

The image shows two forms of activated carbon on a white surface. One is a large, dark, irregularly shaped block of carbon, and the other is a smaller, dark, granular pile of carbon. The text 'TERTIARY TREATMENTS' is overlaid in white capital letters on the large block of carbon.

TERTIARY TREATMENTS

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TERTIARY TREATMENT

•NATURE

- Physical processes.
- Chemical processes.
- Biological processes.

•OBJECTIVES

- Removal of specific substances

•RESULTING FLOWS

- treated aqueous effluent
- sludge
- reusable substances
- Gases

NITROGEN AND PHOSPHOROUS REMOVAL

- MACRONUTRIENTS**

- C, H, O

- MESONUTRIENTS**

- N, P, S, Ca, Mg, Na, K, Si

- MICRONUTRIENTS**

- Fe, Cu, Mo, Mn, Zn

[Nutrient] ↓ growth inhibited

- MACRONUTRIENTS**

Can be taken from environment (CO_2 , H_2O)

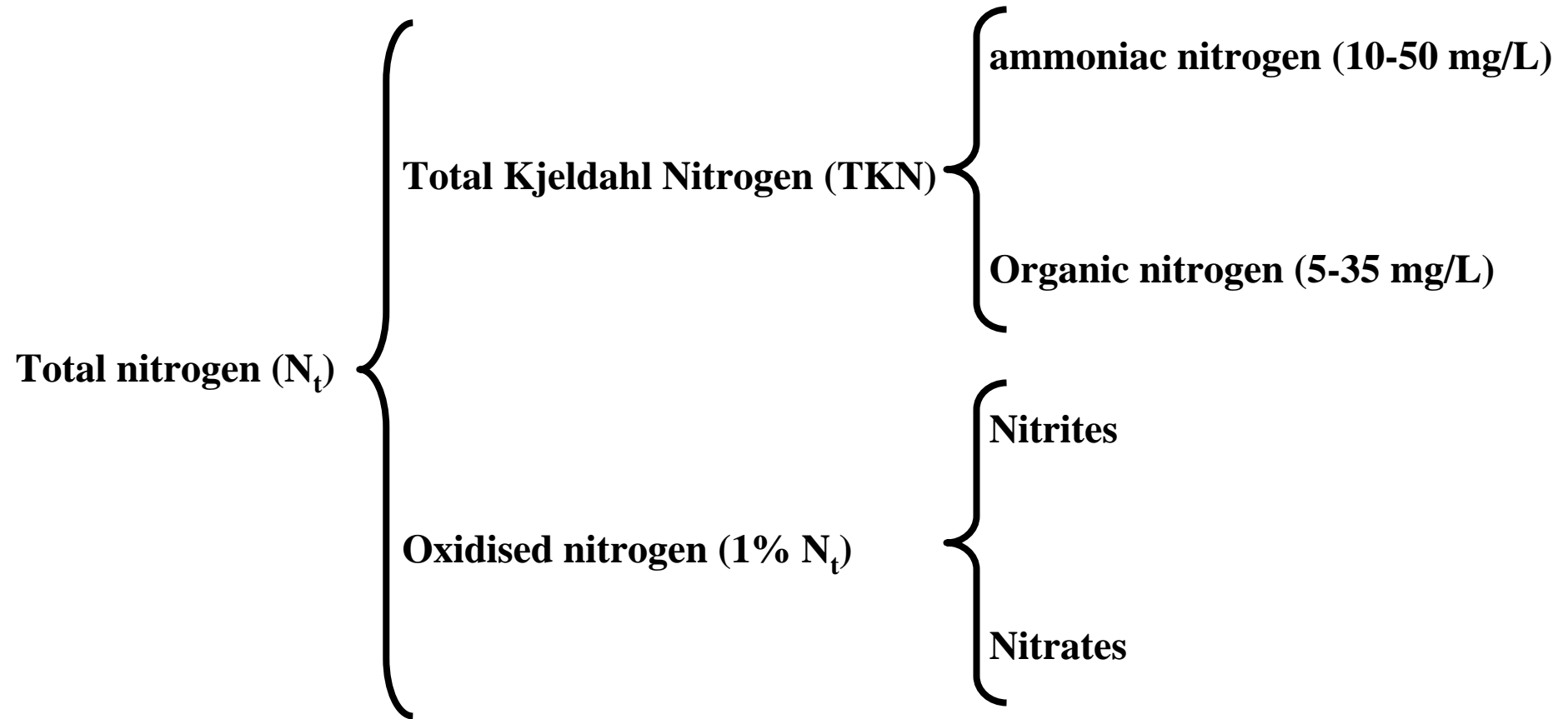
- MESONUTRIENTS**

Best option. N (3-10%), P (0,5-1%)

- MICRONUTRIENTS**

Very small quantities, total removal very expensive

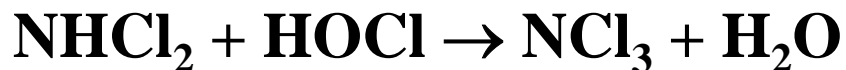
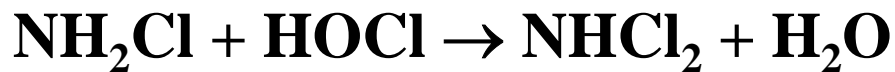
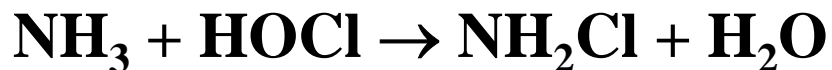
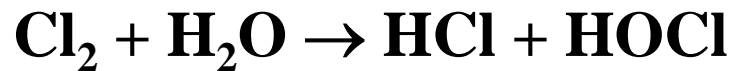
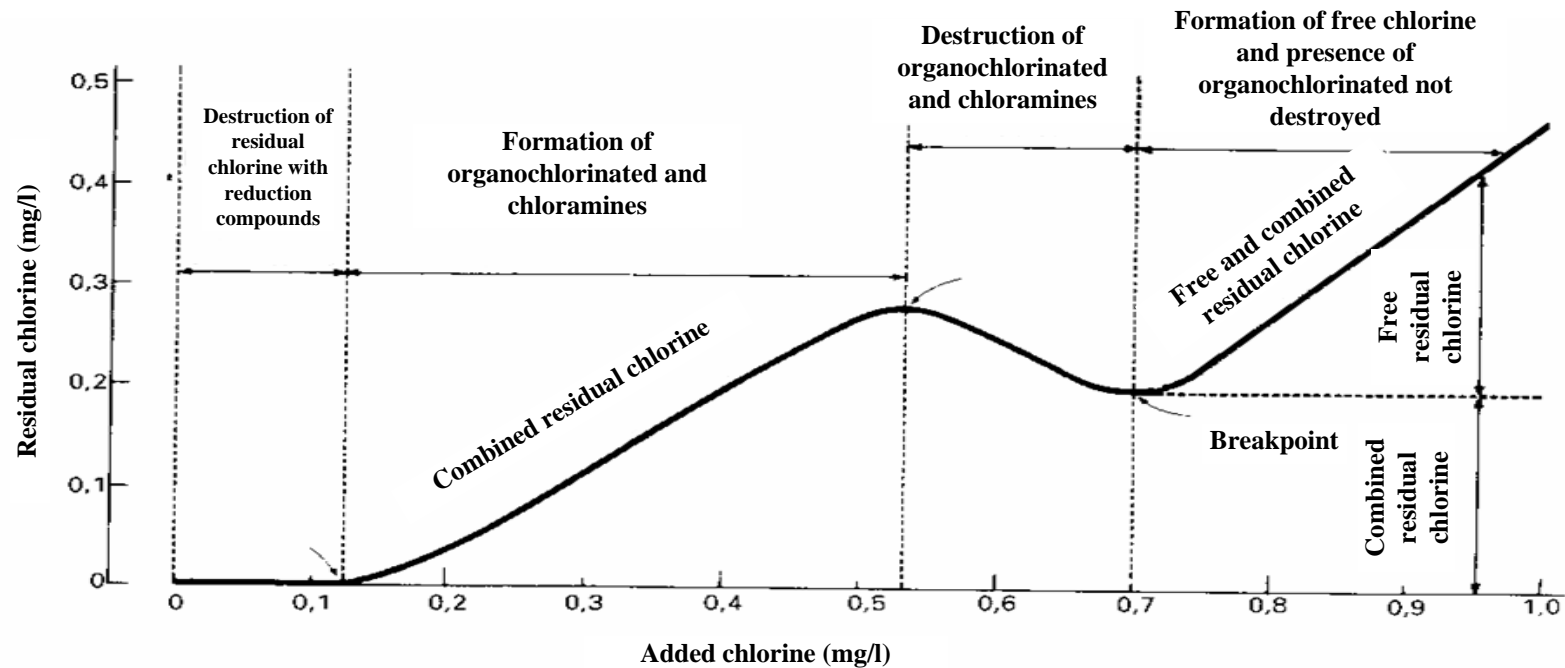
NITROGEN AND PHOSPHOROUS REMOVAL



NITROGEN REMOVAL (I)

•PHYSICO-CHEMICAL METHODS.

•Chlorination breakpoint



$$\frac{\text{Cl}_2}{\text{N}_{\text{NH}_3}} = 8 - 10$$

$$\frac{\text{mg CaCO}_3}{\text{mg N}_{\text{NH}_3}} = 14,3$$

$$\text{mg N}_{\text{NH}_3}$$

NITROGEN REMOVAL (II)

•PHYSICO-CHEMICAL METHODS.

