UNIVERSITAT DE BARCELONA

AOPs PhD School

2nd Summer School on
Environmental applications of Advanced Oxidation Processes

University of Porto, Department of Department of Chemical Engineering
Porto (Portugal), July 10-14, 2075

Wastewater treatment by ozonation

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Departament d'Enginyeria Química

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OUTLINE

❑ Introduction

- Ozone. Properties
- Ozone generation

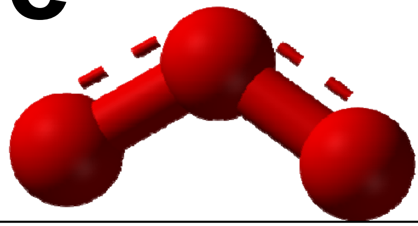
❑ WW O_3 treatment

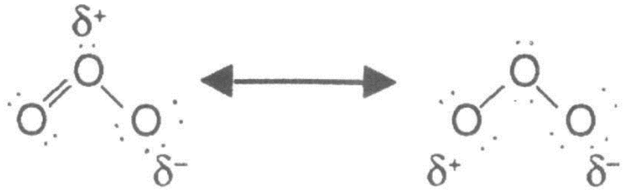
- WW characteristics
- Modeling of O_3 mass transfer
- IOD, TOD, K_La, k_d
- WW changes and pollutants removal

❑ Conclusions

Ozone

O_3





- 1785: M. van Marun . Oxygen with electric discharges gives a peculiar odor (irritant).

- 1840: Schönbein discovered Ozone, a different substance based on Oxygen (from Greek *ozein*, smell)

- 1856: Thomas Andrews demonstrate that **Ozone is only formed by Oxygen**

- 1863: Soret found the relation Oxygen-Ozone (**three volumes of oxygen produces two volumes of ozone)**

Ozone tropospheric – stratospheric

Contaminant - UV filter

Thermodynamically unstable ⇒ have to be produced "in situ"

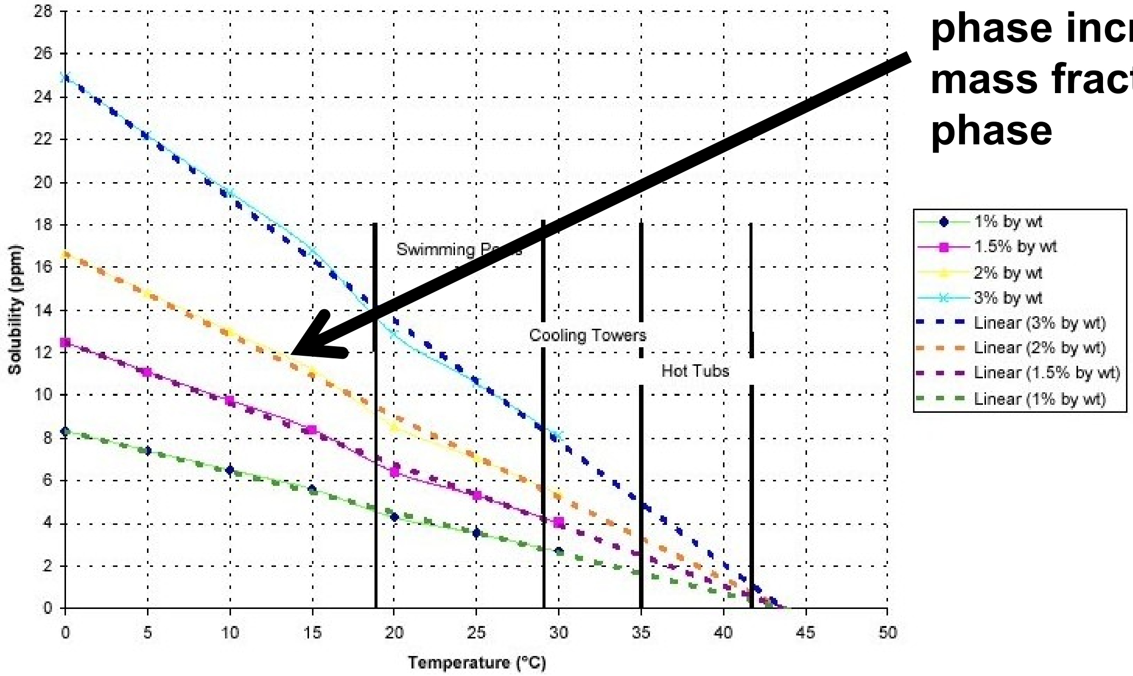
$3\ O_2 \leftrightarrow 2\ O_3$

ozone% explosion limit = 30%

Physical properties of Ozone

- Blue gas, irritant and more heavy than air
- Very reactive and unstable. It has to be generated “in situ”.
- 14 times more soluble in water than oxygen .
- Water solubility increases with pressure
- Water solubility decreases with temperature

equilibrium in aqueous phase increases with mass fraction in gas phase



Chemical properties of Ozone

Ozone reactivity

$$O_3 \longrightarrow 3/2\ O_2 \quad \Delta H^\circ = -\ 34.61\ \text{kcal/mol} = 144.8\ \text{kJ/mol}$$

$$O_3 + 2\ H^+ + 2\ e^- \longrightarrow O_2 + H_2O \quad E^\circ = 2.07\ V$$

Oxidation inorganics

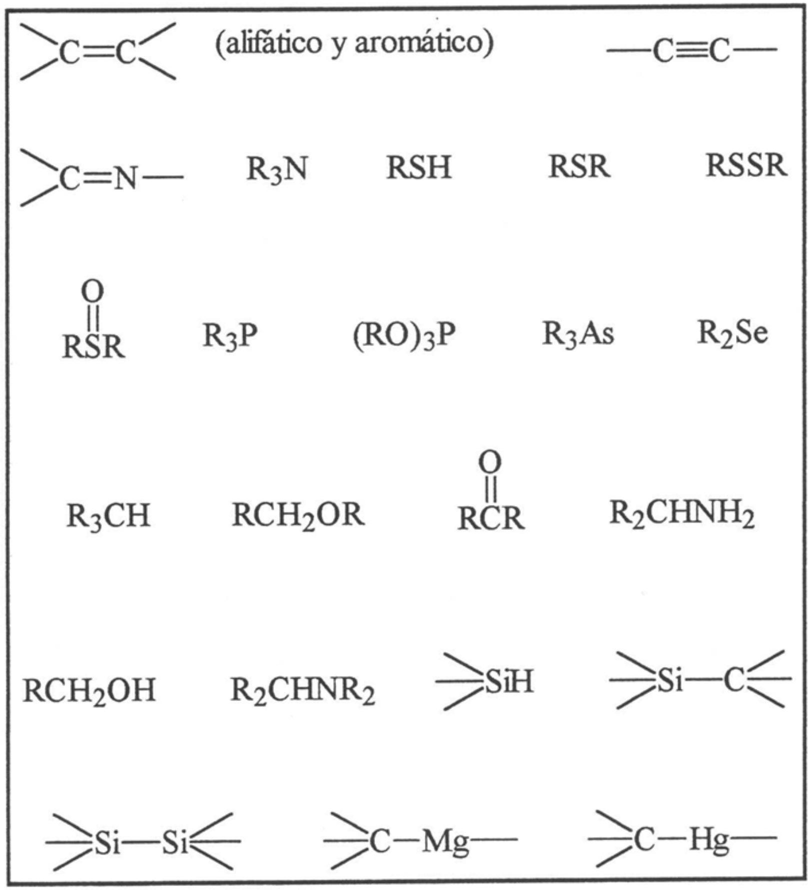
$$Mn^{2+} + O_3 + H_2O \rightarrow MnO_2 + O_2 + 2H^+$$

