AOPs PhD School

1st Summer School on
Environmental applications of Advanced Oxidation Processes

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Wastewater treatment by ozonation

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OUTLINE

☐ Introduction

- Advanced treatment
- Ozone and AOPs _ Fundamentals

☐ WW O_3 treatment

- WW characteristics
- Modeling of O_3 mass transfer
- IOD, K_La, k_d estimation
- WW changes and pollutants removal

☐ Conclusions

Advanced treatment

Why advanced treatment of wastewaters?

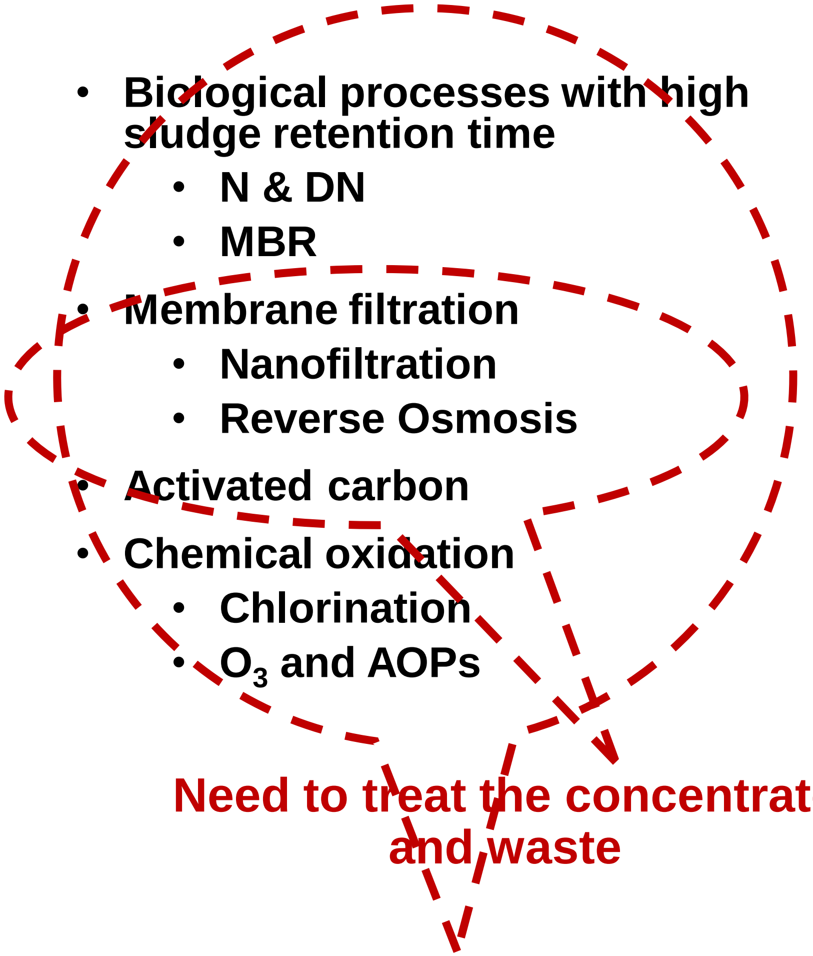
- ☐ Improvement of water quality
- ☐ Wastewater reuse: increase of water availability

Objective : *Sustainable use of water*

- ☐ Answer to water shortage
- ☐ Minimization of environmental and health risks

New challenge : *Emerging micropollutants removal*

Advanced treatment μcontaminants removal

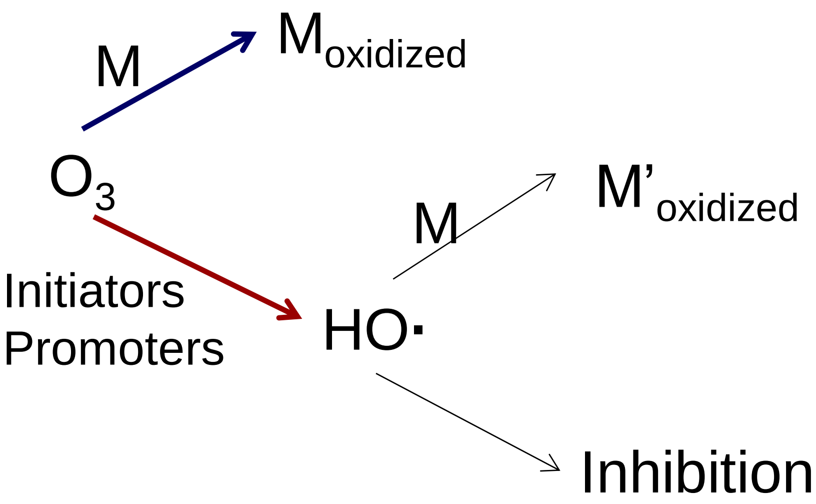


- Biological processes with high sludge retention time
  - N & DN
  - MBR
- Membrane filtration
  - Nanofiltration
  - Reverse Osmosis
- Activated carbon
- Chemical oxidation
  - Chlorination
  - O_3 and AOPs

Need to treat the concentrate and waste

Need to evaluate both the fate of the parent compounds as well as conjugates and bioactive by-products

O_3 AND AOPs _ Fundamental notions



M

$M_{oxidized}$

O_3

Initiators
Promoters

HO·

M

$M'_{oxidized}$

Inhibition

Standards redox potentials (298 K, H_2)

Name	E° (V)
Fluor	3,03
Hydroxyl radical	**2,80**
Ozone	**2,07**
Hydrogen peroxide	1,78
Potassium permanganate	1,68