Air stripping

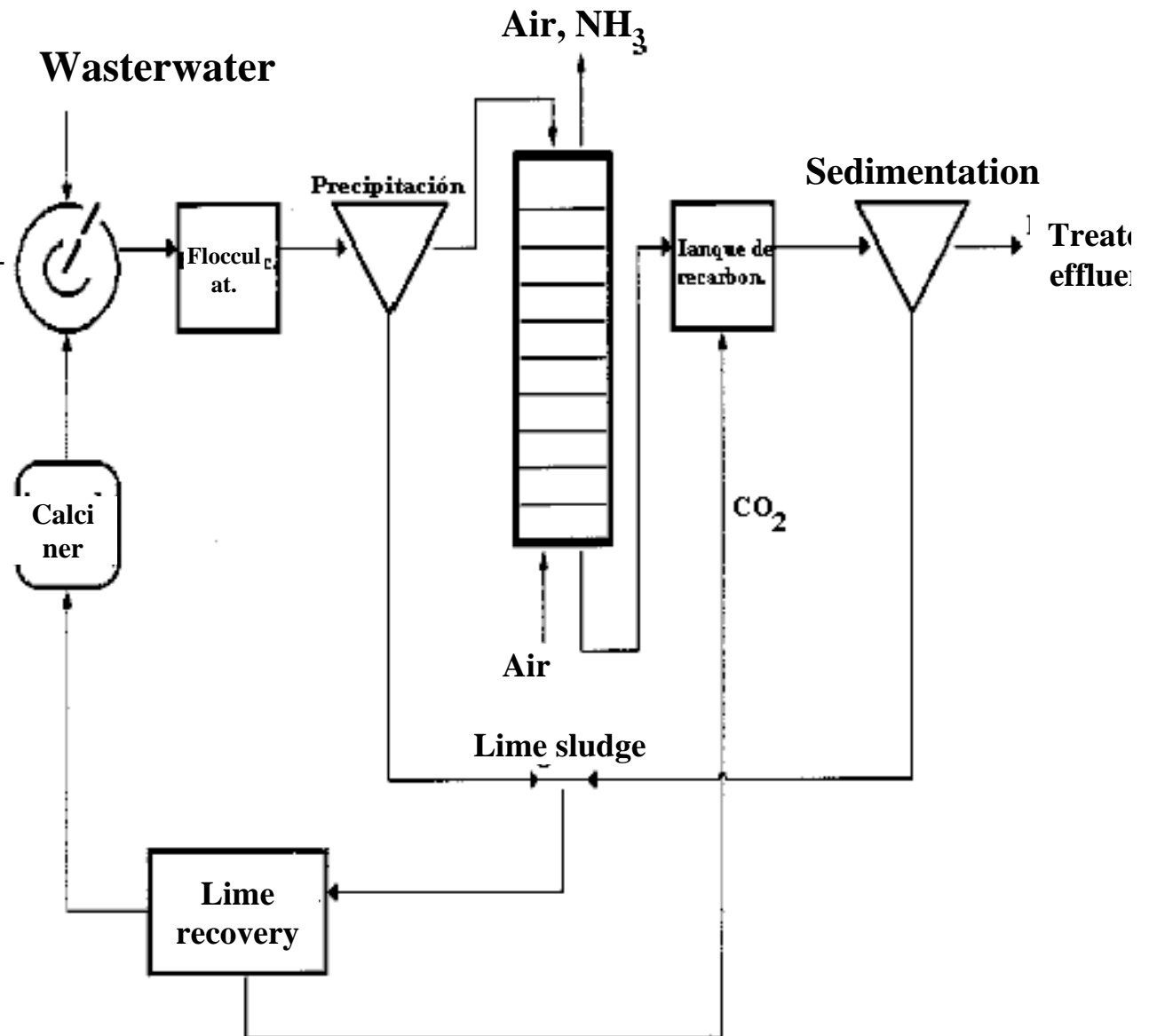
Desorption process

Countercurrent system

$\text{pH} \approx 10 \quad \text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$

$Q_{\text{air}} = 2,5 \text{ m}^3/\text{L}$

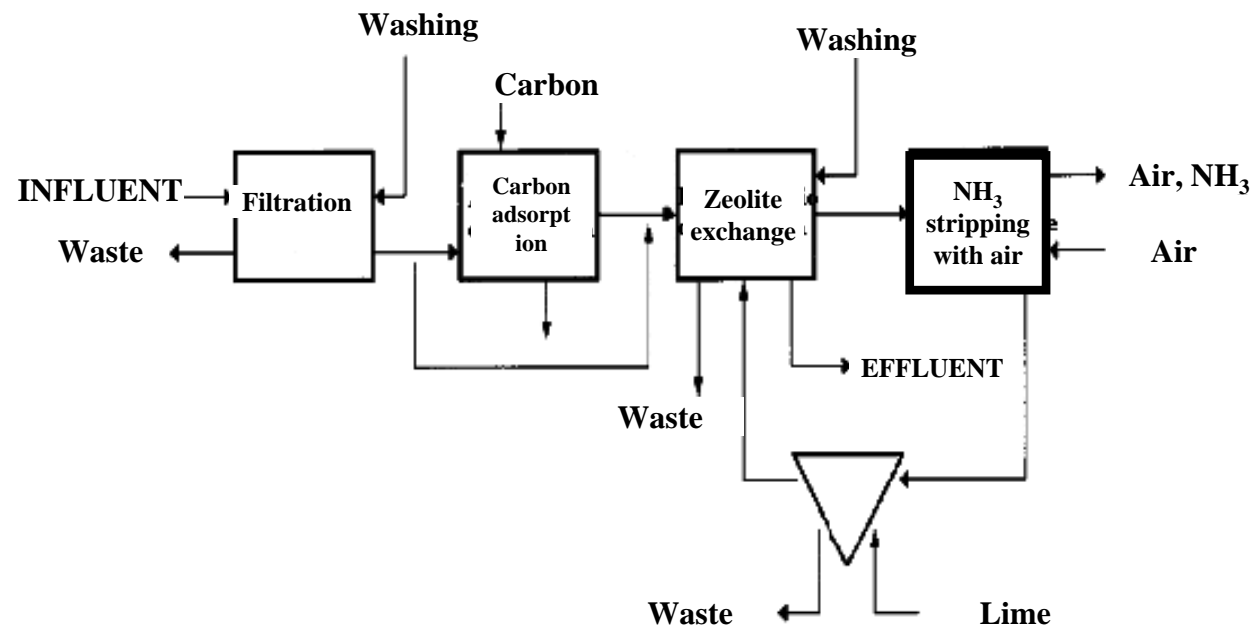
Performance $\approx 90\%$



NITROGEN REMOVAL (III)

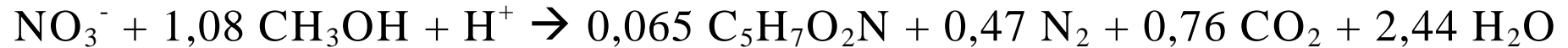
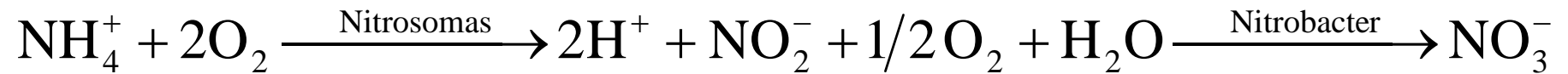
•PHYSICO-CHEMICAL METHODS.

•Ion exchange

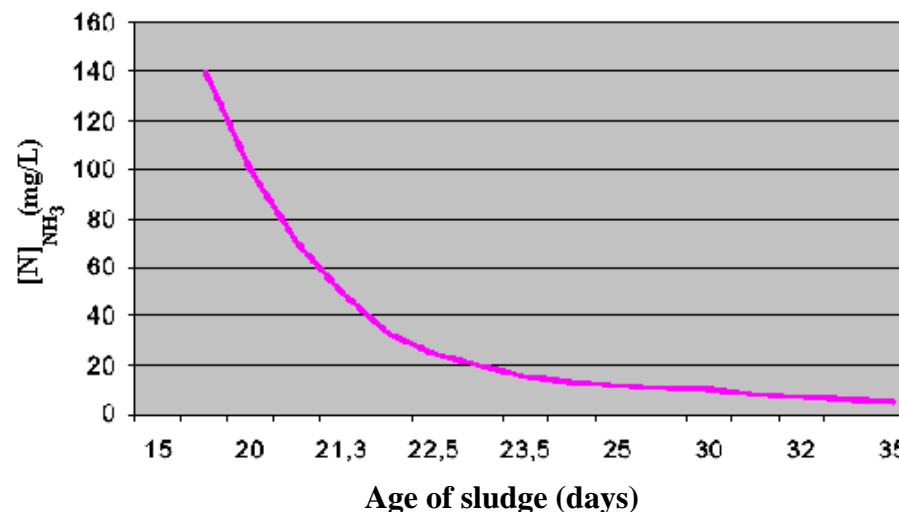


NITROGEN REMOVAL (IV)

•BIOLOGICAL METHODS.