$$Fe^{2+} + O_3 \rightarrow Fe\text{-}O^{2+} + O_2$$

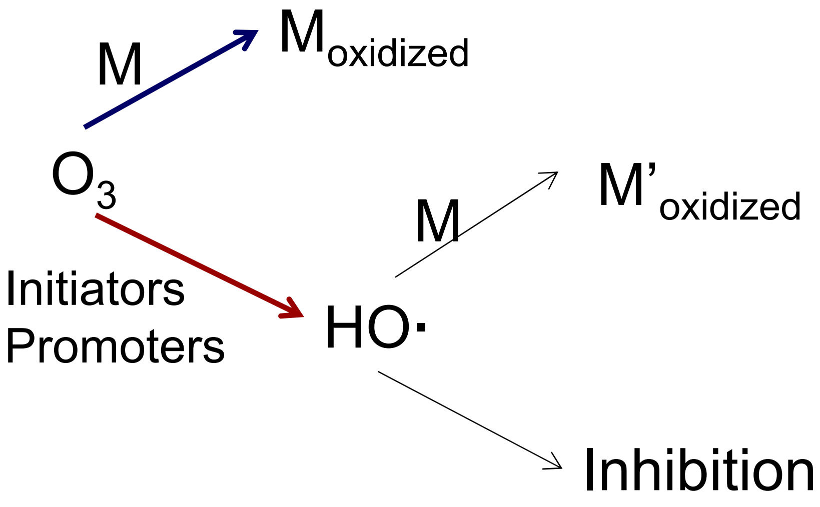
$$Fe\text{-}O^{2+} + Fe^{2+} \rightarrow 2Fe^{3+} + H_2O$$

....

Oxidation organics



Chemical properties of Ozone



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.

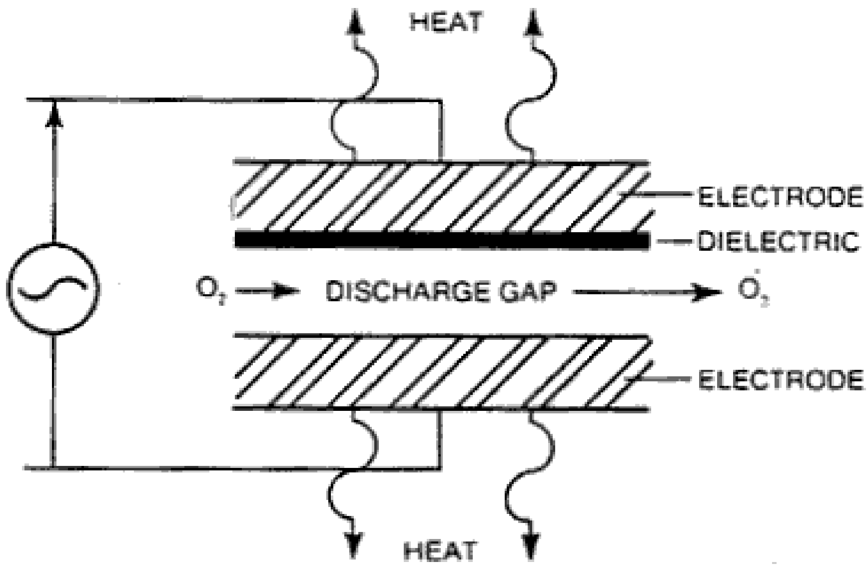
HO· attack is much more unselective : few compounds resist to its action.

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

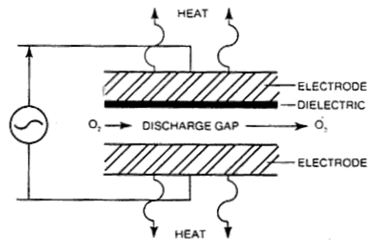
Ozone generation

Irradiation of air or oxygen with UV radiation (185 nm). Low ozone concentrations (0.25% in weight) and small flow rate. Used when small productions are required (labs)

Electric discharge: The most used method in water and wastewater treatment. The electrical discharge breaks the oxygen bond and produces two oxygen atoms.



Ozone generation



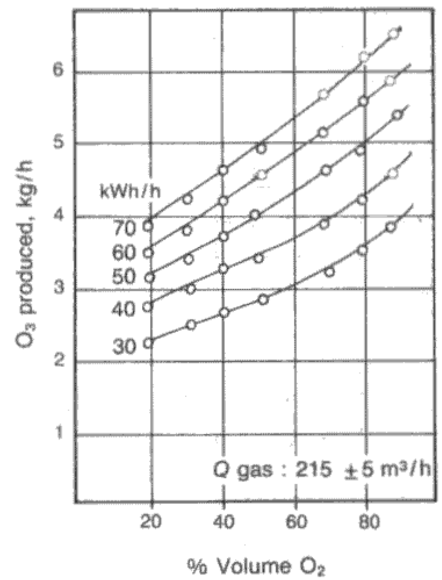
Electric discharge

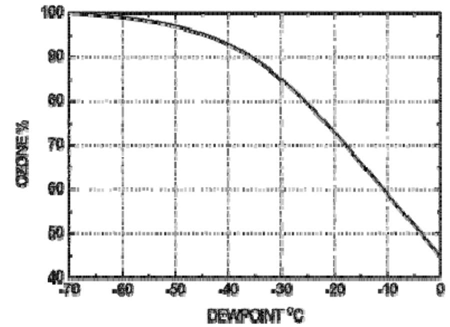
- the inlet gas :**air or oxygen**
- 2-3 times more production of ozone when using oxygen instead of air. Additionally it is avoided the NOx formation.