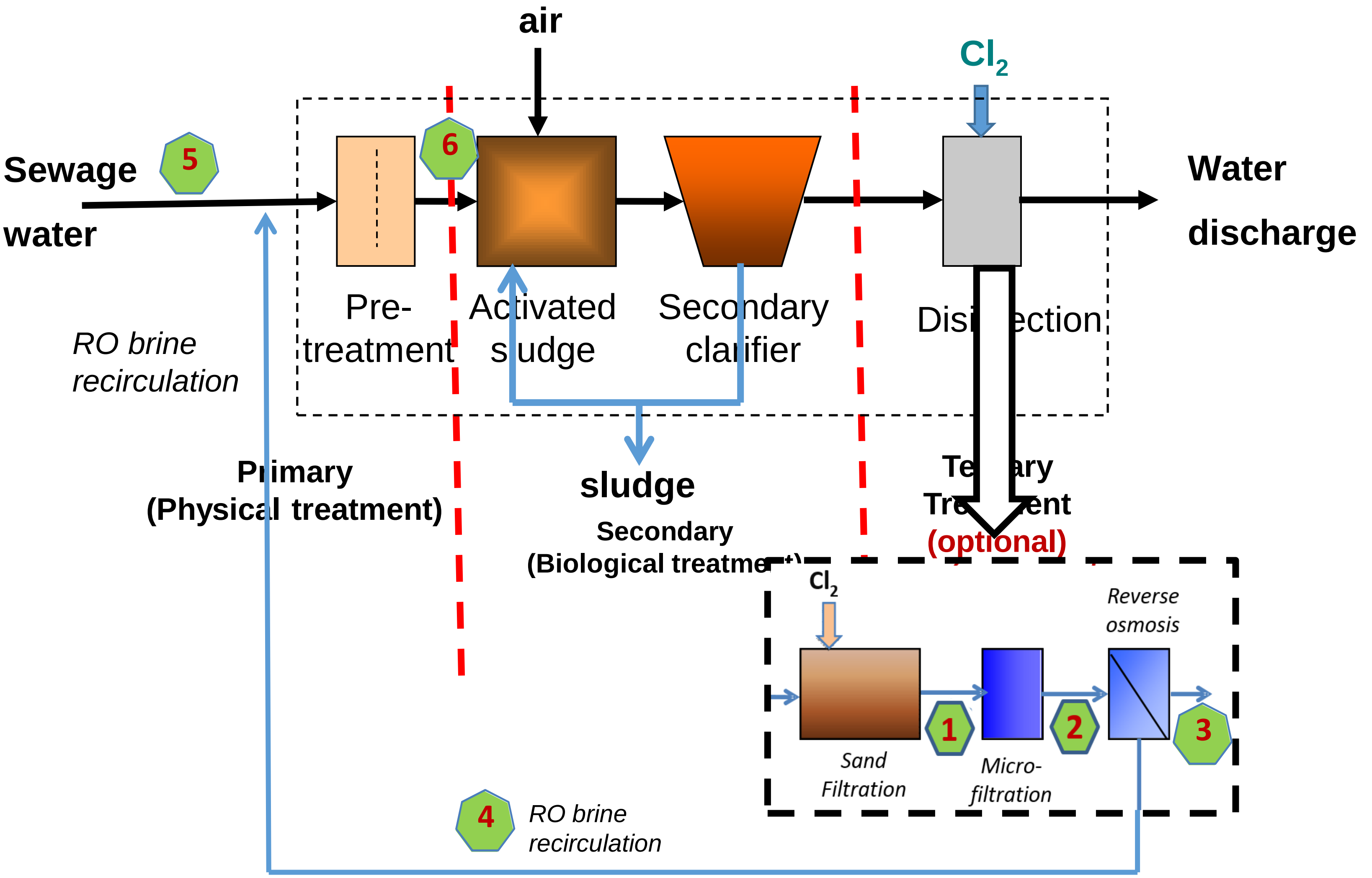
Molecular O_3 attack is selective : attack on high electronic density sites.

HO· attack is much more unselective : few compounds resist to its action.

HO· Initiators	HO· Promoters	HO· Inhibitors
Hydroxide ions Hydrogen peroxide UV_{254} radiation Heterogeneous catalysts Organic matter	Ozone Hydrogen peroxide Organic Matter	Hydrogen peroxide Carbonates Organic Matter Ter-butanol

O_3 in Wastewater treatment

CLASICAL WASTEWATER TREATMENT PLANT (WWTP)



Water and Wastewater parameters

Conventional parameters

- Chemical Oxygen Demand
- Biological Oxygen Demand
- Dissolved Organic Carbon
- UV-Absorbance at 254 nm
- Suspended Solids
- Turbidity
- Inorganic Carbon
- pH
- Nitrate and ammonia content

Micropollutant analysis

- VOCs
- PAHs
- Pesticides
- Phtalates
- Octylphenols//nonylphenols
- …..

Organic matter fractionation

- LC-OCD-ON-UVA

Water and Wastewater parameters

LC-OCD ANALYSIS

LC-OCD-OND-UVAD stands for Liquid Chromatography (size exclusion) Organic Carbon Detection, Organic Nitrogen Detection and Ultra-Violet Detection.

Fraction	Molecular weight	Description
Biopolymers	>> 20,000 Da	Polysaccharides and proteins. High molecular weight, hydrophilic and non-UV absorbable.
Humic substances	≈ 1,000 Da	Calibration based on Suwannee River standard from IHSS.
Building blocks or humic-like substances	350 – 500 Da	Breakdown products of humic substances.
Acids and low-molecular weight humics	< 350 Da	Aliphatic and low molecular weight organic acids
Low-molecular weight neutrals	< 350 Da	Weakly or uncharged low molecular weight compounds as well as low molecular weight slightly hydrophobic compounds

Modeling of O_3 mass transfer

Ozonation is an absorption process

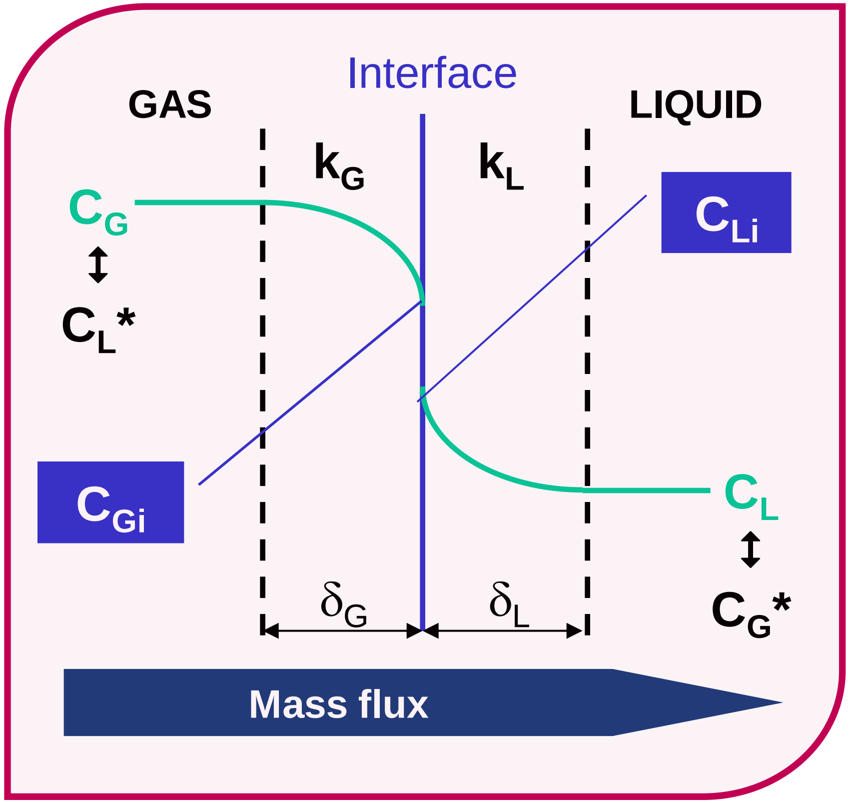
- Mass transfer rate dependent on
    - Physical properties of phases
    - Concentrations at the interface
    - Degree of turbulence