- Anoxic conditions (anaerobic)
- Provide organic material BOD_5



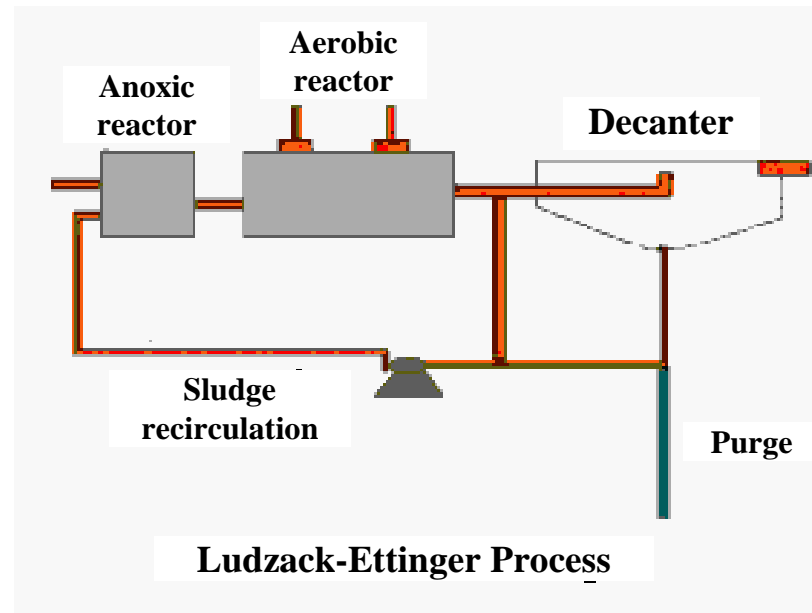
NITROGEN REMOVAL (V)

•BIOLOGICAL METHODS.

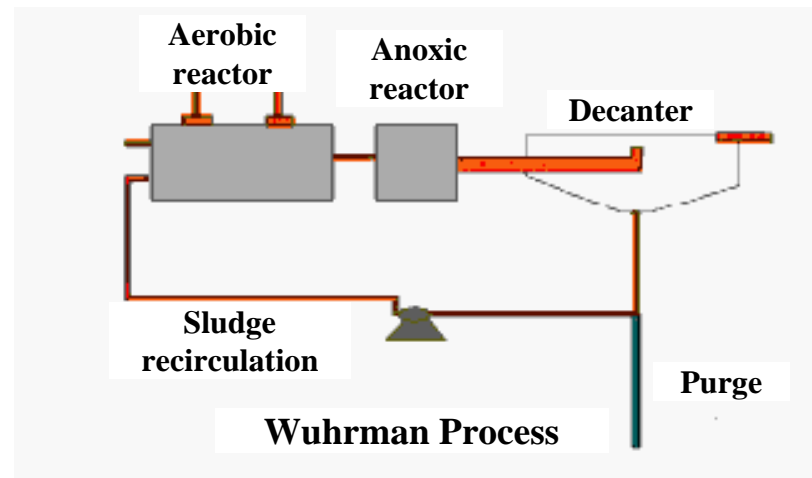
	NITRIFICATION	DENITRIFICATION
Carbon source for cellular synthesis	Inorganic	Organic
Energy source for cellular synthesis	Oxidation N(NH ₄)	Oxidation organic material
Oxygen source for oxidation reactions	O ₂ free	NO ₃ ⁻
Medium	Aerobic	Anaerobic
Microorganisms	Aerobic autotrophic	Facultative heterotrophic
Decrease of the BOD ₅	Associated to oxidised NH ₄ ⁺	Associated to oxidised organic material
Variation of the alkalinity of medium	Alkalinity consumption 7 g HCO ₃ ⁻ /g NH ₄ ⁺	Production of alkalinity 4,5 g HCO ₃ ⁻ / g NO ₃ ⁻
Production of biomass	0,16 g SS _v / g NH ₄ ⁺	————
Consumption of free oxygen	4,2 g O ₂ / g NH ₄ ⁺	————
Oxygen retrieval	————	2,85 g O ₂ / g NO ₃ ⁻

NITROGEN REMOVAL (VI)

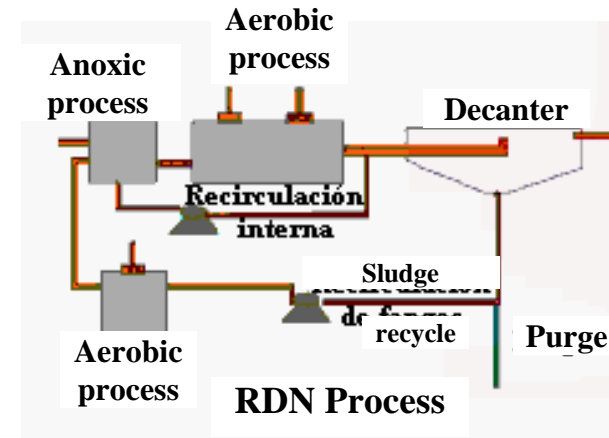
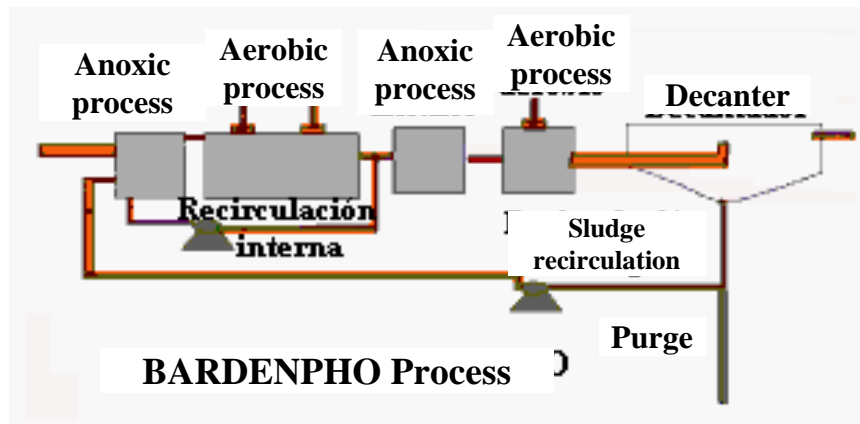
Predenitrification



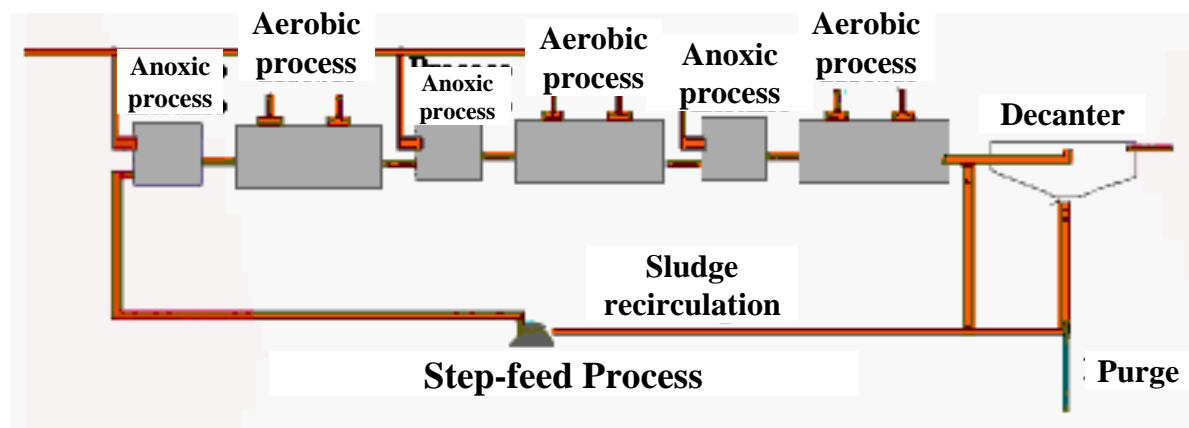
Postdenitrification



NITROGEN REMOVAL (VII)



Step-feed processes



NITROGEN REMOVAL (VIII)

Processes in oxidation channels



Oxidation ditch channel

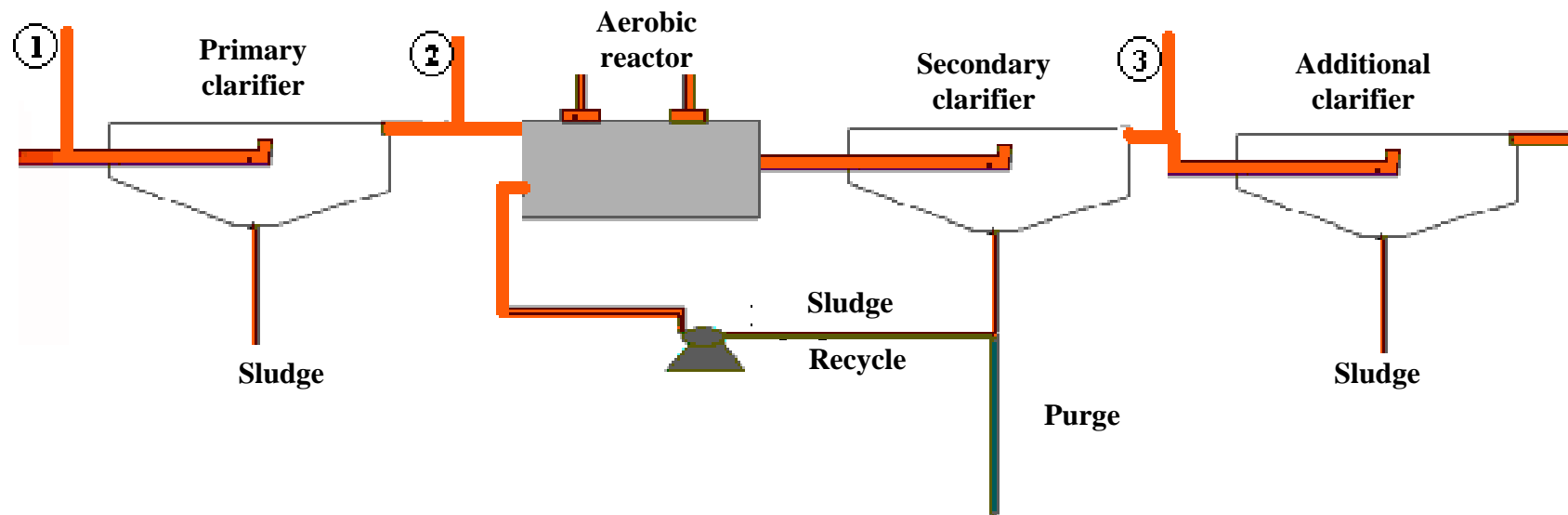


Orbal

PHOSPHOROUS REMOVAL (I)

- **PHYSICAL METHODS** : ultrafiltration, reverse osmosis
- **CHEMICAL METHODS**: precipitation.