-**pre-treatment of gas needed**

1) gas compression
2) gas filtering (to avoid foreign particles)
3) gas drying to a very low % of humidity to increase the production performance and to avoid NOx formation.
4) Unit of gas-liquid contact (ozone transfer)
5) Thermic or catalytic ozone killer

- **main drawback only the 5% of the used electric energy goes to the oxygen-oxygen bonds. The rest appears as light radiation and heat. Consequently the dielectrics have to be cooled with air or water.**

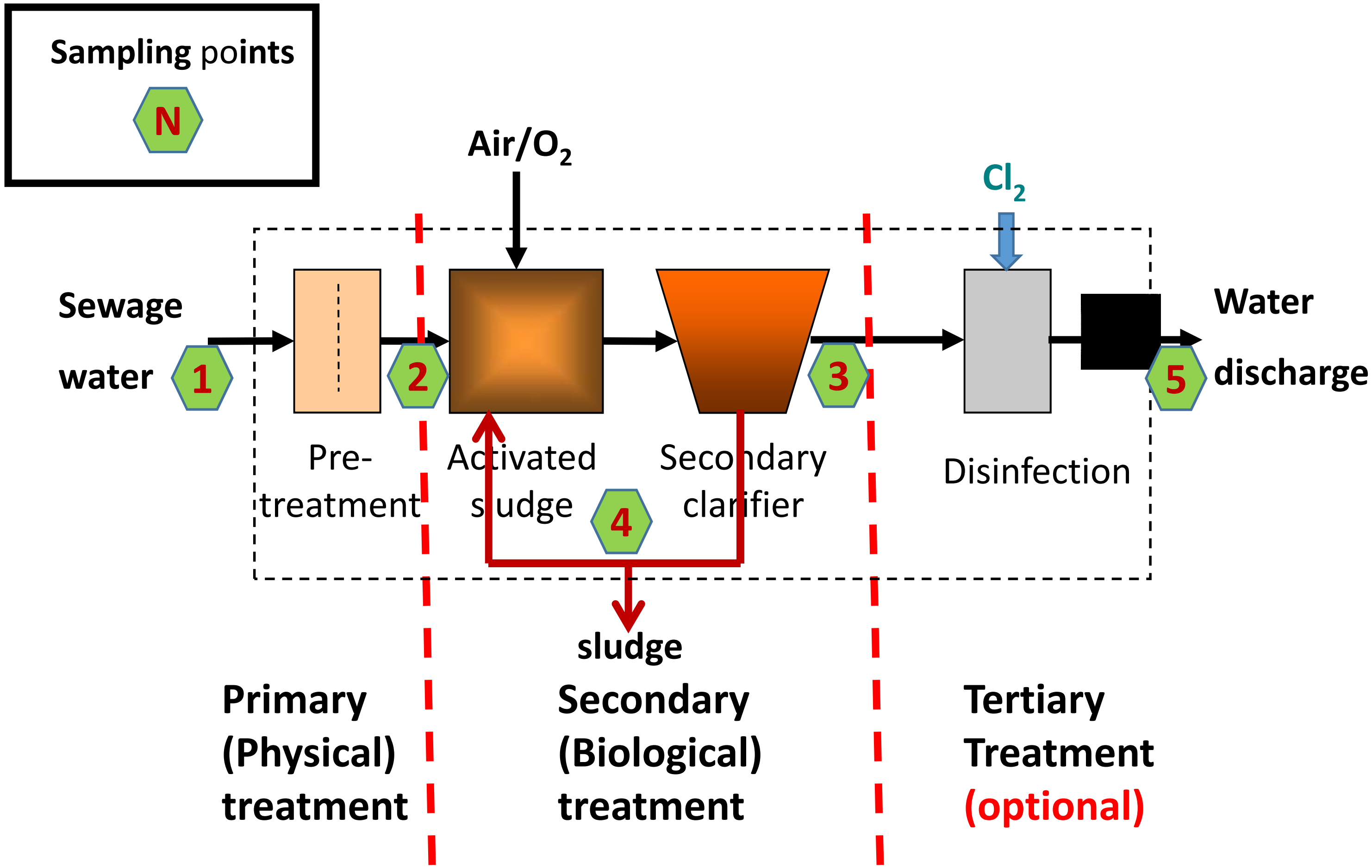




COST (2013) 11- 16 kW.h/kg Ozone

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
- Phthalates
- Octylphenols//nonylphenols
- …..

