: 691.2 kg/d, the same value for the two effluents*

$$1\ \text{ppm} = \frac{1\ \text{mg}}{\text{kg}} \approx \frac{1\ \text{mg}}{\text{L}}$$

Only if the solution density is $\rho = 1$ (very diluted aqueous solutions)

Mineral extraction: $$\frac{20\ \text{mg COD}}{\text{L}} \cdot \frac{400\ \text{L}}{\text{s}} \cdot \frac{1\ \text{kg}}{10^6\ \text{mg}} \cdot \frac{86400\ \text{s}}{1\ \text{day}} = 691.2\ \text{kg COD/day}$$

Palm oil: $$\frac{80000\ \text{mg COD}}{\text{L}} \cdot \frac{0.1\ \text{L}}{\text{s}} \cdot \frac{1\ \text{kg}}{10^6\ \text{mg}} \cdot \frac{86400\ \text{s}}{1\ \text{day}} = 691.2\ \text{kg COD/day}$$

## Exercise

**2.** A sewage treatment plant will be designed to serve a city for the next 15-25 years, with a present population of 50000 people. Determine the "population equivalent" or "unit per capita loading, PE", for the design of the sewage treatment plant assuming an annual population growth rate of 1.2 %. Consider the fluctuating population will be 15 %. The fresh water consumption is 300 L/hab day and the $BOD_5$ is 140 mg/L. DATA 1 PE = 60 g/day $BOD_5$.

*Answer: 54235 PE*

a) Population growth

$$P_t = P_0(1+\alpha)^t = 50000 \text{ inhab} \cdot (1+0.012)^{25} = 67373 \text{ inhab.}$$

Annual growth rate

Population at time 0 (present time)

Population at time t (t=25 years)

b) Total population: + 15% foreigners

67373 inhab·1.15 = 77478 inhab.

c) Contamination generated by the 77478 inhab. and population equivalent (PE)

1 PE = 60 g $BOD_5$/day

$$77478 \text{ inhab} \cdot \frac{300 \text{ L}}{\text{inhab day}} \cdot \frac{140 \text{ mg DBO}_5}{\text{L}} \cdot \frac{1 \text{ g}}{10^3 \text{ mg}} = 3254076 \text{ g BOD}_5/\text{day}$$

$$3254076 \text{ g BOD}_5/\text{day} \frac{1 \text{ PE}}{60 \text{ g BOD}_5/\text{day}} = 54235 \text{ PE}$$

## Exercise. Hard water.

**3.** A natural water contains $4·10^{-4}$ M of $Mg^{2+}$, $5·10^{-4}$ M of $Ca^{2+}$ and $6·10^{-4}$ M of $HCO_3^-$. Determine the amount of $Ca(OH)_2$ and $Na_2CO_3$ per $m^3$ of water in its softening.

Answer: 51.8 g/$m^3$ $Ca(OH)_2$, 63.6 g/$m^3$ $NaCO_3$

Basis of calculation: 1 $m^3$ ($10^3$ L)

$4·10^{-4}$ mol/L de $Mg^{2+}$ · $10^3$ L = 0.4 mol $Mg^{2+}$
$5·10^{-4}$ mol/L de $Ca^{2+}$ · $10^3$ L = 0.5 mol $Ca^{2+}$
$6·10^{-4}$ mol/L de $HCO_3^-$ · $10^3$ L = 0.6 mol $HCO_3^-$

1st step: removal of $Mg^{2+}$ vith $Ca(OH)_2$

$$Mg^{2+} + Ca(OH)_2 \longrightarrow Mg(OH)_2 \downarrow + Ca^{2+}$$

| | $Mg^{2+}$ | $Ca(OH)_2$ | $Mg(OH)_2$ | $Ca^{2+}$ | |
|---|---|---|---|---|---|
| initial | 0.4 | 0.4 | - | - | mol |
| final | 0 | 0 | 0.4 | 0.4 | mol |