- Two-film model

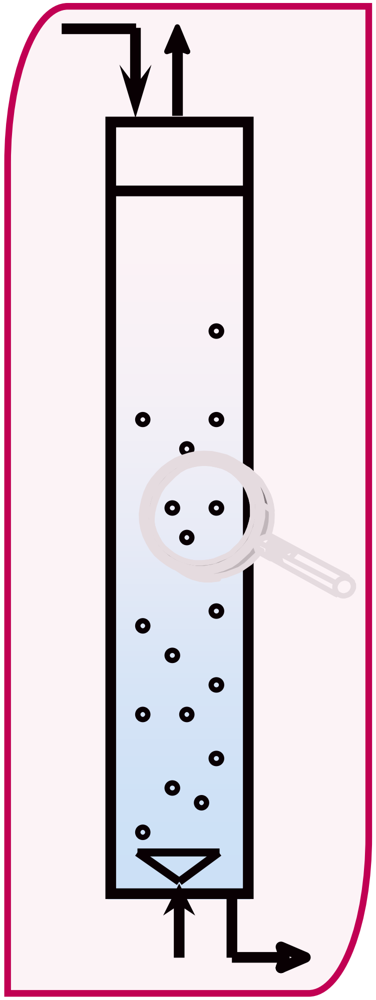
  $N = (k_L.a).(C_L^*-C_L).V_L$

    - $C_L^* = f(C_G, P, T)$ - Henry's law
    - $C_L = f(\text{mixing conditions})$
    - $k_L.a = f(\text{hydrodynamic \& operating conditions, reactor configuration})$

- gas hold-up and bubble size



Modeling O_3 mass transfer



Mass transfer & kinetics ➔Reaction regime

- Kinetics: first-order reaction for M, for Oxidant (O_3, OH°)

  $O_3 + n\,M \rightarrow$ Products $r_{O3} = k.[O_3].[M]$, $r_M = n.k.[O_3].[M]$

  n : stoichiometric coefficient

  - Idem for reaction from HO°
  - Side reactions: scavenging effect, competition with OM oxidation

- Hydraulics: plug flow for the liquid phase

- Reaction regime

$$Ha = \frac{\sqrt{D_{O_3}.k.[M]}}{k_L}$$

Hatta number

Modeling O_3 mass transfer

$$Ha = \frac{\sqrt{D_{O_3} . k . [M]}}{k_L}$$

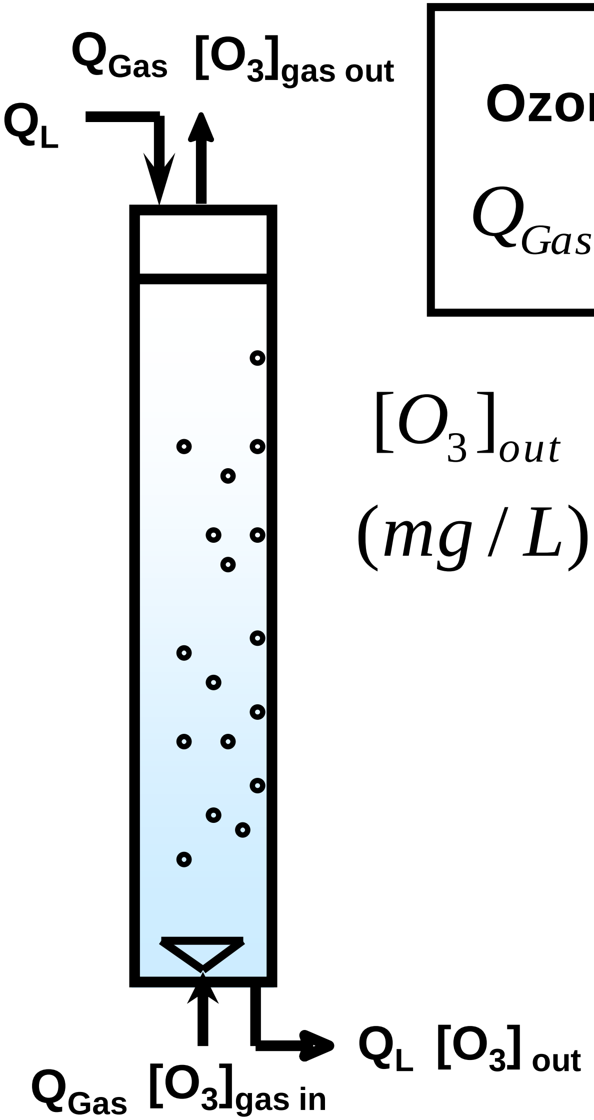
Hatta number

O_3 and O_3-AOP reactors

	Determining characteristic(s)	**Reactor type**
Ha<0.02 - Very slow reaction	Liquid hold-up	Bubble column
0.02<Ha<0.3 – Slow reaction	Chemical regime	Bubble column Stirred tank
0.3<Ha<3 – Quite fast reaction	Liquid hold-up Interfacial area	Stirred tank
Ha > 3 – Fast reaction	Interfacial area	Packing column
Ha >>3 – Instantaneous reaction	Transfer coefficient Interfacial area	Static mixer Ejector