Organic matter fractionation

- LC-OCD-ON-UVAD

Water and Wastewater parameters

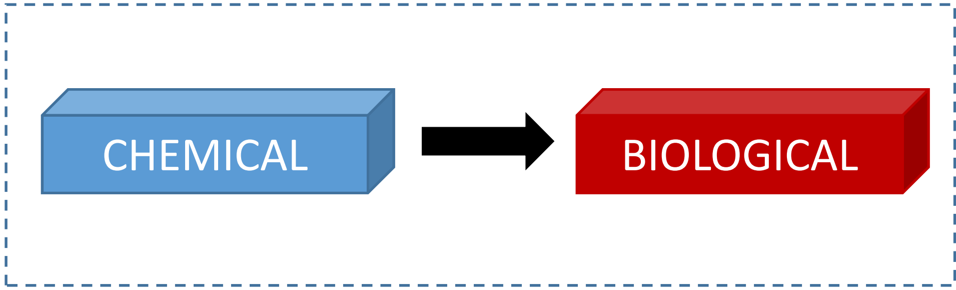
LC-OCD ANALYSIS

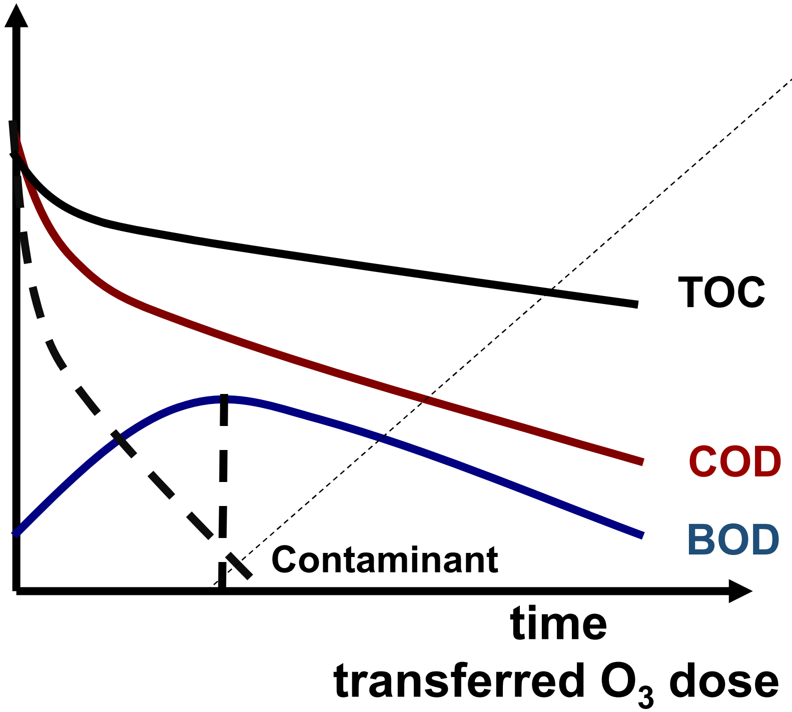
LC-OCD-OND-UVAD stands for Liquid Chromatography (size exclusion) Organic Carbon Detection, Organic Nitrogen Detection and Ultra-Violet Detection.

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

O_3 in wastewater treatment

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





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

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

Maximum of BOD

Modeling of O_3 mass transfer & Chemical Reaction

Ozonation is an mass transfer process

- Mass transfer rate dependent on
  - Physical properties of phases
  - Concentrations at the interface
  - Degree of turbulence
  - gas hold-up and bubble size

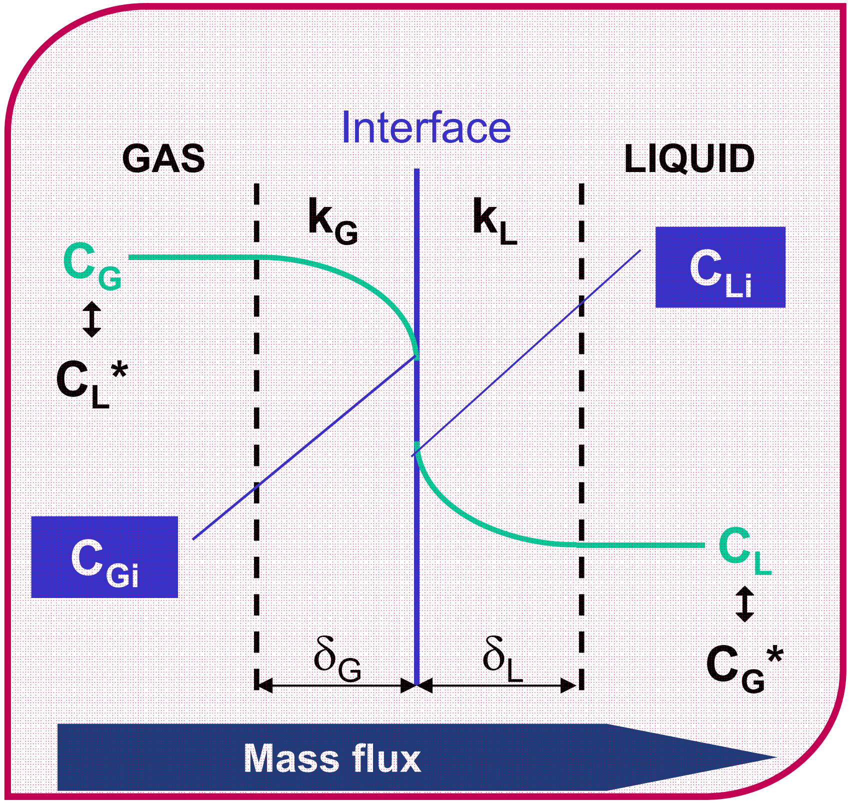
- Two-film model

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

  - $N = O_3$ flux density ($g/(m^2.s)$)
  - $C_L^* = f(C_G, P, T)$ - Henry's law (g/m^3)
  - $C_L = f$(mixing conditions) (g/m^3)
  - $K_L.a = f$(hydrodynamic & operating conditions, reactor configuration) (s^{-1})
  - A = interfacial area (m^{-1})