2nd step: removal of $Ca^{2+}$ and $HCO_3^-$ with $Ca(OH)_2$

$$Ca^{2+} + 2\,HCO_3^- + Ca(OH)_2 \longrightarrow 2\,CaCO_3 \downarrow + 2\,H_2O$$

| | $Ca^{2+}$ | $HCO_3^-$ | $Ca(OH)_2$ | $CaCO_3$ | $H_2O$ | |
|---|---|---|---|---|---|---|
| initial | 0.4+0.5 | 0.6 | 0.3 | - | - | mol |
| final | 0.6 | 0 | 0 | 0.6 | 0.6 | mol |

3rd step: removal of $Ca^{2+}$ with $Na_2CO_3$

$$Ca^{2+} + Na_2CO_3 \longrightarrow CaCO_3 \downarrow + 2\,Na^+$$

| | $Ca^{2+}$ | $Na_2CO_3$ | $CaCO_3$ | $Na^+$ | |
|---|---|---|---|---|---|
| initial | 0.6 | 0.6 | - | - | mol |
| final | 0 | 0 | 0.6 | 1.2 | mol |

Consumption of $Ca(OH)_2$

$$\frac{0.4 + 0.3\text{ mol}}{m^3}\,\frac{74\text{ g}}{1\text{ mol }Ca(OH)_2} = 51.8\text{ g/m}^3$$

Consumption of $Na_2CO_3$

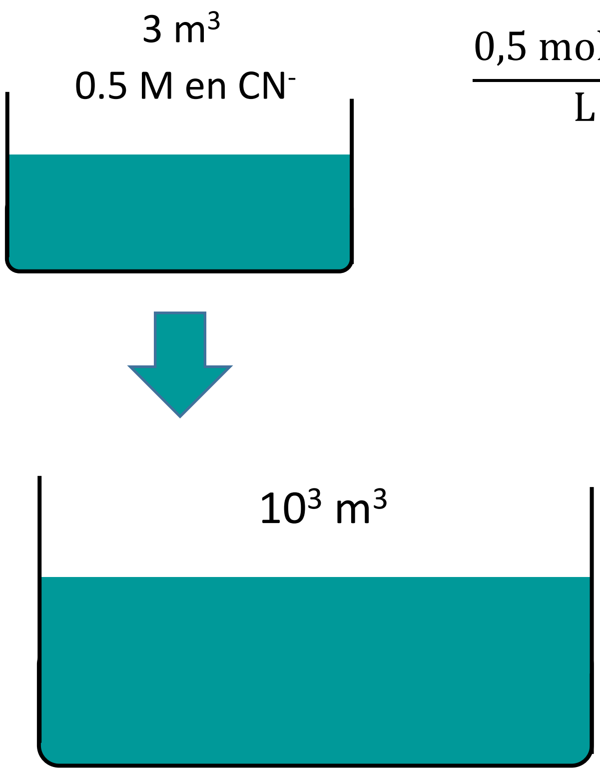
$$\frac{0.6\text{ mol}}{m^3}\,\frac{106\text{ g}}{1\text{ mol }Na_2CO_3} = 63.6\text{ g/m}^3$$

## Exercise

**4.** The production of galvanized iron uses zinc cyanide. A spent zinc cyanide bath 0.5 M contains 3 $m^3$ of the solution, which is diluted with water in a tank of $10^3$ $m^3$. Determine the COD of the initial and final $ZnCN_2$ solutions?

$$2\,CN^- + 5\,O_2 + 12\,H^+ \longrightarrow 2\,CO_2 + N_2 + 6\,H_2O$$

*Answer: Initial COD: 40000 mg $O_2$/L, Final COD: 120 mg $O_2$/L*




$$\frac{0{,}5 \text{ mol } CN^-}{L} \cdot \frac{5 \text{ mol } O_2}{2 \text{ mol } CN^-} \cdot \frac{32 \cdot 10^3 \text{ mg } O_2}{1 \text{ mol } O_2} = 4 \cdot 10^4 \text{ mg } O_2/L \quad \text{mg COD/L}$$

$$\frac{0{,}5 \text{ mol } CN^-}{L} \cdot \frac{3 \text{ m}^3}{10^3 \text{ m}^3} = 1.5 \cdot 10^{-3} \text{ mol/L} = 1.5 \text{ mmol/L}$$