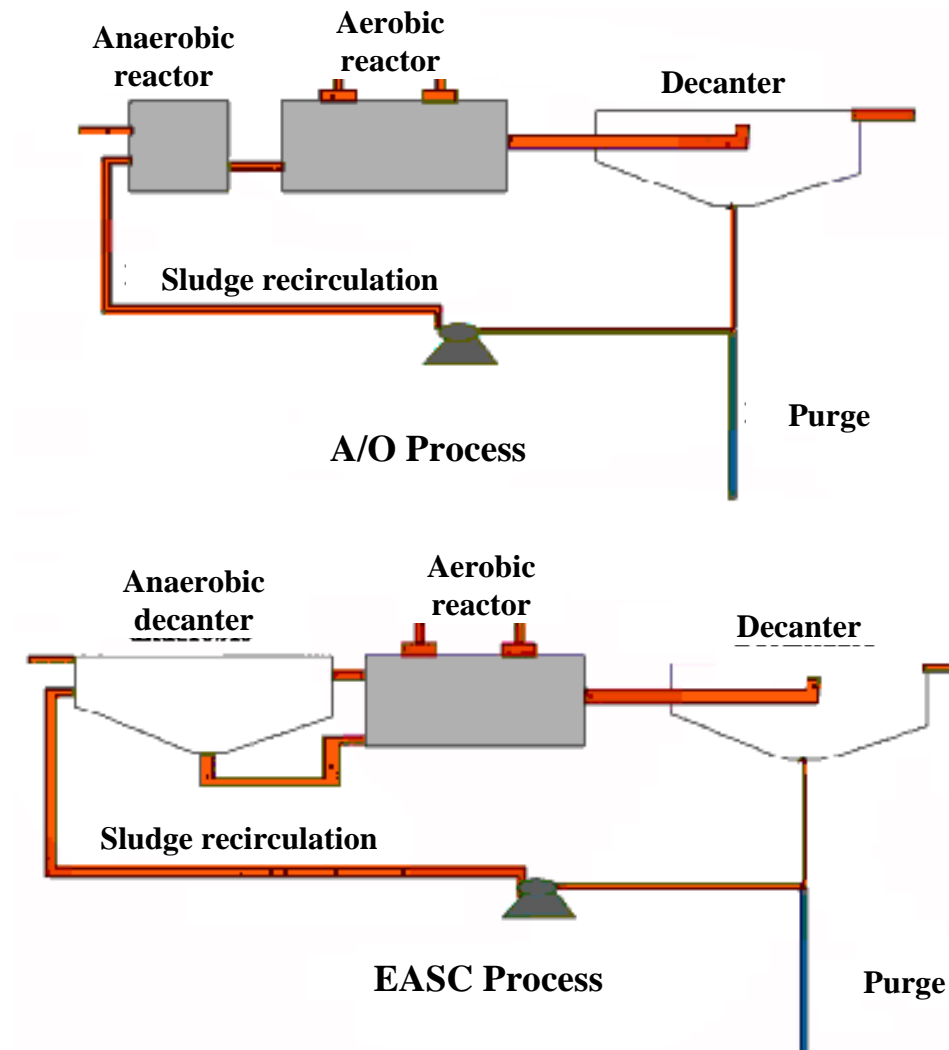
Alternatives to addition of reactants



- ⌚ Precipitation in the primary clarifier
- ⌚ Simultaneous precipitation
- ⌚ Separate precipitation

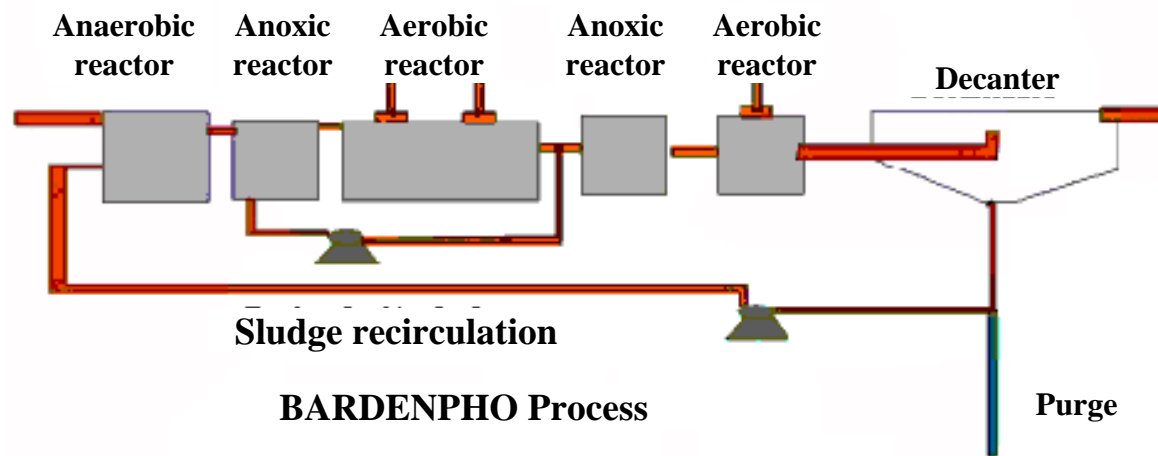
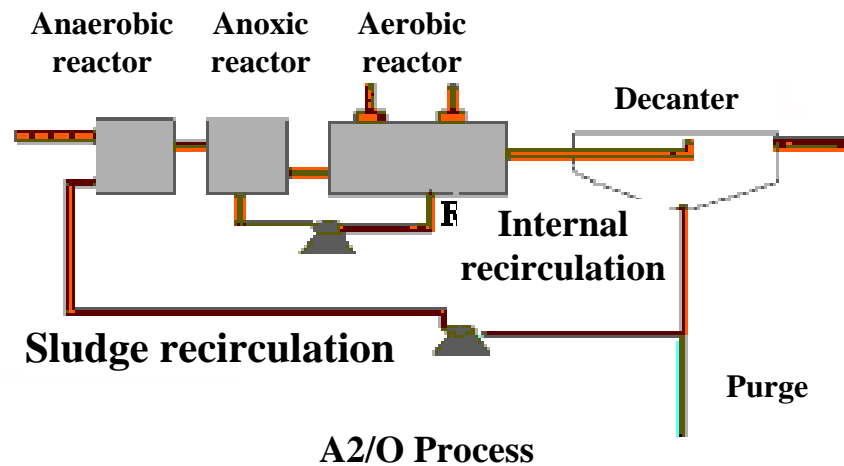
PHOSPHOROUS REMOVAL (II)

•BIOLOGICAL METHODS.



NITROGEN AND PHOSPHOROUS REMOVAL

•BIOLOGICAL METHODS.



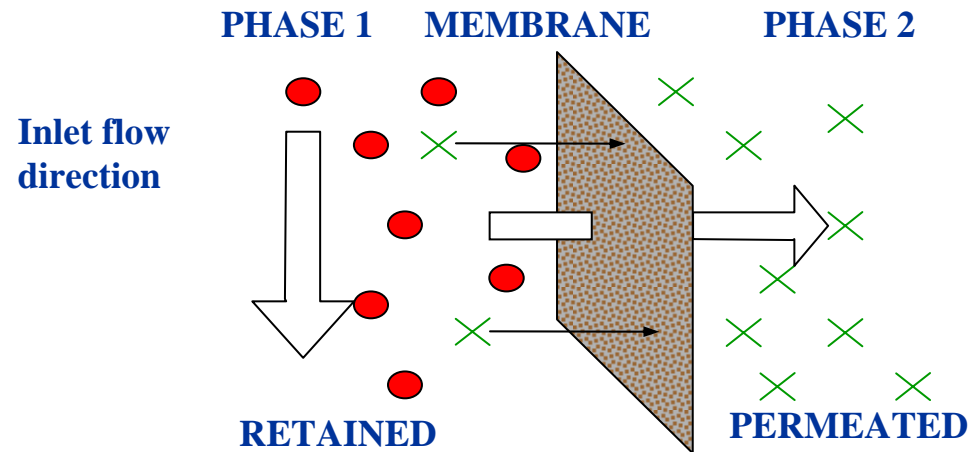
NITROGEN AND PHOSPHOROUS REMOVAL

•BIOLOGICAL METHODS.