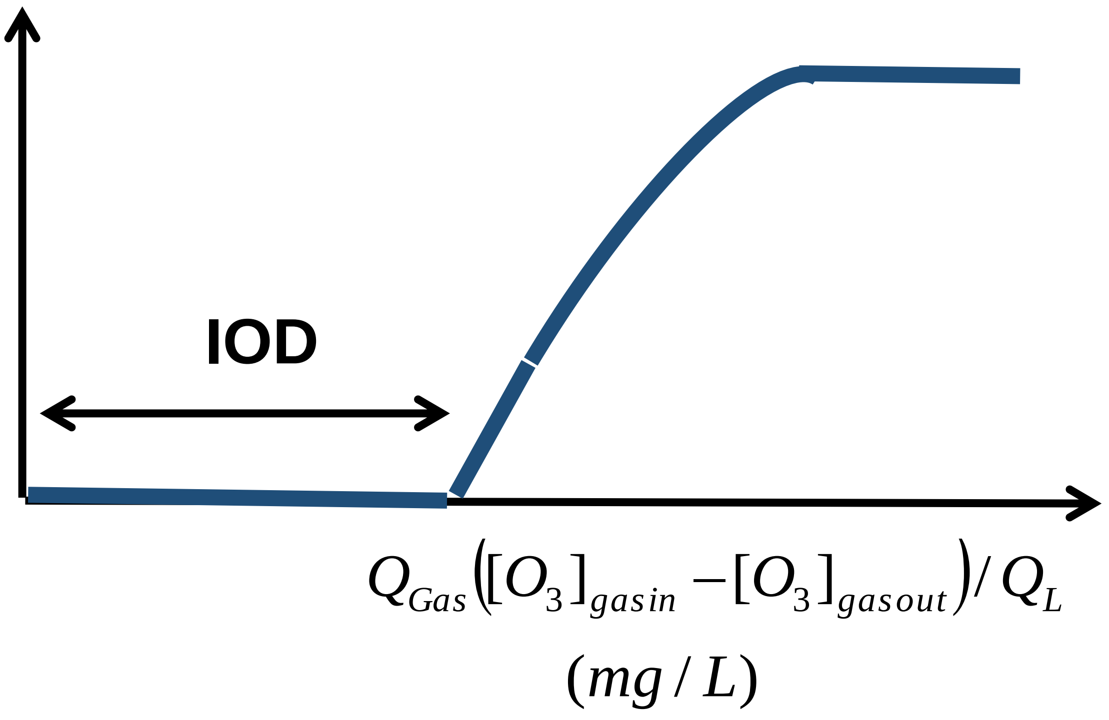
IOD (Immediate Ozone Demand)

IOD : minimum amount of ozone dose (mg/L) to be transferred to have dissolved ozone in water (continuous flow)

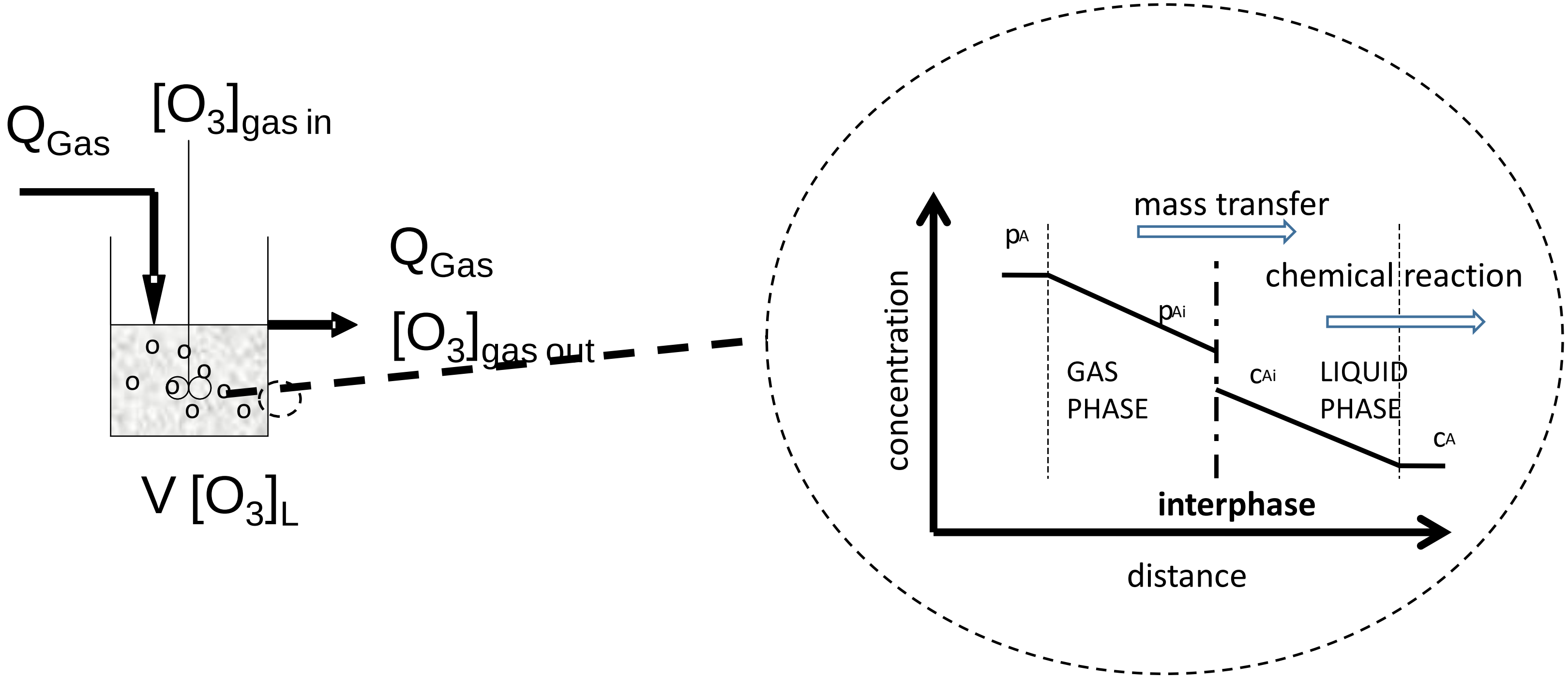


Ozone balance **(steady state)**

$$Q_{Gas}\left([O_3]_{gas\,in} - [O_3]_{gas\,out}\right) - R_{O3} = Q_L [O_3]_{out}$$



IOD estimation al lab scale



$$N_{O3}(mol/(m^2.s)) = k_g(p_{o3} - p_{o3*}) = k_L([O3]^* - [O3])$$

$$N_{O3}(mol/(m^2.s)) = k_G(p_{o3} - H[O3]) = k_L\left(\frac{p_{o3}}{H} - [O3]\right)$$