$$\frac{1.5 \cdot 10^{-3} \text{ mol } CN^-}{L} \cdot \frac{5 \text{ mol } O_2}{2 \text{ mol } CN^-} \cdot \frac{32 \cdot 10^3 \text{ mg } O_2}{1 \text{ mol } O_2} = 120 \text{ mg } O_2/L \quad \text{mg COD/L}$$

$$\frac{4 \cdot 10^4 \text{ mg } O_2}{L} \cdot \frac{3 \text{ m}^3}{1000 \text{ m}^3} = 120 \text{ mg } O_2/L \quad \text{mg COD/L}$$

# Exercise

**5.** The flow of an industrial wastewater effluent is 1200 $m^3/h$ and its characteristics are as follows:

Suspended solids: 600 mg/L

Palmitic acid ($CH_3$-$(CH_2)_{14}$-COOH): 100 mg/L

The effluent must be treated to reach the legal discharged limits:

Suspended solids: 35 mg/L

BOD: 25 mg $O_2$/L

Determine:

a) The sludge production, expressed in t/day, due to the removal of the suspended solids, considering that the moisture content of the sludge is 40 %.

b) The BOD of the wastewater

c) The efficiency to the treatment process to meet the legal DBO discharge limit

*Answer: 27.12 t/day, 287.5 mg $O_2$/L; 91.30 %*

Exercise

a) Moist sludge in t/day:

$$\left(\frac{600\ \mathrm{mg\ SS}}{\mathrm{L}} - \frac{35\ \mathrm{mg\ SS}}{\mathrm{L}}\right) \cdot \frac{1200 \cdot 10^3\ \mathrm{L}}{\mathrm{h}} \cdot \frac{24\ \mathrm{h}}{1\ \mathrm{day}} \cdot \frac{1\ \mathrm{t}}{10^9\ \mathrm{mg}} \cdot \frac{100\ \mathrm{t\ moist\ sludge}}{(100-40)\ \mathrm{t\ SS}} = 27.12\ \mathrm{t/day}$$

b) BOD of the wastewater due to the palmitic acid.

Oxidation of the palmitic acid: $CH_3(CH_2)_{14}COOH + O_2 \longrightarrow CO_2 + H_2O$

$$CH_3(CH_2)_{14}COOH + 23\ O_2 \longrightarrow 16\ CO_2 + 16\ H_2O$$

$$\frac{100\ \mathrm{mg\ Palmitic}}{\mathrm{L}} \cdot \frac{1\ \mathrm{mol\ Palmitic}}{256 \cdot 10^3\ \mathrm{mg\ Palmitic}} \cdot \frac{23\ \mathrm{mol}\ O_2}{1\ \mathrm{mol\ Palmitic}} \cdot \frac{32 \cdot 10^3\ \mathrm{mg}\ O_2}{1\ \mathrm{mol}\ O_2} = 287.5\ \mathrm{mg}\ O_2/\mathrm{L}$$

c) Inlet BOD: 287.5 mg $O_2$/L; Outlet BOD: 25 mg $O_2$/L. Efficiency:

$$\frac{(287.5\ \mathrm{mg}\ O_2/\mathrm{L} - 25\ \mathrm{mg}\ O_2/\mathrm{L})}{287.5\ \mathrm{mg}\ O_2/\mathrm{L}} \cdot 100 = 91{,}30\ \%$$

**Example:** Calculate the discharge fee of the extraction of anthracite and coal industry that discharges water after treatment, in an area intended for the collection of drinking water. The discharge flow is 400 L/s. Calculate the fee in 2 scenarios: water subjected to adequate treatment and water not subjected to adequate treatment.