MAIN BIOLOGICAL METHODS TO REMOVE PHOSPHORUS AND NITROGEN

Method	Removes		Applied to line	Sequence	Detention time (h)	Observations
	N (%)	P(%)				
A/O	25	90	Main	anaerobic-aerobic	2-4	Sludge phosphorous-rich, use as fertilizer
PhoStrip	25	95	Auxiliary	aerobic-anaerobic-precipitation	4-6	Less use of chemicals than in conventional precipitation
Sequencing batch reactor (SBR)	variable	variable	——	anaerobic-aerobic-anoxic	3-24	Very versatile process, recommended for small flows
A ² /O	75	90	Main		5-8	Modification of the A/O process
Bardenpho	80	70	Main	anaerobic-anoxic-aerobic-anoxic-aerobic	15-20	Recirculation from the 1 st aerobic step to the anoxic step. Low production of sludge with phosphorous.
Orbal	90	30	Main	anoxic-aerobic (cyclic)	14-24	Concentric circular channels. High mineralization

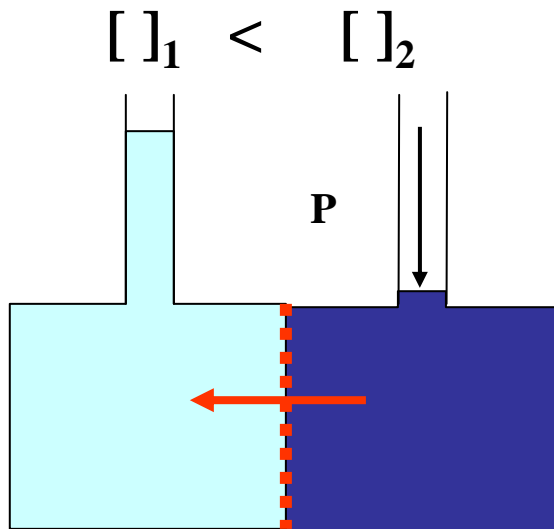
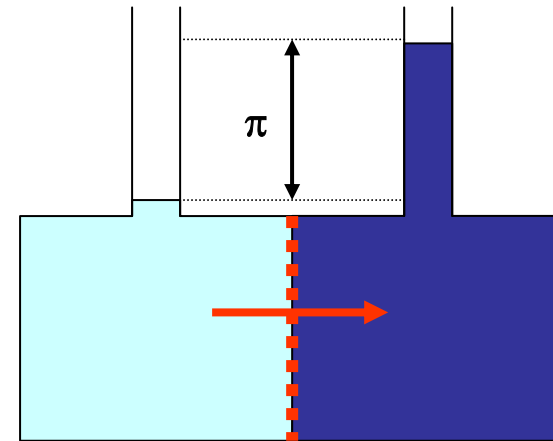
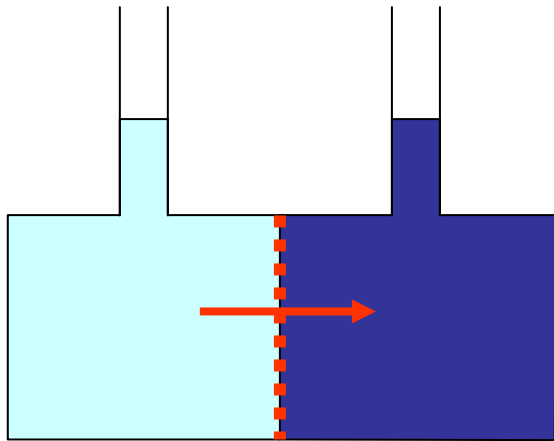
MEMBRANES (I)



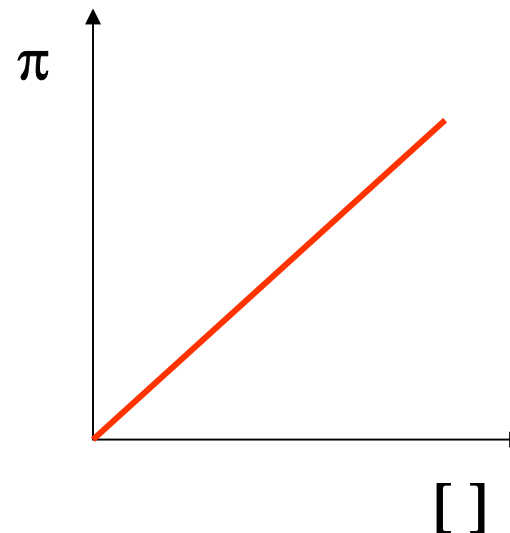
Technique	Driving force	Type of barrier	Ø particle (µm)	Operation pressure (atm)	Removes
Filtration	Pressure	Inert	> 10	1-2	suspended solids
Microfiltration	Pressure	Inert	0,1-10	1-4	suspended solids, bacteria, latex, etc.
Ultrafiltration	Pressure	Inert	0,01-0,1	5-10	Virus, proteins, oil, colloids, etc.
Nanofiltration	Pressure	Inert	10⁻³-10⁻²	20-40	Colorants, antibiotics, lactose, etc.
Reverse osmosis	Pressure	Inert or active	10⁻⁴-10⁻³	30-60	Organic and inorganic salts
Pervaporation	Pressure	Inert or active	10⁻⁵-10⁻³	0-1	Separation of solvents
Separation of gases	Pressure or concentration	Inert	< 10⁻⁴	0-1	Separation of gases
Dialysis	concentration	Inert or active	10⁻³-10⁻²	---	Macromolecules, sales, etc.
Electrodialysis	Electric potential	Active	10⁻³-10⁻²	---	Deacidification, desalting, etc.

MEMBRANES (II)

REVERSE OSMOSIS : recovery of diluted solutions



$$\pi = 1,12 \cdot T \cdot \Sigma m$$

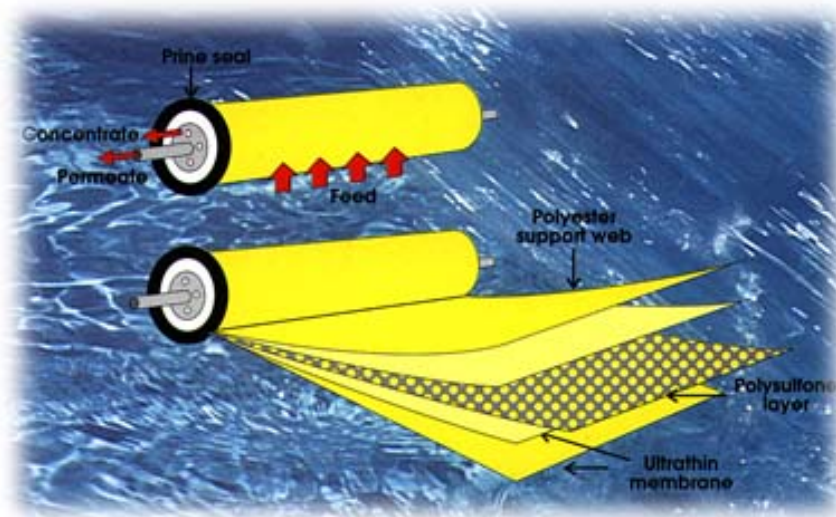


$P > 1,4 + \pi$ (Mpa)
 Saline water : 4,2-5,6 MPa
 Marine water: 7,0-8,4 MPa

MEMBRANES (III)

REVERSE OSMOSIS

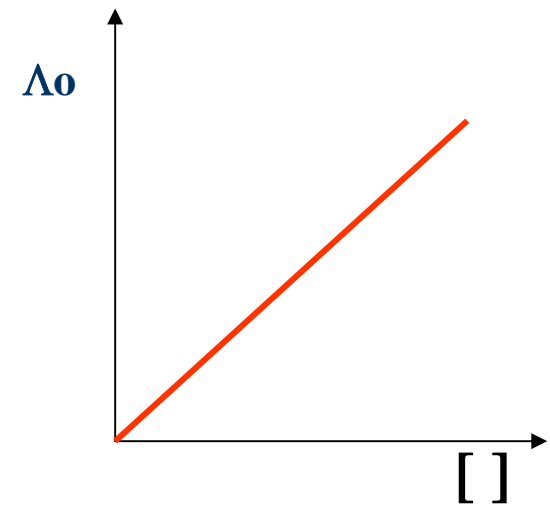
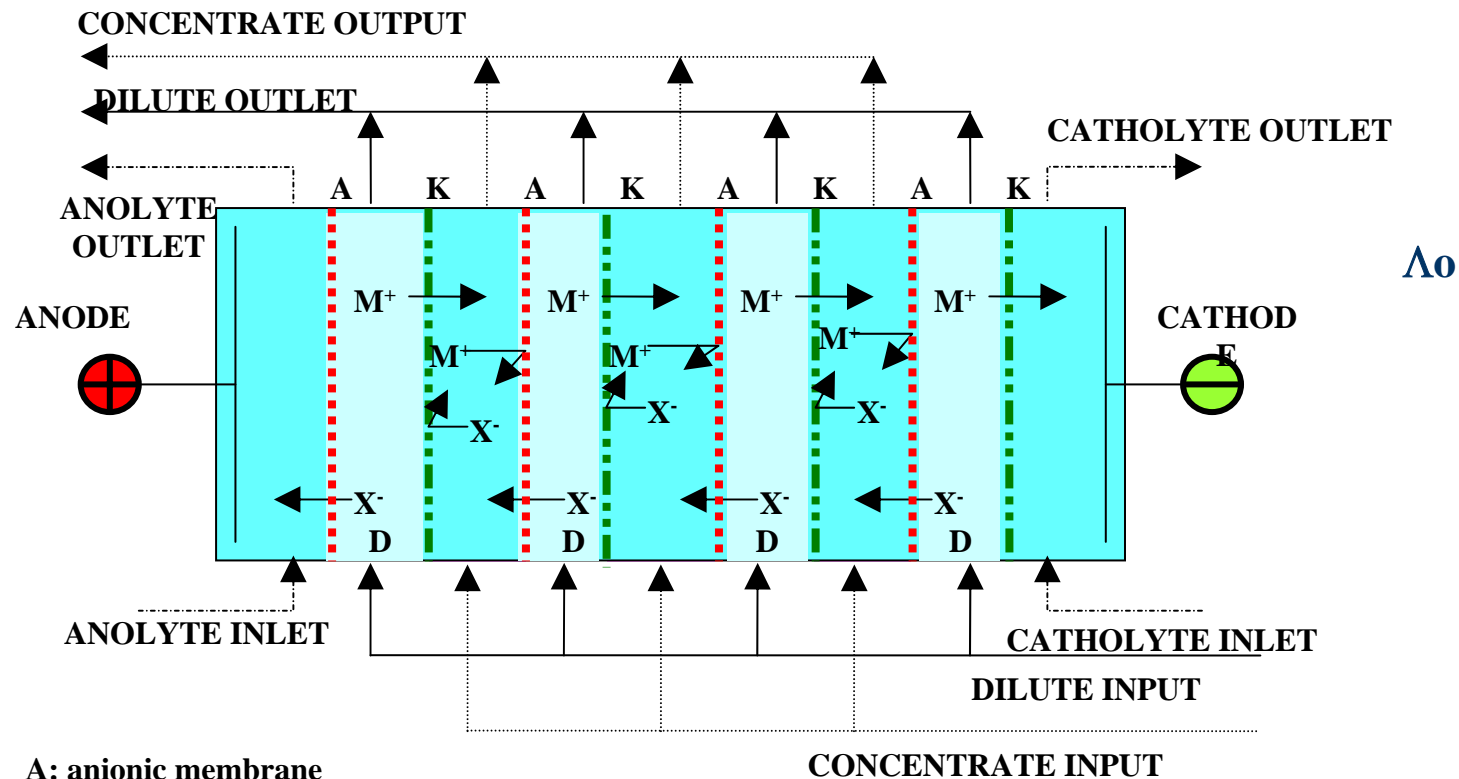
	Cellulose acetate	Polyamide	TFC	Polysulfone
pH	4-7	4-11	2-12	2-12
Tolerance to chlorine	Tolerance	0,1 ppm	poor	poor
Resistance to bacteria	None	Good	Good	Good
Temperature limit (°C)	35	38	50-80	70
Rejection (%)	90-80	95-95	97-99,5	90-98