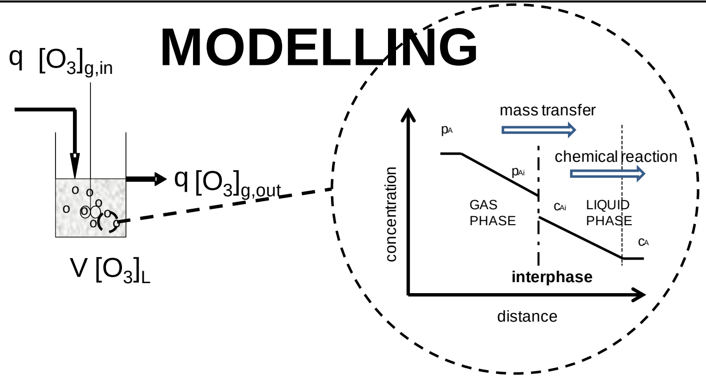
HENRY`S constant

$$p_{O3} = H[O3]$$

$$p_{O3} = Hx_{O3}$$

IOD estimation al lab scale

MODELLING



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HENRY\`S constant

$$p_{O3} = H[O3]$$

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Transferred Ozone Dose

$$TOD = \int_0^t \frac{Q_{Gas}}{V_{Liq}} \times ([O3]_{gas\ in} - [O3]_{gas\ out}) \times dt_r$$

Immediate Ozone Demand (IOD) minimum amount of ozone to be transferred to have dissolved ozone in water

Ozone balance in liquid phase

TOD < IOD $[O3] = 0$

TOD > IOD $$\frac{d[O3]}{dt} = K_La \times ([O3]^* - [O3]) - k_d \times [O3]$$

$$P_{O3} = Hx_{O3^*}$$ Henry's law

$$H = 3.8 10^7 [HO^-]^{0.035} \exp(-2428/T)$$

$$276.5K < T < 333K \quad 0.65 < pH < 10.2$$

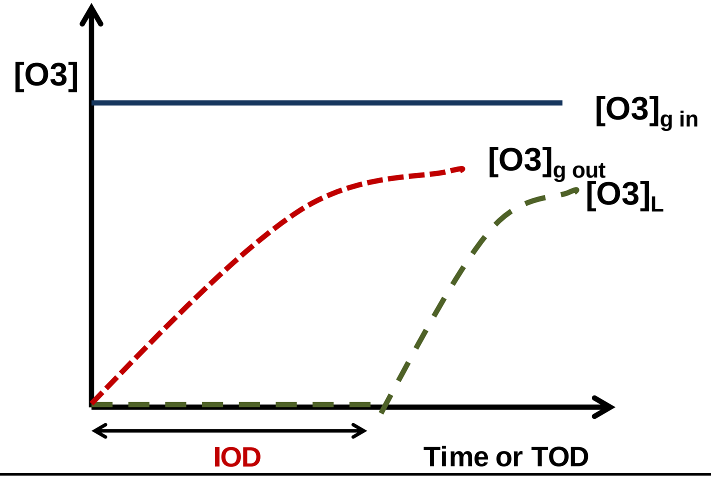
Roth and Sullivan equation

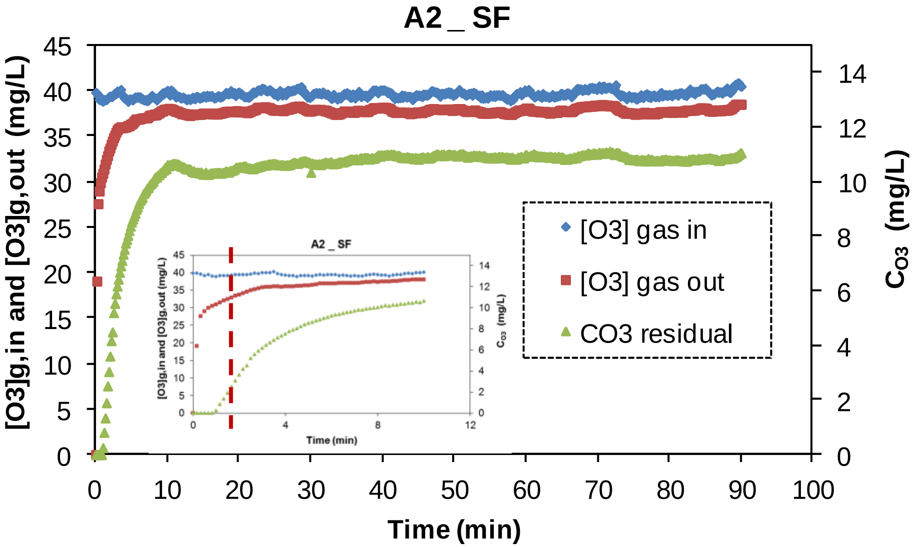
Ozone balance in gas phase

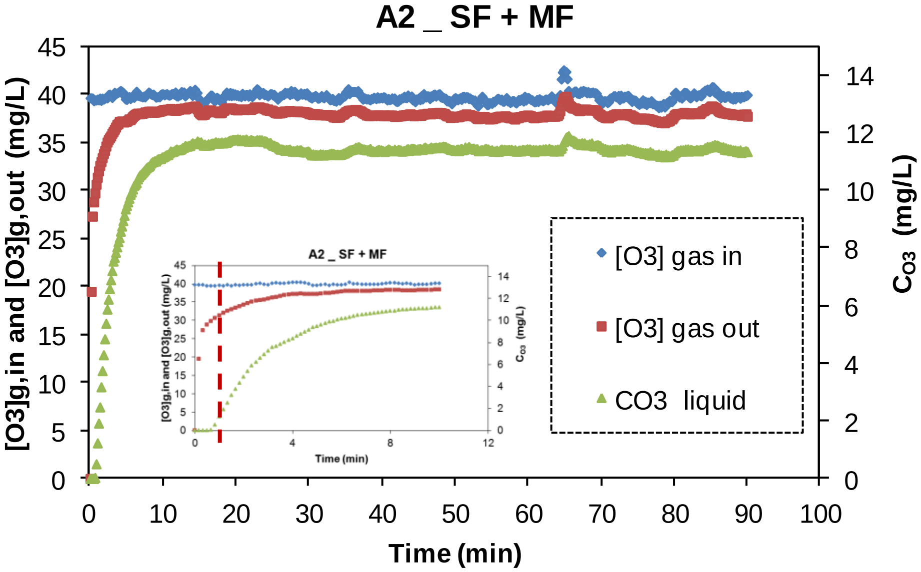
$$Q_{Gas}\left([O3]_{gasin} - [O3]_{gasout}\right) = K_La([O3]^* - [O3])V_{Liq} = k_d[O3]\ V_{Liq} + \frac{d[O3]}{dt}V_{Liq}$$

IOD estimation al lab scale

A THEORETICAL
BEHAVIOUR
(K_La and k_d constant)