Ozone – water : control in the liquid

$$k_L = K_L$$



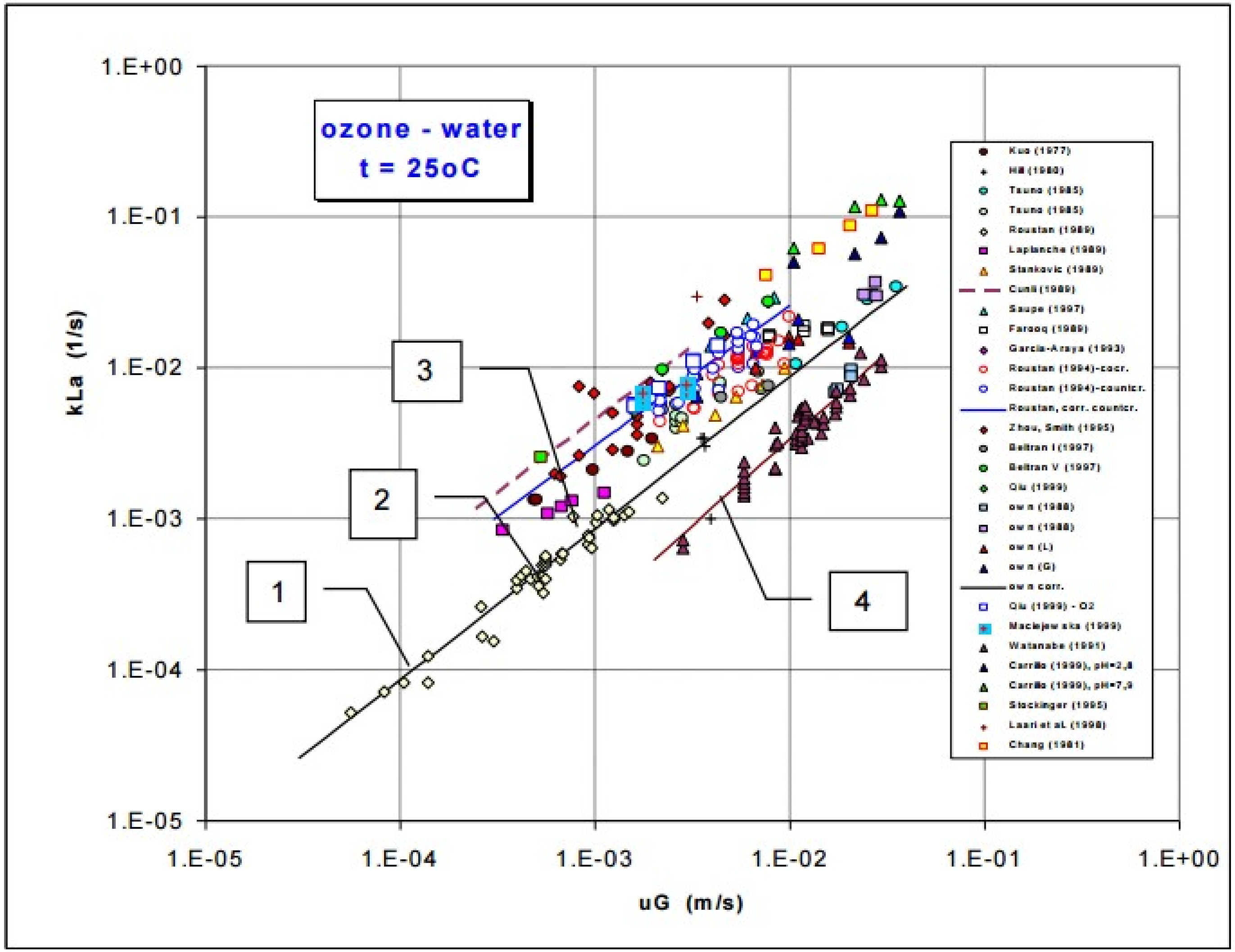
Absorption with Chemical Reaction

$$r_{O3} = k_{O3}.[O_3].[M]$$

$$Ha = \frac{\sqrt{D_{O3} k_{O3} [M]}}{k_L}$$

Hatta number

O_3 mass transfer



Experimental data of k_La vs. u_G in the bubble columns:

(1)- $k_La = 0.867u_G$; (2) - $k_La = 1.89u_G^{0.932}$; (3) - $k_La = 4.12u_G^{1.02}$; (4) - $k_La = 0.67u_G^{1.15}$

$$r_{O3} = k_{O3}.[O_3].[M]= k_d.[O_3]$$

$$\frac{dS}{dt} = -k_{O3}(O_3)(S) - k_{\cdot OH}(^{\cdot}OH)(S)$$

Substance	k_{O3} [M^{-1} s^{-1}]	k_{OH} [10^9 M^{-1} s^{-1}]
pCBA[a]	0.15	5.2
Ketoprofen[d]	0.4	8.4
Ibuprofen[b]	9.1	7.4
Clofibric acid[b, c]	20	4.7
Bezafibrate[b]	590	7.4
Ciprofloxacin[e]	1.9×10^4	4.1
Naproxen[b, c]	2×10^5	9.6
Trimethoprim[e]	2.7×10^5	6.9
Carbamazepine[b]	3×10^5	8.8
Enrofloxacin[e]	6.7×10^5	4.5
Diclofenac[b]	1×10^6	7.5
Sulfamethoxazole[b]	2.5×10^6	5.5

U. Hubner, S. Keller, M. Jekel. Evaluation of the prediction of trace organic compound removal during ozonation of secondary effluents using tracer substances and second order rate kinetics. Water Research 47 (2013) 6467-6474