MEMBRANES (IV)

ELECTRODIALYSIS (ED):

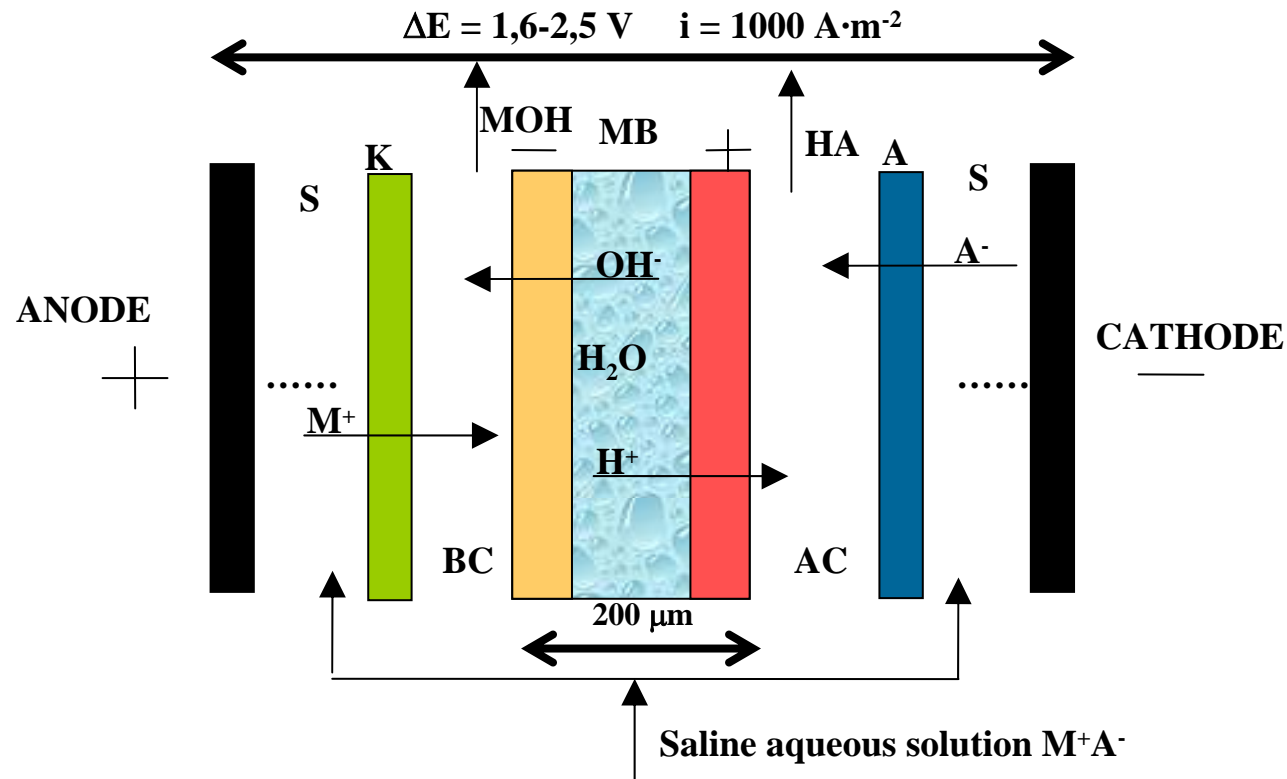
Recovery of concentrated solutions



MEMBRANES (V)

ELECTRO-ELECTRODIALYSIS (EED):

Synthesis of concentrated solutions



EED cell with 3 compartments with bipolar membranes (BM).

K: monopolar cationic membrane.

A: monopolar anionic membrane.

S: saline compartment.

AC: acid compartment.

BC: basic compartment.

OXIDATION TECHNOLOGIES (I)

● CONVENTIONAL

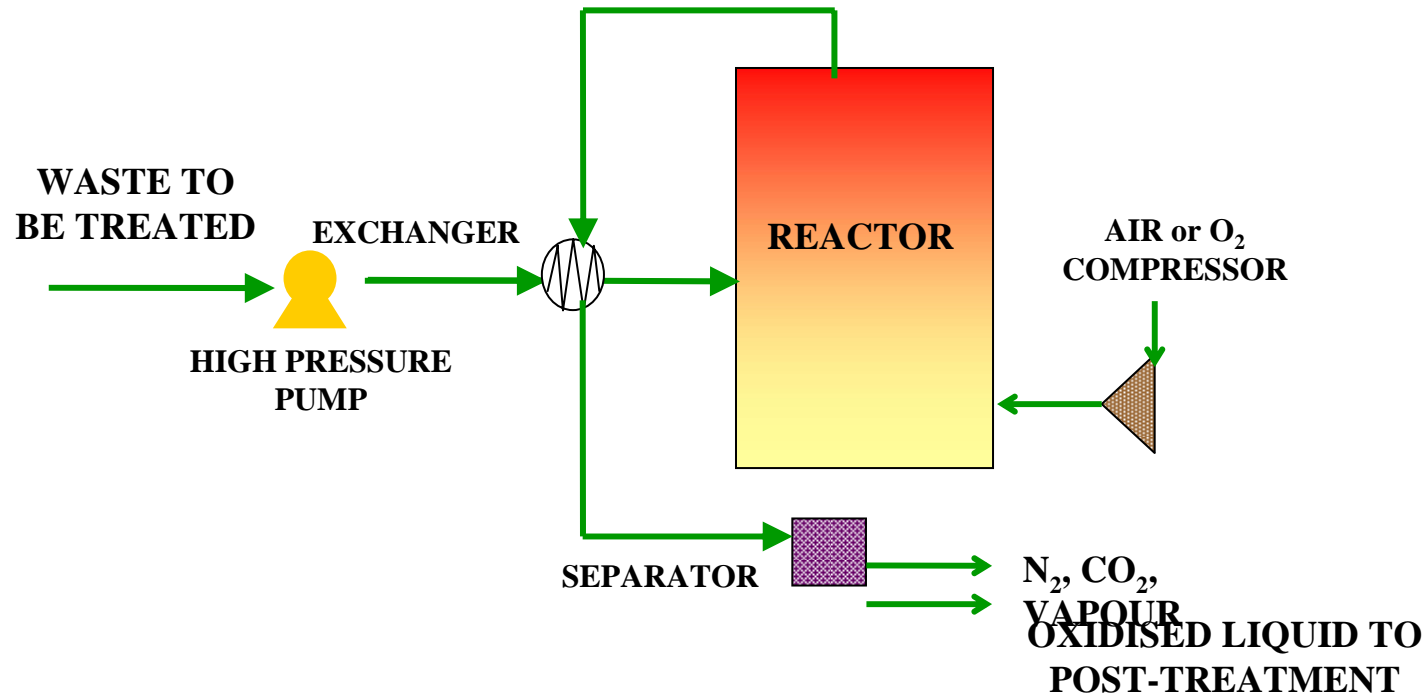
- ✓ Moderate Temp and P
- ✓ H_2O_2 , Cl_2 , O_3 , NaClO , KMnO_4 , $\text{H}_2\text{O}_2/\text{Fe}^{2+}$, ...
- ✓ $\text{COD} > 5000 \text{ mg/L}$
- ✓ Critical variables: pH and Temp
- ✓ Difficult to destroy hydrocarbons and halogenated compounds