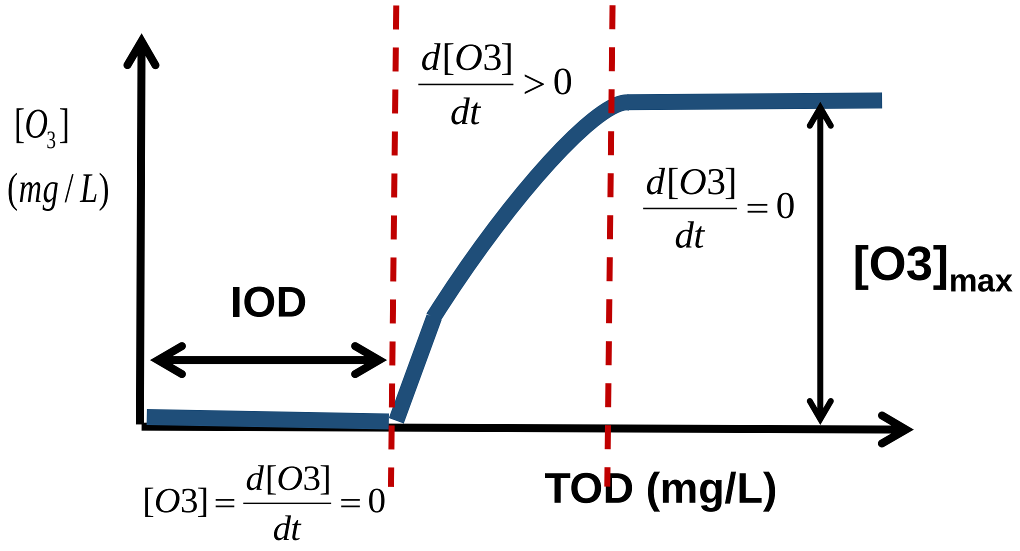


IOD = 6 mg/L, contact time = 1 min

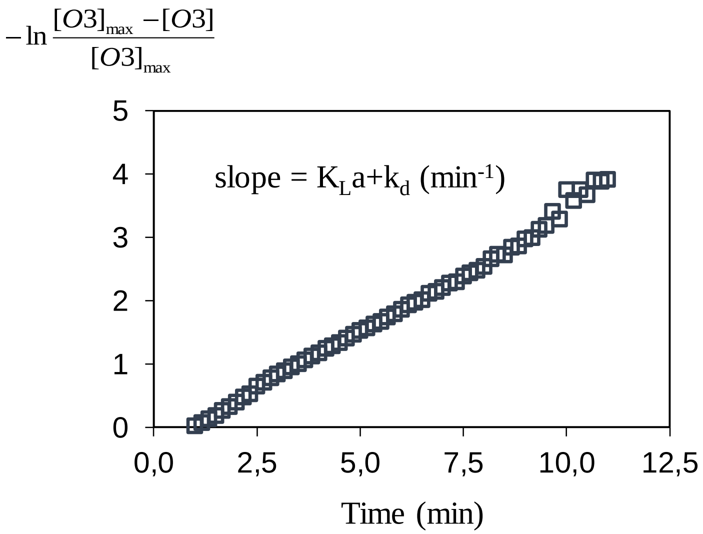
From these data it is easilty possible to estimate K_La and k_d

Estimation K_La , k_d at lab scale

Behavior ozone in water



$$\frac{d[O3]}{dt} > 0 \qquad \ln \frac{[O3]_{max} - [O3]}{[O3]_{max}} = -(K_La + k_d)t$$



$$\frac{d[O3]}{dt} = 0 \qquad \frac{[O3]^*}{[O3]_{max}} = \frac{K_La + k_d}{K_La}$$

$$P_{O3} = Hx_{O3^*}$$

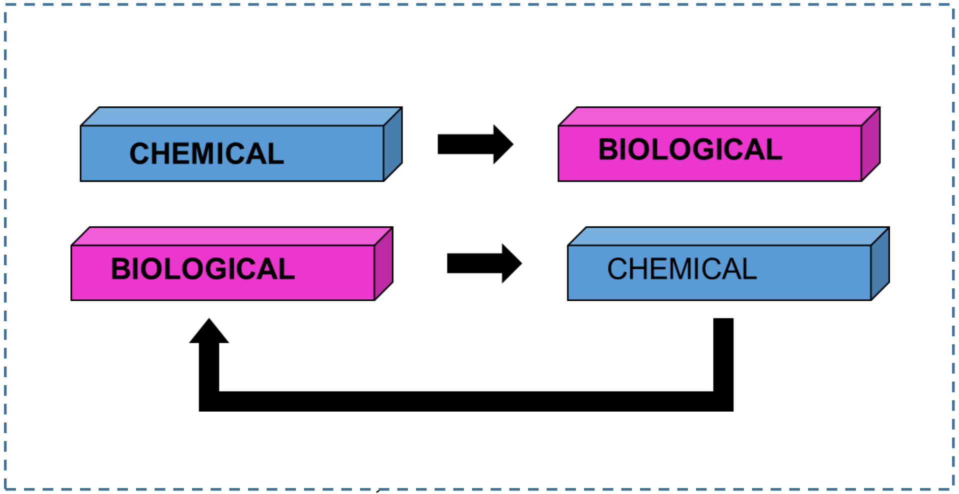
Roth and Sullivan

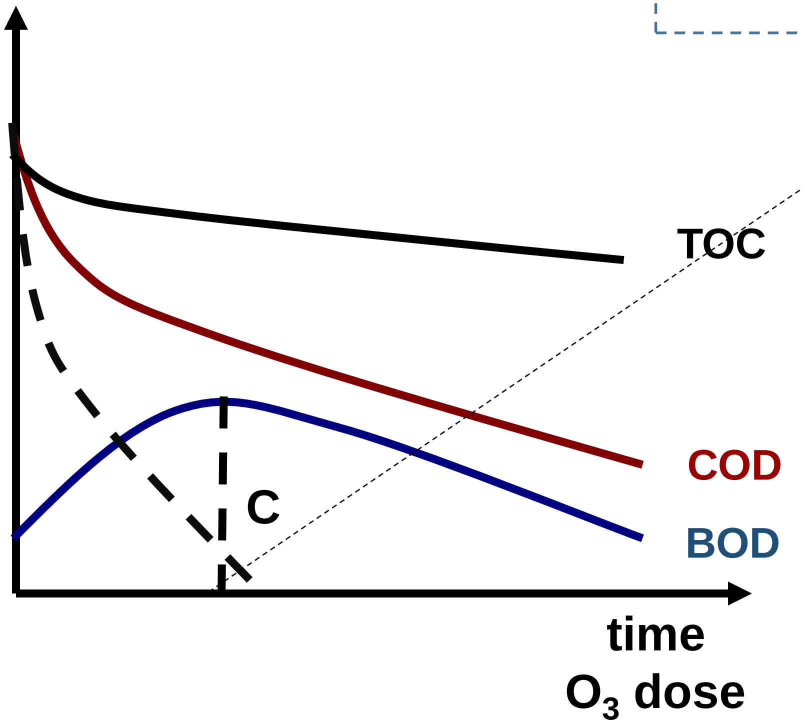
$$H = 3.810^7[HO^-]^{0.035}\exp(-2428/T)$$