Data:

Fee of urban water discharge: 0.01683 €/$m^3$

Fee of industrial water discharge 0.04207 €/$m^3$

**a) Discharged volume per year:**

$$\frac{400\ \mathrm{L}}{\mathrm{s}} \cdot \frac{60\ \mathrm{s}}{\mathrm{min}} \cdot \frac{60\ \mathrm{min}}{\mathrm{h}} \cdot \frac{24\ \mathrm{h}}{\mathrm{day}} \cdot \frac{365\ \mathrm{days}}{\mathrm{año}} \cdot \frac{1\ \mathrm{m}^3}{10^3 \mathrm{L}} = 12614400\ \mathrm{m}^3/\mathrm{year}$$

**b) Type of discharged effluente** — Industrial water

**c) Class of industrial activity** — Class II: coeficient k1 = 1.09

**d) Water treatment** — Discharged effluent after proper treatment, coeficient k2: 0.5
Non proper treatment, coeficient k2 = 2.5

**e) Discharge point** — Category I, coeficient k3 = 1.25

1. Proper treatment: CCV = V · P · k1 · k2 · k3 = 0.04207 €/$m^3$ · 12614400 $m^3$/año · 1.09 · 0.5 · 1.25 = 361531 €/año

2. Non-proper treatment: CCV = V · P · k1 · k2 · k3 = 0.04207 €/$m^3$ · 12614400 $m^3$/año · 1.09 · 2.5 · 1.25 = 1807655 €/año

**Exercise**: Calculate the discharge fee for a wastewater with a flow rate of 400 L/s in an area that belongs to category II. This water has a suspended solid (SS) content of 5 mg/L.

Data: 1 Population equivalent (PE) = 60 g $O_2$ $BOD_5$/day or 90 g SS/day
Fee of urban water discharge: 0.01683 €/m$^3$
Fee of industrial water discharge 0.04207 €/m$^3$

**a) Discharged volumen per year**

$$\frac{400\ \text{L}}{\text{s}} \cdot \frac{60\ \text{s}}{\text{min}} \cdot \frac{60\ \text{min}}{\text{h}} \cdot \frac{24\ \text{h}}{\text{day}} \cdot \frac{365\ \text{days}}{\text{año}} \cdot \frac{1\ \text{m}^3}{10^3\text{L}} = 12614400\ \text{m}^3/\text{year}$$

**b) Type of wastewater**

Municipal wastewater, urban wastewater, sewage wastewater

**c) PE**

$$\frac{400\ \text{L}}{\text{s}} \cdot \frac{60\ \text{s}}{\text{min}} \cdot \frac{60\ \text{min}}{\text{h}} \cdot \frac{24\ \text{h}}{\text{day}} \cdot \frac{5\ \text{mg SS}}{\text{L}} \cdot \frac{1\ \text{g}}{10^3\ \text{mg}} \cdot \frac{1\ \text{PE}}{90\ \text{g SS/day}} = 1920\ \text{PE}$$

Coeficient k1 = 1 (Municipal watewater up to 1999 PE)

**d) Water treatment**

Watewater discharge after proper treatment, coeficient k2: 0.5
Non proper treatment, coeficient k2 = 2.5

**e) Discharge point**

Category I, coeficient k3 = 1.12

1. Fee for proper treatment: CCV = V · P · k1 · k2 · k3 = 0.01683 €/m$^3$ · 12614400 m$^3$/year · 1 · 0.5 · 1.12 = 118888 €/year

2. Fee for non proper treatment: CCV = V · P · k1 · k2 · k3 = 0.01683 €/m$^3$ · 12614400 m$^3$/year · 1 · 2.5 · 1.12 = 594440 €/year

**6.** A metallurgical industry generates a liquid effluent that is discharged at 3 L/s. The effluent has a COD of 864 mg $O_2$/L due to the content in toluene ($C_6H_5$-$CH_3$), the suspended solids content is 500 mg/L, and chromium (III) concentration is 30 mg/L. Determine:

a) The toluene concentration in the discharge, expressed in mg/L.

b) If the suspended solids are removed by settling, with a yield of 90%, generating a sludge with a density of 1.2 g/cm$^3$ and moisture content of 65%, determine the volume of sludge, expressed in m3, generated per year.

c) If the chromium is removed by precipitation with calcium hydroxide, determine the amount of the precipitating reagent per day to completely remove the chromium from the effluent.