Modeling O_3 mass transfer & chemical reaction

$$Ha = \frac{\sqrt{D_{O3} k_{O3} [M]}}{k_L}$$

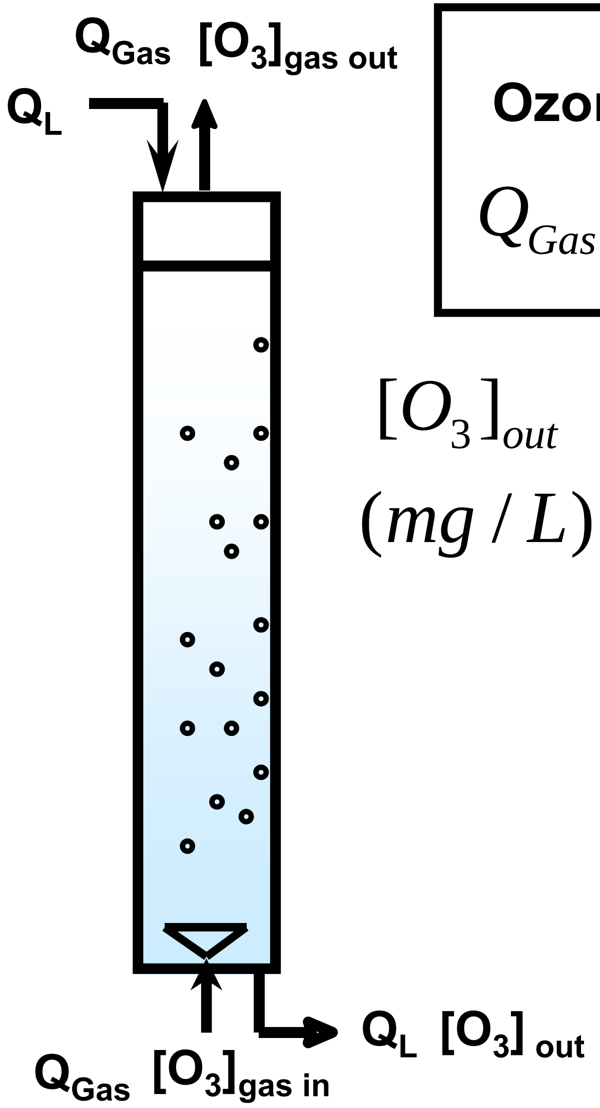
Hatta number

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

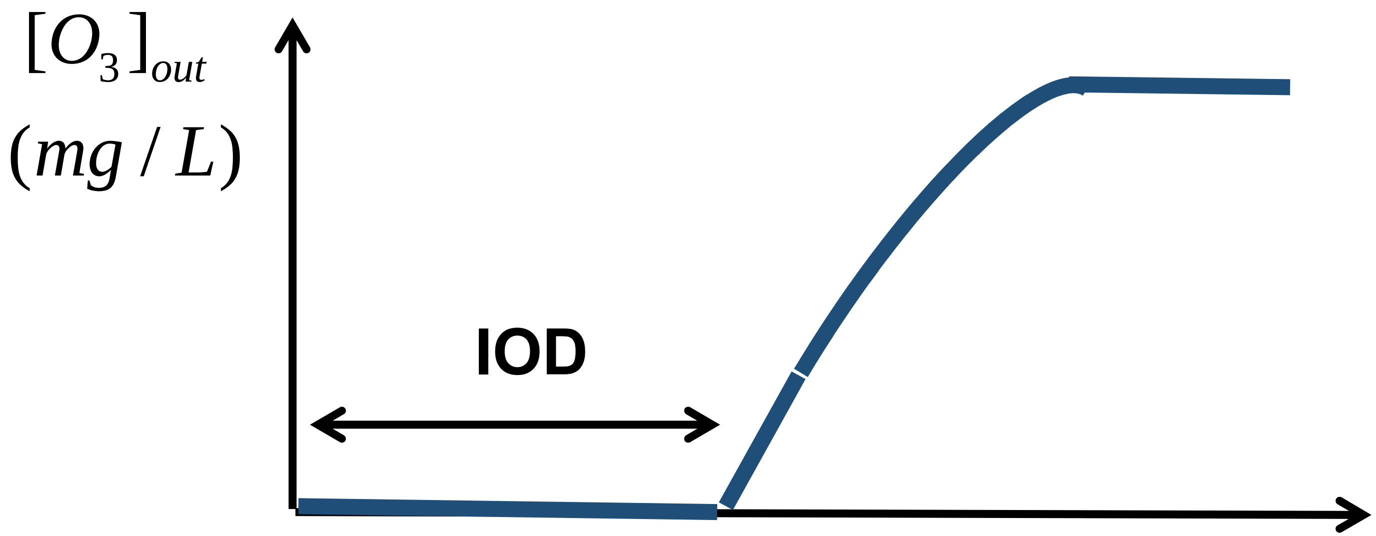
IOD (immediate O_3 demand) TOD (transferred O_3 dose)

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



Ozone balance **(steady state)**

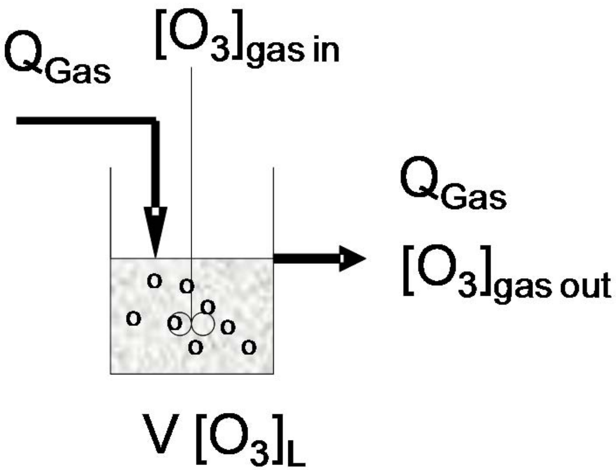
$$Q_{Gas}\left([O_3]_{gas\ in} - [O_3]_{gas\ out}\right) - R_{O3} = Q_L[O_3]_{out}$$



$$\text{TOD} = Q_{Gas}\left([O_3]_{gas\ in} - [O_3]_{gas\ out}\right)/Q_L$$

$$(mg/L)$$

Semicontinuous ozonation: simple model



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

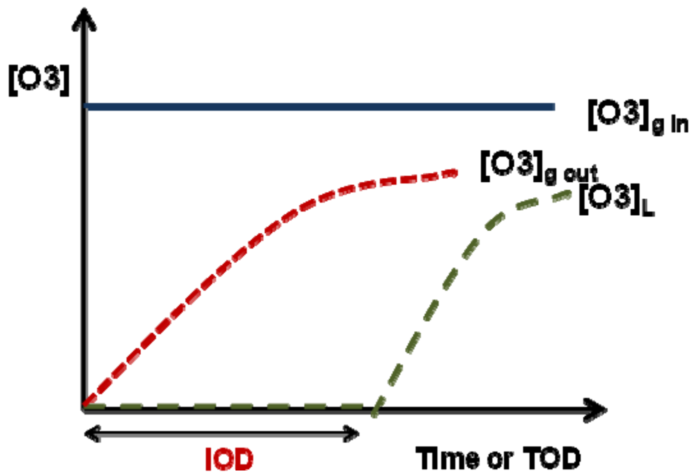
Ozone balance in liquid phase

TOD < IOD $\quad [O3] = 0$

TOD > IOD $\quad \dfrac{d[O3]}{dt} = K_L a \times ([O3]^* - [O3]) - k_d \times [O3]$

Ozone balance in gas phase

$$Q_{Gas}\left([O3]_{gas\ in} - [O3]_{gas\ out}\right) = K_L a([O3]^* - [O3])V_{Liq} = k_d [O3]\ V_{Liq} + \frac{d[O3]}{dt} V_{Liq}$$