$$276.5K < T < 333K \quad 0.65 < pH < 10.2$$

Wastewater changes

- **Contaminant removal**
- **COD removal**
- **TOC removal**
- **BOD changes**

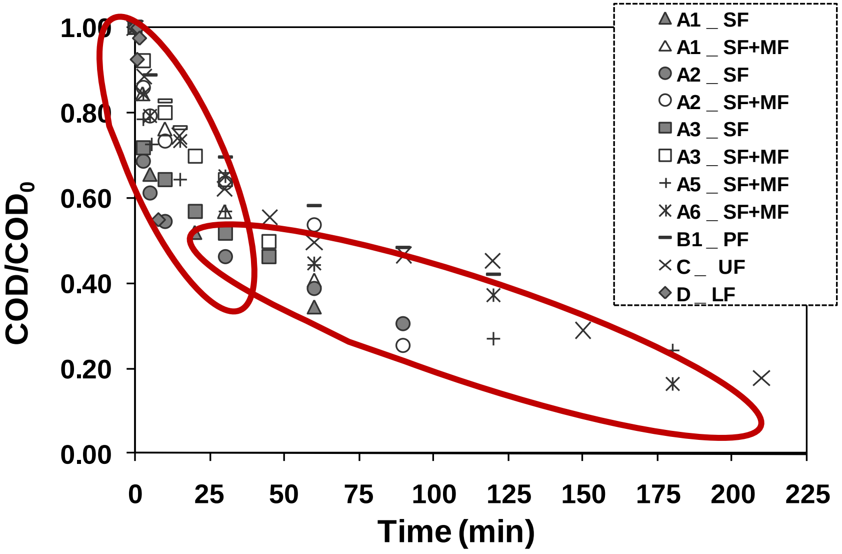


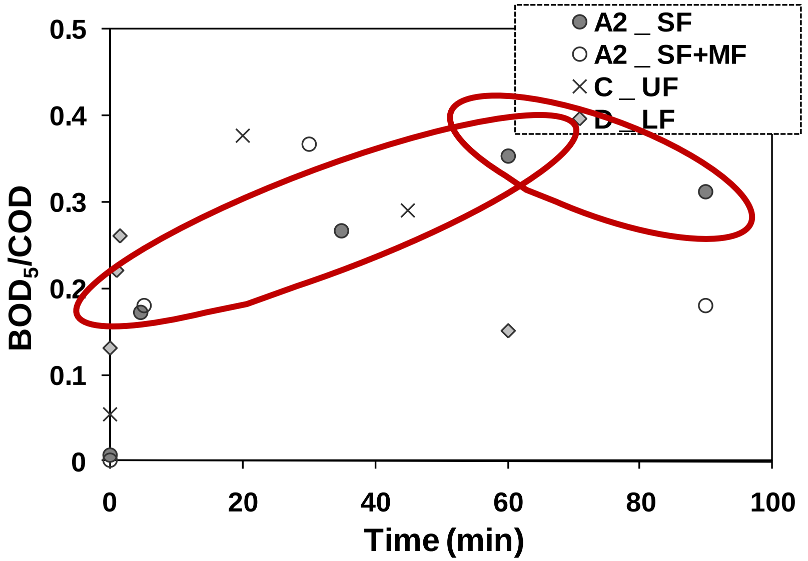


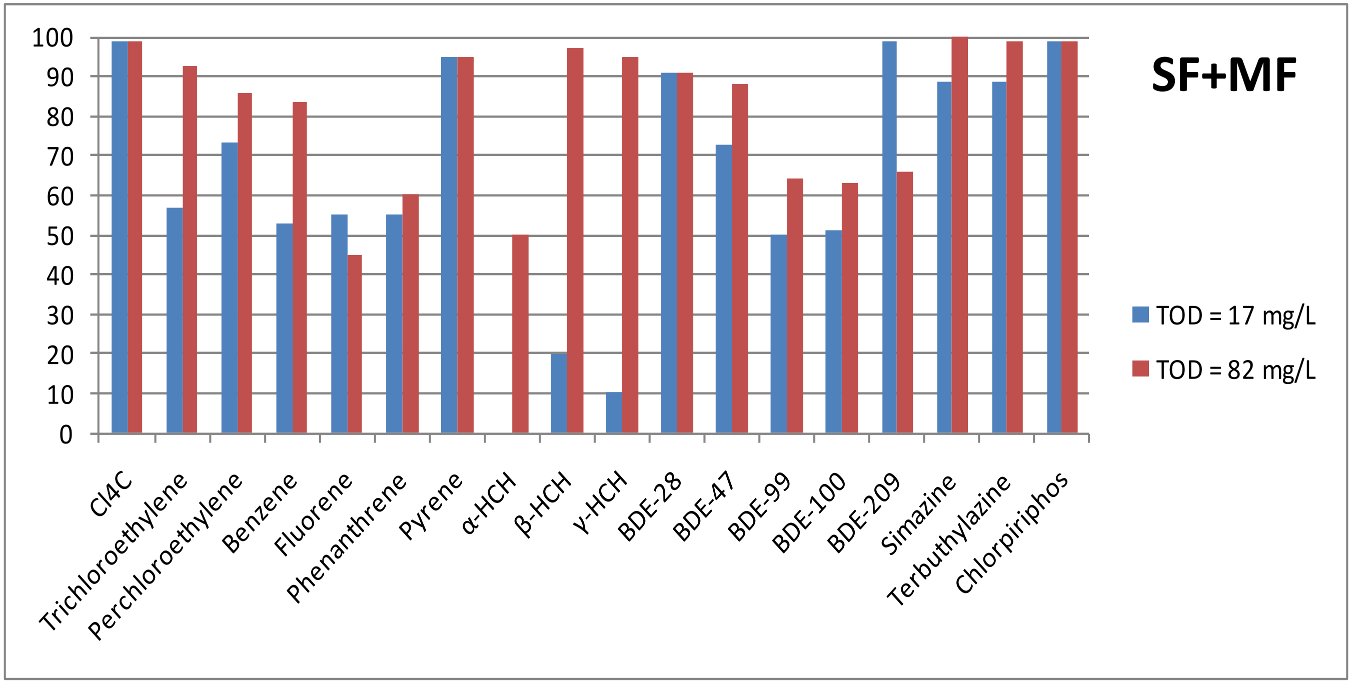
Stoichiometry
g (C, TOC, COD,UVA) removed/g O_3