d) The population equivalent of the discharged effluent. 1 population equivalent = 60 g BOD/day (assume that COD = BOD, biodegradable effluent)

Exercise

## a) The toluene concentration in the discharged effluent, expressed as mg/L

Toluene ($C_6H_5$-$CH_3$): 864 mg $O_2$/L $\Rightarrow$ mg/L

$$C_6H_5\text{-}CH_3 + 9\,O_2 \longrightarrow 7\,CO_2 + 4\,H_2O$$

$$\frac{864 \text{ mg } O_2}{\text{L}} \cdot \frac{1 \text{ mol } O_2}{32 \cdot 10^3 \text{ mg}} \cdot \frac{1 \text{ mol } C_7H_8}{9 \text{ mol } O_2} \cdot \frac{92 \text{ g } C_7H_8}{1 \text{ mol } C_7H_8} \cdot \frac{10^3 \text{ mg}}{1 \text{ g}} = 276 \text{ mg/L}$$

b) If the suspended solids are removed by settling, with a yield of 90%, generating a sludge with a density of 1.2 g/cm$^3$ and moisture content of 65%, determine the **volume of sludge, expressed in m$^3$, generated per year**.

$$\frac{500 \text{ mg SS}}{\text{L}} \cdot \frac{3 \text{ L}}{\text{s}} \cdot \frac{60 \text{ s}}{\text{min}} \cdot \frac{60 \text{ min}}{\text{h}} \cdot \frac{24 \text{ h}}{\text{day}} \cdot \frac{365 \text{ day}}{\text{year}} \cdot 0.90 \cdot \frac{100 \text{ mg sludge}}{35 \text{ mg SS}} \cdot \frac{1 \text{ cm}^3 \text{ sludge}}{1.2 \cdot 10^3 \text{ mg sludge}} \cdot \frac{1 \text{ m}^3}{10^6 \text{ cm}^3} = 101.37 \text{ m}^3\text{/year}$$

Exercise

c) If the chromium is removed by precipitation with calcium hydroxide, determine the **amount of the precipitating reagent per day** to completely remove the chromium from the effluent.

30 mg/L Cr(III)
3 L/s

$2\,Cr^{3+} + 3\,Ca(OH)_2 \longrightarrow 2\,Cr(OH)_3 + 3\,Ca^{2+}$

$$\frac{30\text{ mg Cr}^{3+}}{\text{L}}\cdot\frac{3\text{ L}}{\text{s}}\cdot\frac{60\text{ s}}{\text{min}}\cdot\frac{60\text{ min}}{\text{h}}\cdot\frac{24\text{ h}}{\text{day}}\cdot\frac{1\text{ mol Cr}^{3+}}{52\cdot10^3\text{ mg Cr}^{3+}}\cdot\frac{3\text{ mol Ca(OH)}_2}{2\text{ mol Cr}^{3+}}\cdot\frac{74\text{ g Ca(OH)}_2}{1\text{ mol Ca(OH)}_2}\cdot\frac{1\text{ kg}}{10^3\text{ g}} = 16.60\text{ kg/day}$$

d) The **population equivalent** of the discharged effluent.

1 population equivalent PE= 60 g BOD/day (assume that COD = BOD, biodegradable effluent)

864 mg $O_2$/L
3 L/s

$\Rightarrow$ 1 PE = 60 g BOD/day

$$\frac{864\text{ mg O}_2}{\text{L}}\cdot\frac{3\text{ L}}{\text{s}}\cdot\frac{86400\text{ s}}{\text{day}}\cdot\frac{1\text{ g}}{10^3\text{ mg}}\cdot\frac{1\text{ PE}}{60\text{ g O}_2/\text{day}} = 3733\text{ PE}$$

**7.** A wastewater treatment plant treats various residual effluents from different sources: flushing waters, runoff streams, dehydration of sludge, etc. The WWTP receives 12 $m^3/h$ from the different sources. The effluents are mixed and treated together in the WWTP. The plant is composed of a primary treatment (settling tank) and a secondary treatment (biological reactor and a secondary settling tank). The primary treatment removes 35% of $BOD_5$ and decreases the suspended solids (SS) content to 30 mg/L. The separation of suspended solids generates a sludge with 93% of moisture content. The raw water has 600 mg/L of SS and 850 mg $O_2$/L of $BOD_5$. The final treated effluent is discharged in a nearby watercourse meeting the following legal limits: SS ≤ 35 mg/L; $BOD_5$ = 25 mg $O_2$/L.

a) Plot a flowchart of the process.