● ADVANCED

- ✓ Wet oxidation: High Temp and P
- ✓ Oxidation with supercritical water ($T > 374^\circ\text{C}$, $p > 220 \text{ atm}$)
- ✓ Oxidant + UV
- ✓ Electrochemical
- ✓ Solar detoxification

OXIDATION TECHNOLOGIES (II)

Wet oxidation



OXIDATION TECHNOLOGIES (III)

Wet oxidation

DESTRUCTION EFFICIENCY OF TOXIC CHEMICAL PRODUCTS

PRODUCT	T _{ox} . (°c)	TIME (h)	Efficacy (%)
Acrolein	275	1	99,96
Acrylonitrile	275	1	99,00
2,4- Dimethylphenol	275	1	99,99
2,4-Dinitrotoluene	275	1	99,74
1,2- diphenylhydrazine	275	1	99,88
Nitrophenol	275	1	99,60
Phenol	275	1	99,80
Formic acid	300	1	99.30
Chloroform	275	1	99,90
Carbon tetrachloride	275	1	99,70
1,2-Dichloroethane	275	1	99,70
n- -Nitrosodimethylamine	275	1	99,60
Hexachlorocyclopentadiene	300	1	99,90
Toluene	275	1	99,70
Dibutyl phthalate	275	1	99,50
Pyrene	275	1	99,95
Polycyclic benzene (PCB)	320	2	63,00

DISINFECTION (I)

OBJECTIVE

- ✓ Conditioning of consumption water
- ✓ Kill pathogens

CLASSIFICATION

- ✓ Preoxidation: plant entrance
- ✓ Primary disinfection : after filtration
- ✓ Secondary disinfection : residual disinfectant

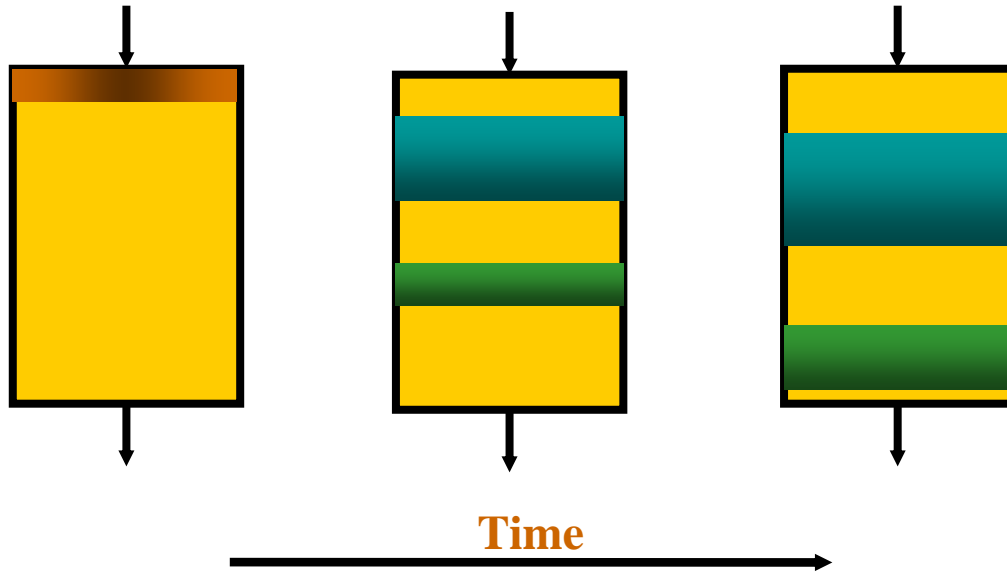
DISINFECTION (II)

DISINFECTANT	ADVANTAGES	DISADVANTAGES	APPLICATION
Chlorine	Effective Cheap Easy to apply Removes NH_3 Primary and secondary disinfectant	Dangerous subproducts pH acid Does not remove Fe(II) and Mn(II)	Towards the end: THMS ↓ Secondary disinfectant
Ozone	Very effective Without THMS Removes organic material Oxidant/disinfectant	High cost Primary disinfectant Expensive Difficult to apply	Before secondary disinfection
UV Radiation	Effective virus and bacteria Without secondary products Easy to apply	Cannot be used with coloured water, with SS, or high BOD Primary disinfectant	Towards the end of the treatment
Chlorine dioxide	Does not produce THMS	Expensive, dangerous subproducts, useless at recommended concentrations	Before filtration Treat with active carbon.
Monochloramines	Long residual times Does not produce THMS	Dangerous subproducts Does not remove NH_3 Not effective against virus Only as a secondary disinfectant	At the end of the process
Potassium permanganate	Does not produce subproducts Removes Fe(II) and Mn(II) Easy to apply Cheap	Poor disinfectant Does not remove ammonia	Before the filtration

Partial and accumulated yields (PR, % and AR, %) usually found in the removal of contaminant load in a effluent treatment plant.

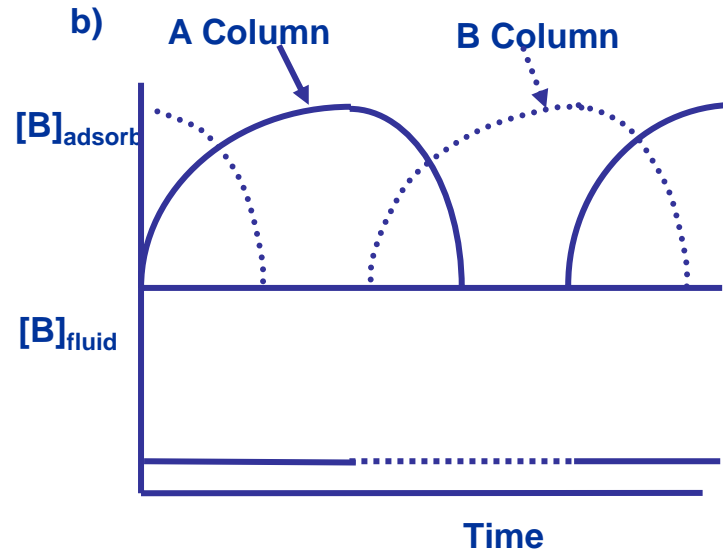
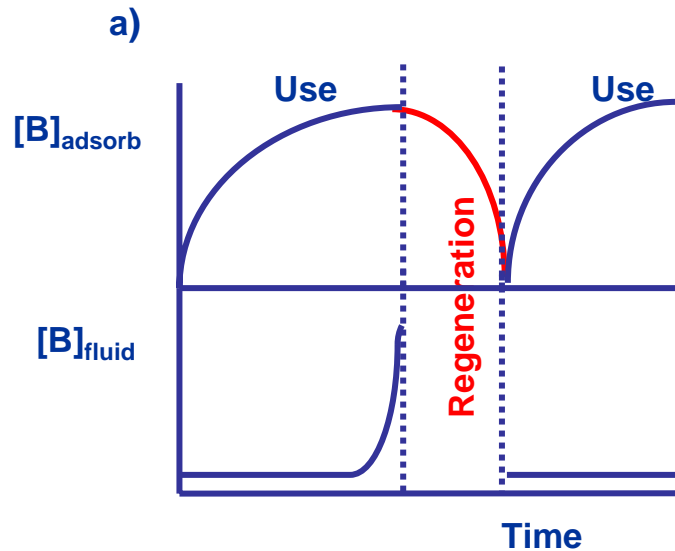
Parameter	Primary treatment		Secondary treatment		Tertiary treatment	
	PR	AR	PR	AR	PR	AR
BOD₅	25	25	90	92,5	33	95
SS	72	72	70	91,5	33	95
Phosphorous	12,5	12,5	16,5	25	91,5	94

ADSORPTION



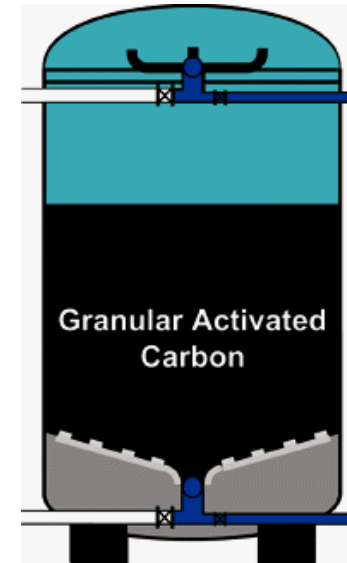
adsorption capacity: amount of substance that can be adsorbed per weight or volume unit of adsorbent,

selectivity, tendency that a substance has to be adsorbed when in presence of other substances that can also be adsorbed.



ADSORPTION WITH ACTIVATED CARBON

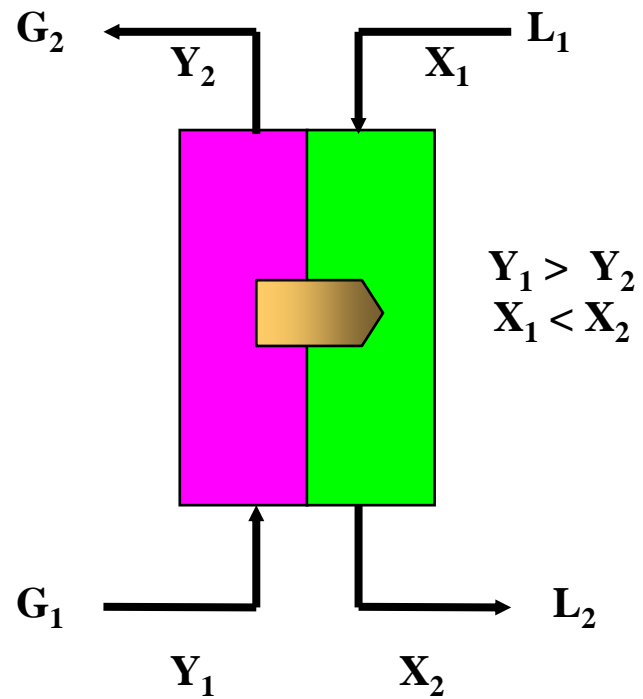
- ❏ Adsorption system
- ❏ Circulation in fixed bed
- ❏ Transference of liquid contaminant → solid
- ❏ Thermal regeneration of the bed.