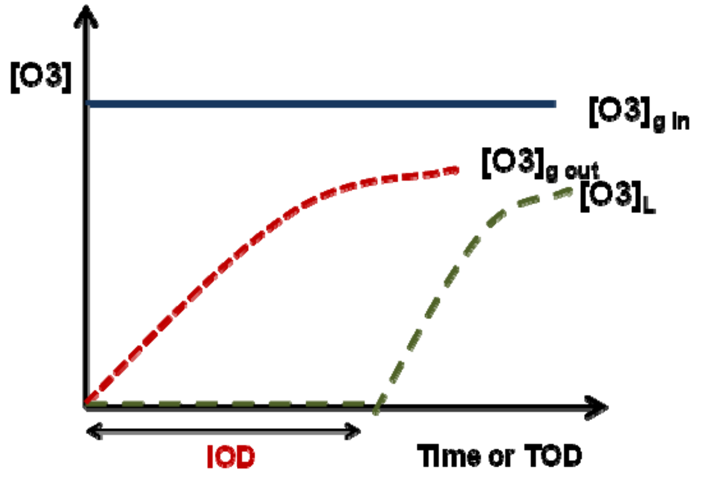
$$P_{O3} = Hx_{O3^*}$$ Henry's law

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

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

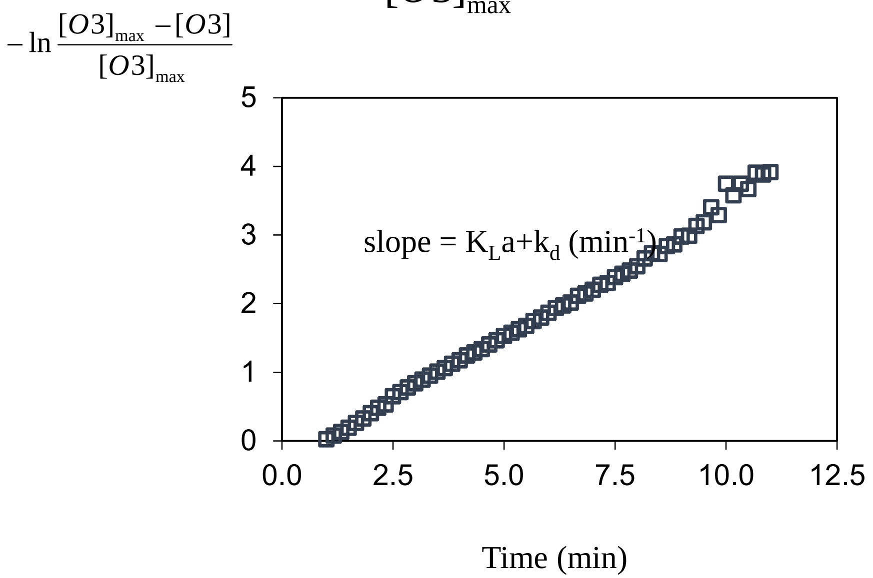
Roth and Sullivan equation

Estimation K_La , k_d at lab scale



when $\frac{d[O3]}{dt} > 0$

$$\ln \frac{[O3]_{\max} - [O3]}{[O3]_{\max}} = -(K_L a + k_d)t$$



when $\frac{d[O3]}{dt} = 0$

$$k_d = \frac{Q_{Gas}\left([O3]_{gas\ in} - [O3]_{gas\ out}\right)}{[O3]\ V_{Liq}}$$

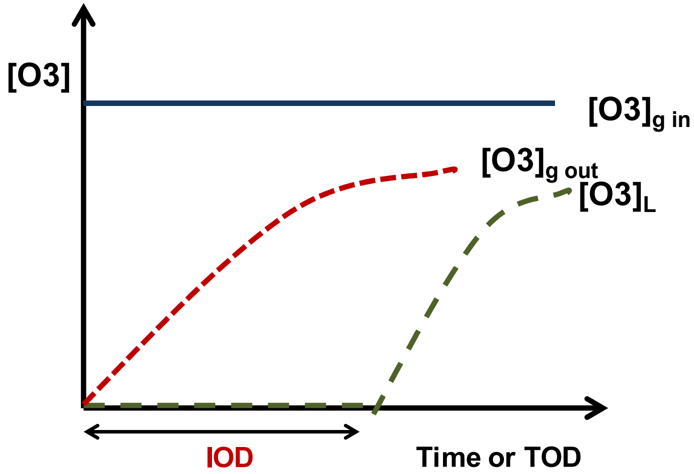
$$\frac{[O3]^*}{[O3]_{\max}} = \frac{K_L a + k_d}{K_L a}$$

$P_{O3} = Hx_{O3^*}$ Roth and Sullivan

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

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

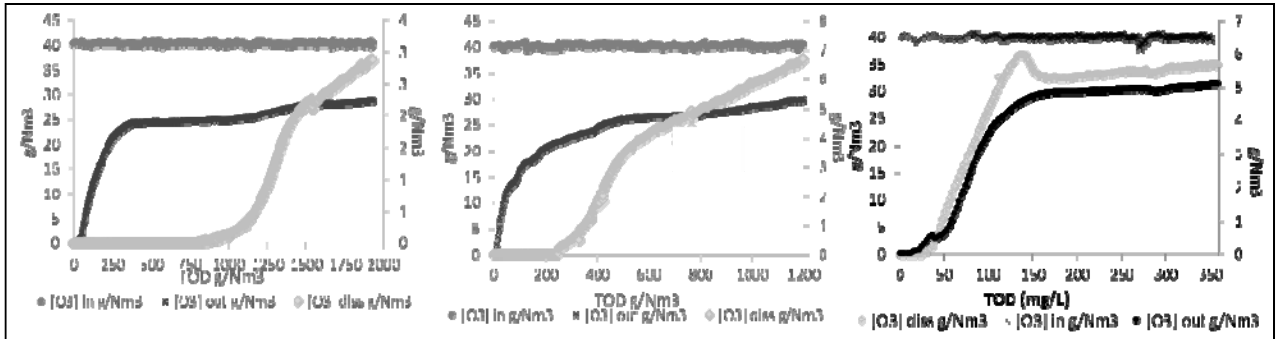
A THEORETICAL BEHAVIOUR
(k_La and k_d constant)



EXPERIMENTAL

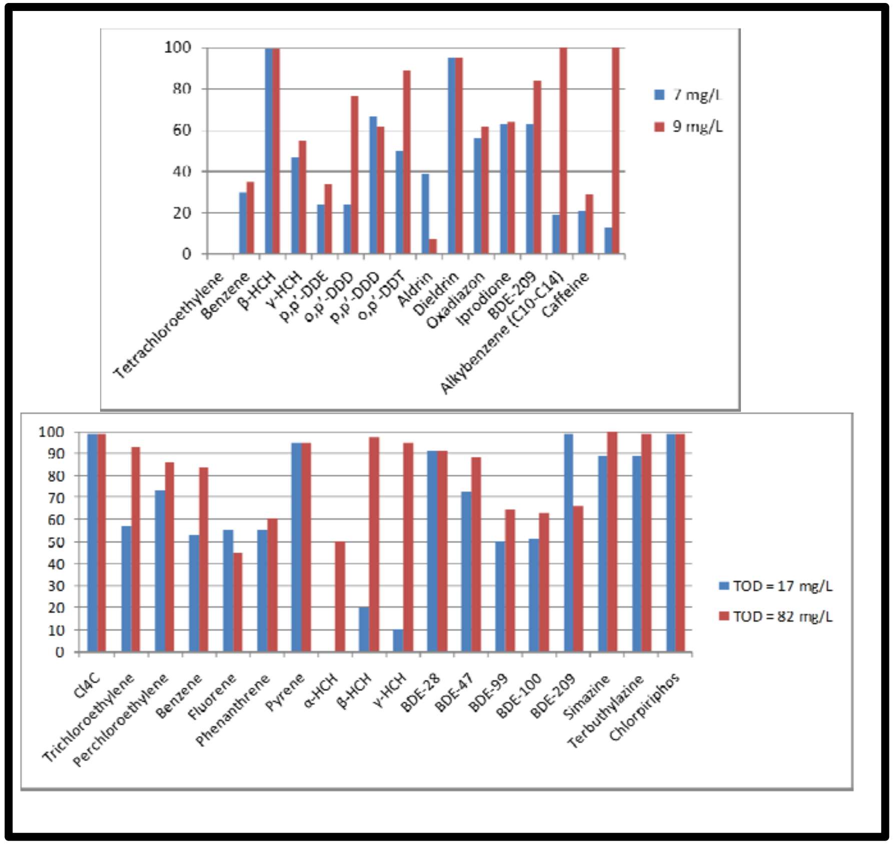
Effluent	DOC	COD	UV254	pH	Turbidity	IC	SS
	mg/L	mg/L	m^{-1}		NTU	mg/L	mg/L
P1	69.5	265	26.9	7.6	131	86	67
P2	59.4	367	36.8	7.6	120	60	97
P3	109.7	778	96.3	7.4	170	107	250
P4	94.7	885	74.2	8.5	285	54	512
S1	6.7	29	12.0	8.1	7.8	65	-
T1	6.5	19	11.4	6.6	0.3	16	-
T2	13.2	50	26.2	8.5	0.1	52	-