Kinetics (C, TOC,COD, UVA)
1st fast reaction
2nd slow reaction

Maximum of BOD

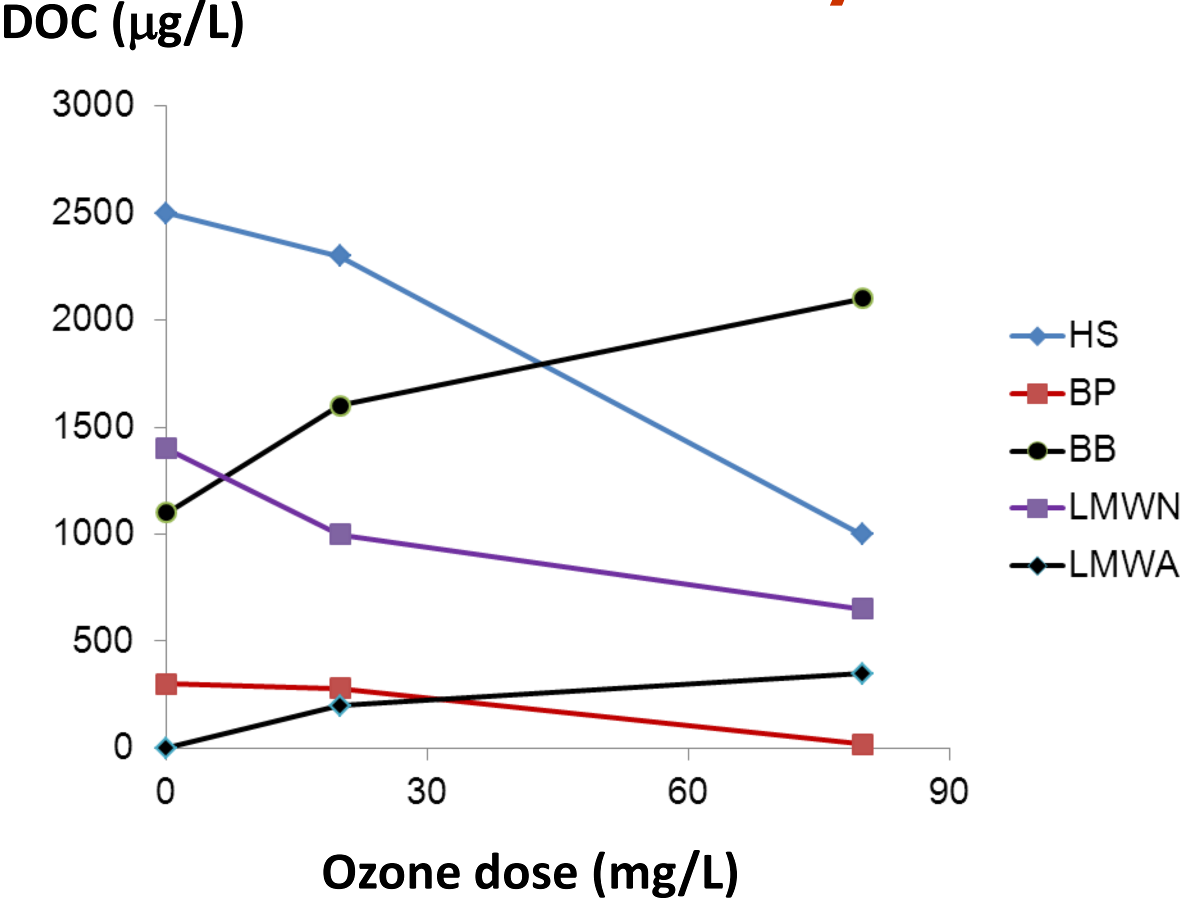

COD/COD$_0$
1.00
0.80
0.60
0.40
0.20
0.00
0
25
50
75
100
125
150
175
200
225
Time (min)
A1 _ SF
A1 _ SF+MF
A2 _ SF
A2 _ SF+MF
A3 _ SF
A3 _ SF+MF
A5 _ SF+MF
A6 _ SF+MF
B1 _ PF
C _ UF
D _ LF


BOD$_5$/COD
0.5
0.4
0.3
0.2
0.1
0
0
20
40
60
80
100
Time (min)
A2 _ SF
A2 _ SF+MF
C _ UF
D _ LF


SF+MF
100
90
80
70
60
50
40
30
20
10
0
Cl4C
Trichloroethylene
Perchloroethylene
Benzene
Fluorene
Phenanthrene
Pyrene
α-HCH
β-HCH
γ-HCH
BDE-28
BDE-47
BDE-99
BDE-100
BDE-209
Simazine
Terbuthylazine
Chlorpiriphos
TOD = 17 mg/L
TOD = 82 mg/L

WW changes: Size Molecular distribution

LC-OCD Analysis



HS and LMW neutrals decrease with ozone dose

Building blocks increase with ozone dose

Cleavage of high MW into lower MW substances and acid formation

Conclusions

- **Ozonation of wastewater effluents** is able to reduce **COD, DOC, UVA, Turbidity** at the same time than the **contaminant concentration.**
- **At low ozonation doses** there is an increase of the biodegradability, **BOD/COD**, of the effluent.
- **During ozonation** there are important changes in the **Size Molecular Distribution of the Organic Matter.**
- Examination of the ozone mass balance provides three fundamental parameters: **the instantaneous ozone demand, ozone mass transfer coefficient and the ozone decay kinetic constant**.
- **Their knowledge is of primary importance for the design of ozone contactors and for the determination of the appropriate operating conditions.**

Universitat de Barcelona

OH•
ADVANCED OXIDATION PROCESS
ENGINEERING
AOP ENGINEERING GROUP

ceqap
Centre d'Enginyeria Química
Ambiental i del Producte

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Thank you

http://www.ub.edu/eq/cat/recerca_AOP.html