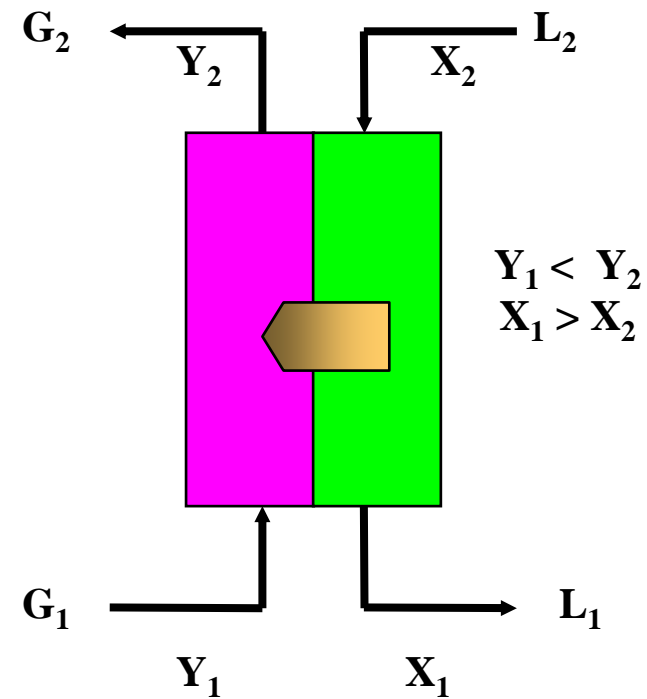
REMOVES

- ❏ Phenols
- ❏ Dyes
- ❏ Toxics in general

ABSORPTION / ADSORPTION:



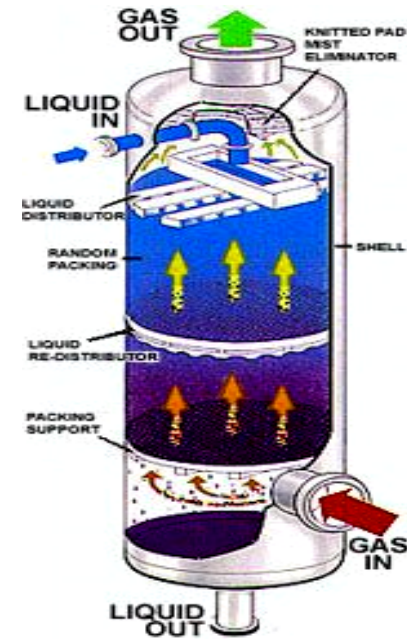
ABSORPTION



ADSORPTION

VAPOUR OR AIR STRIPPING

- 📄 Desorption system
- 📄 Countercurrent flow
- 📄 Transference of contaminant liquid → gas



REMOVES

- 📄 Ammonia
- 📄 Solvents (VOCs)
- 📄 Volatile substances

GAS WASHING: STRIPPING

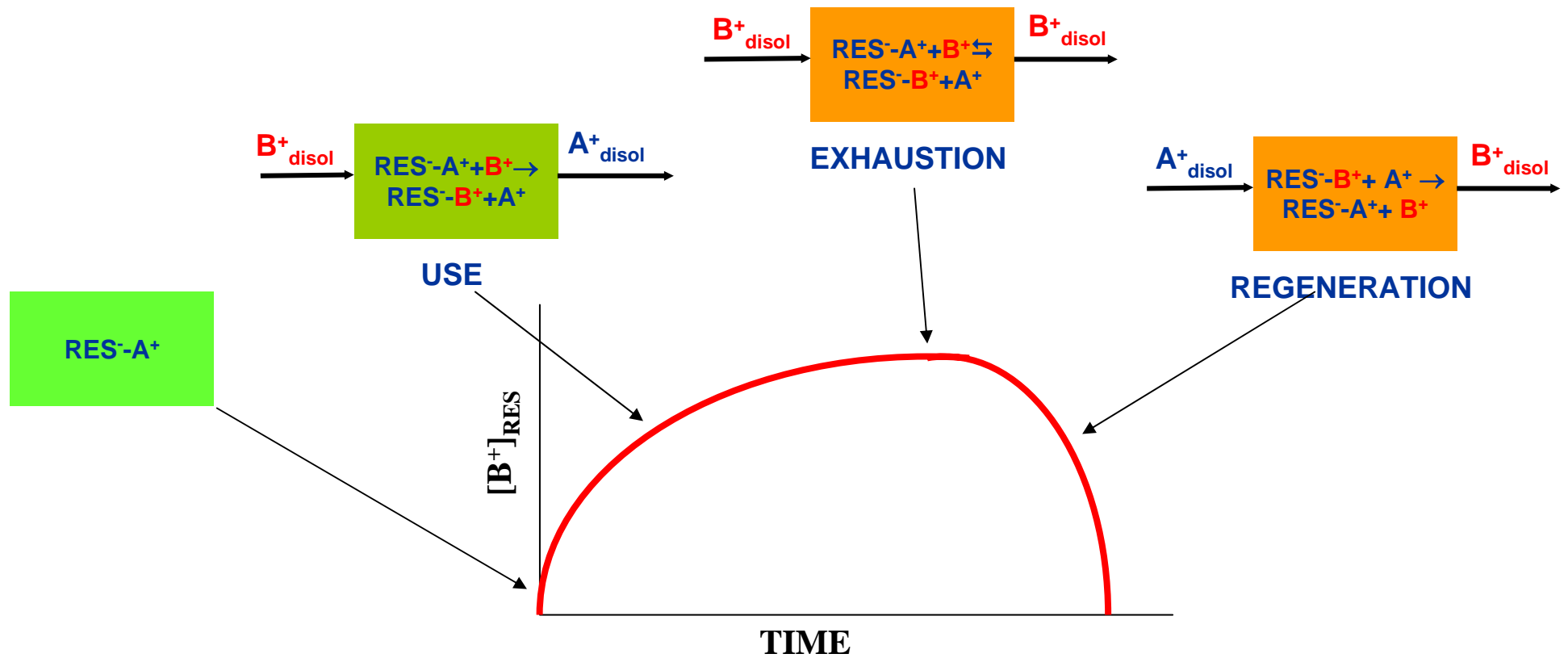
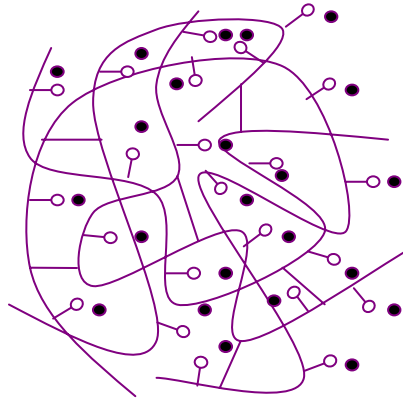
- 📄 Absorption system
- 📄 Bubbling through the liquid
- 📄 With or without reaction (neutralization, oxidation-reduction)
- 📄 Transfer of contaminant gas → liquid

REMOVES

- 📄 Unpleasant odors
- 📄 Solvents (VOCs)



ION EXCHANGE



Ionic exchange Columns

Exchange system: anionic, cationic or mixed

Organic, inorganic and hybrid resins.

Circulation in fixed bed

Transference de contaminant
liquid → solid

REMOVES

Metallic ions

Water softening

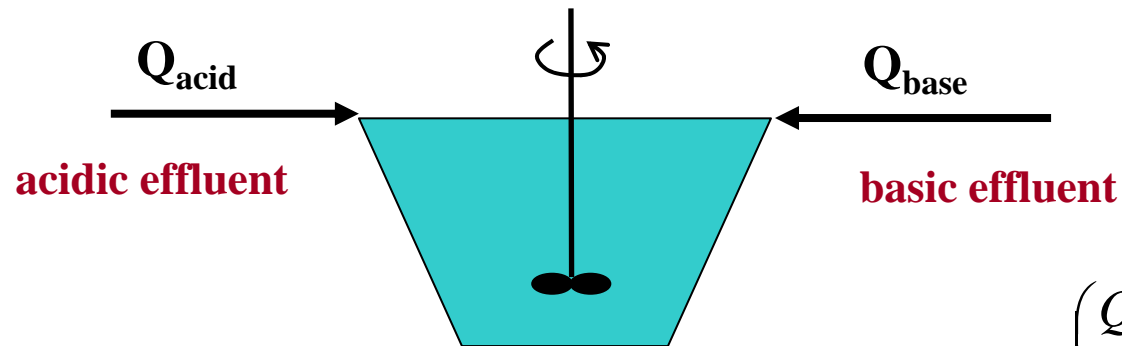
Nitrates

Ionic organic compounds.



ADJUSTING pH

HOMOGENIZATION



$$pH_{final} = -\log_{10} \frac{\left(\frac{Q_{acid}}{10^{pH_{acid}}} \right) \cdot \left(\frac{Q_{base}}{10^{pH_{base}}} \right)}{Q_{acid} + Q_{base}}$$

DOSAGE