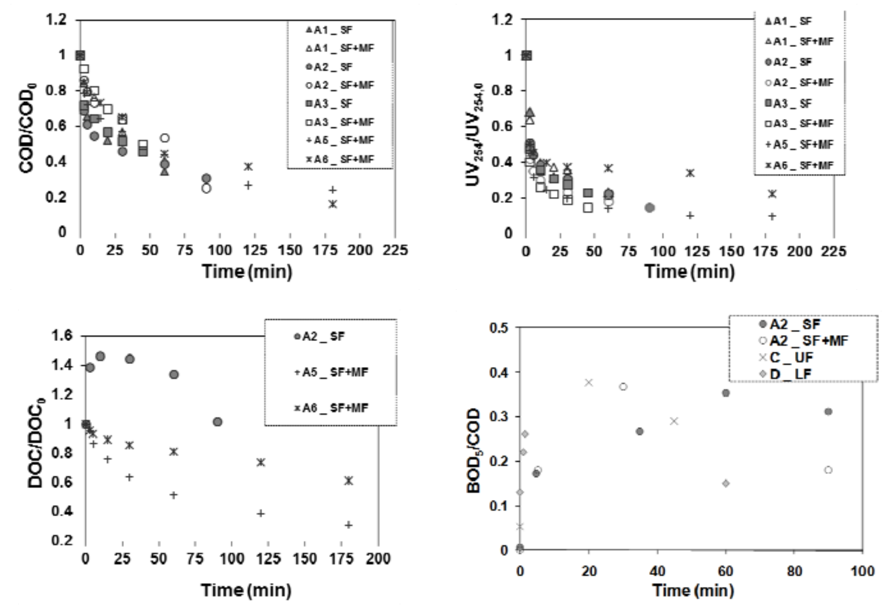
Effluent	IOD	K_La	k_d
	mg/L	min^{-1}	min^{-1}
P1	64	0.83	0.80
P2	83	0.76	0.19
P3	348	0.50	0.66
P4	249	0.79	0.30
S1	6.5	0.29	0.087
T1	10	1.90	0.08
T2	12	0.67	0.10



Sludge
Primary effluent
Secondary effluent

Removal of CECs by O_3





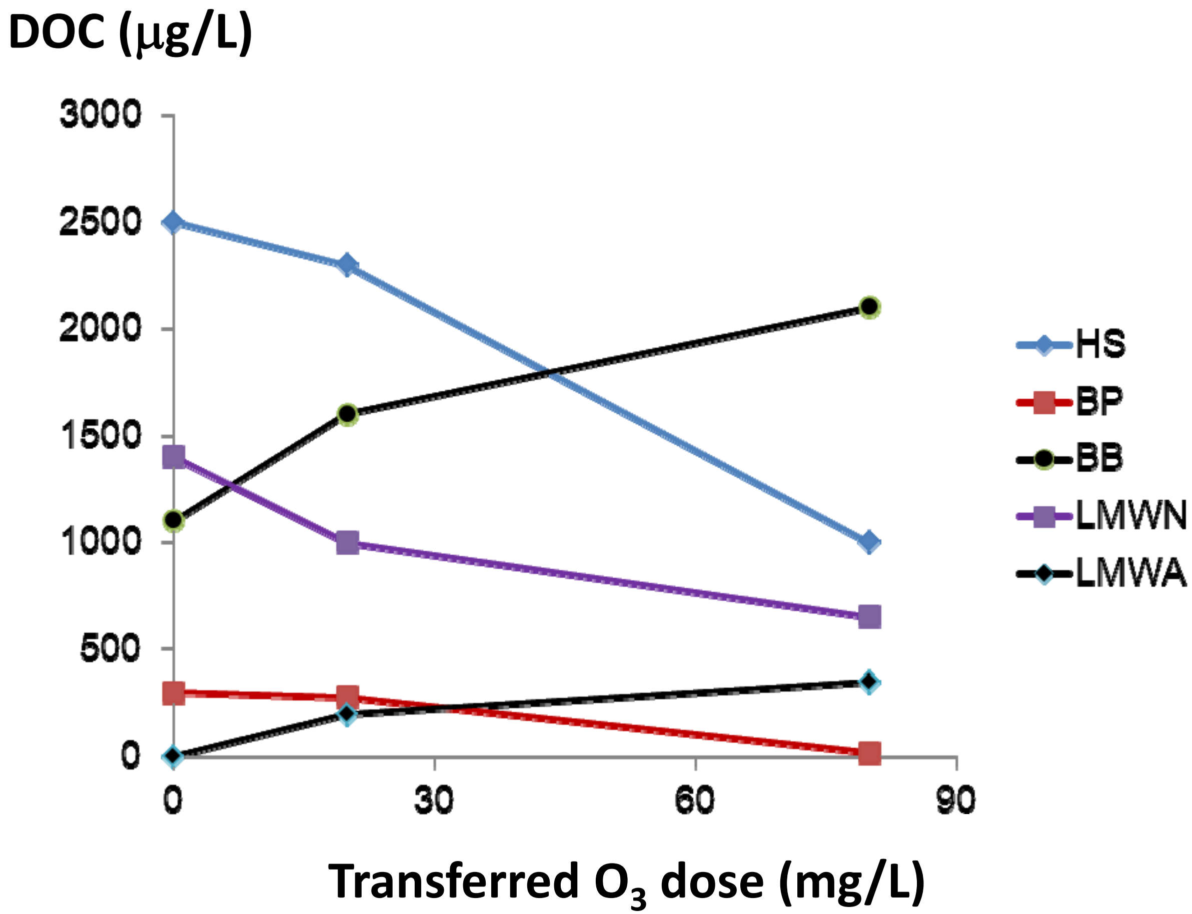
Water Quality Parameters

Marce et al CEJ 283 (2016) 768-777

Marce et al O_3 World Congress. Barcelona October 2015

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 relatively 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.**

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AOPs PhD School

2nd Summer School on
Environmental applications of Advanced ` Processes

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Wastewater .ent by ozonation

Thank you

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