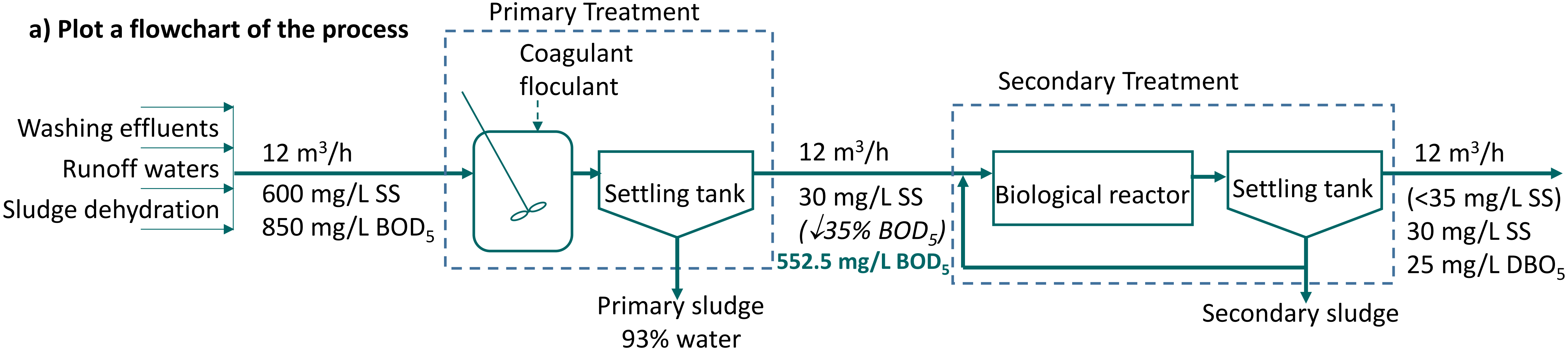
b) Determine de daily production of primary sludge (only consider the removal of suspended solids)

c) Determine the efficiency of the biological reactor to meet the legal discharge limit for $BOD_5$

d) Using the $BOD_5$ for the raw water, determine the population equivalent for the WWTP.

Assume that the flow of water is 12 $m^3/h$ throughout the plant.

**a) Plot a flowchart of the process**




Exercise

b) Determine de **daily production of primary sludge** (only consider the removal of suspended solids)

$$(600-30)\frac{\text{mg SS}}{\text{L}}\cdot\frac{12\text{ m}^3}{\text{h}}\cdot\frac{10^3\text{L}}{1\text{ m}^3}\cdot\frac{24\text{ h}}{1\text{ day}}\cdot\frac{100\text{ mg sludge}}{7\text{ mg SS}}\cdot\frac{1\text{ t}}{10^9\text{ mg}}=2.35\text{ t/day}$$

c) Determine the **efficiency of the biological reactor** to meet the legal discharge limit for BOD5

$$850\text{ mg/L}\cdot(1-0.35)=552.5\text{ mg/L BOD}_5$$

$$\frac{552.5\text{ mg/L}-25\text{ mg/L}}{552.5\text{ mg/L}}\cdot 100=95.5\%$$

d) Using the $BOD_5$ for the raw water, determine the **population equivalent** for the WWTP

$$850\frac{\text{mg BOD}_5}{\text{L}}\cdot\frac{12\,m^3}{\text{h}}\cdot\frac{10^3\text{ L}}{1\,m^3}\cdot\frac{24\text{ h}}{1\text{ day}}\cdot\frac{1\text{ g}}{10^3\text{ mg}}\cdot\frac{1\text{ PE}}{60\text{ g BOD}_5\text{/day}}=4080\text{ PE}$$