GENERAL DISCUSSION ABOUT ADVANCED OXIDATION PROCESSES (AOPs)

Montserrat Pérez Moya (montserrat.perez-moya @upc.edu)
Departament d'Enginyeria Química (DEQ)
Universitat Politècnica de Catalunya (UPC)
EEBE, Barcelona, Spain

AOPs PhD School

www.upc.edu

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2nd Summer School on Environmental applications of AOPs, University of Porto,
Faculdade de Engenharia, Porto (Portugal), July 10-14, 2017

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OVERVIEW

- **INTRODUCTION**
  - ✓ **Water**
  - ✓ **Conventional water treatments**
  - ✓ **Wastewater quality parameters**
  - ✓ **AOPs**
- **AOPs**
  - ✓ **Classification**
  - ✓ **Process description – Recent Studies**
- **WHAT IS REQUIRED TO AOPs IMPLEMENTATION?**
- **STRATEGIES TO IMPROVE AOPs**
  - ✓ **Dosage of reagents**
  - ✓ **On-line monitoring**
- **CONCLUSIONS**

WHAT'S THE PROBLEM WITH WATER?

- **LIMITED (97,5% salty water, 2,5 % fresh water)**
- **NECESSARY FOR HUMAN (human dies after 5-10 days without water)**
  - ✓ **LIVING**
  - ✓ **DEVELOPMENT**

Water treatment and recycling is required

- **RESTRICTIVE LEGISLATION ABOUT WATER CONTAMINATION**
- **MAJOR SOCIAL AWARENESS**

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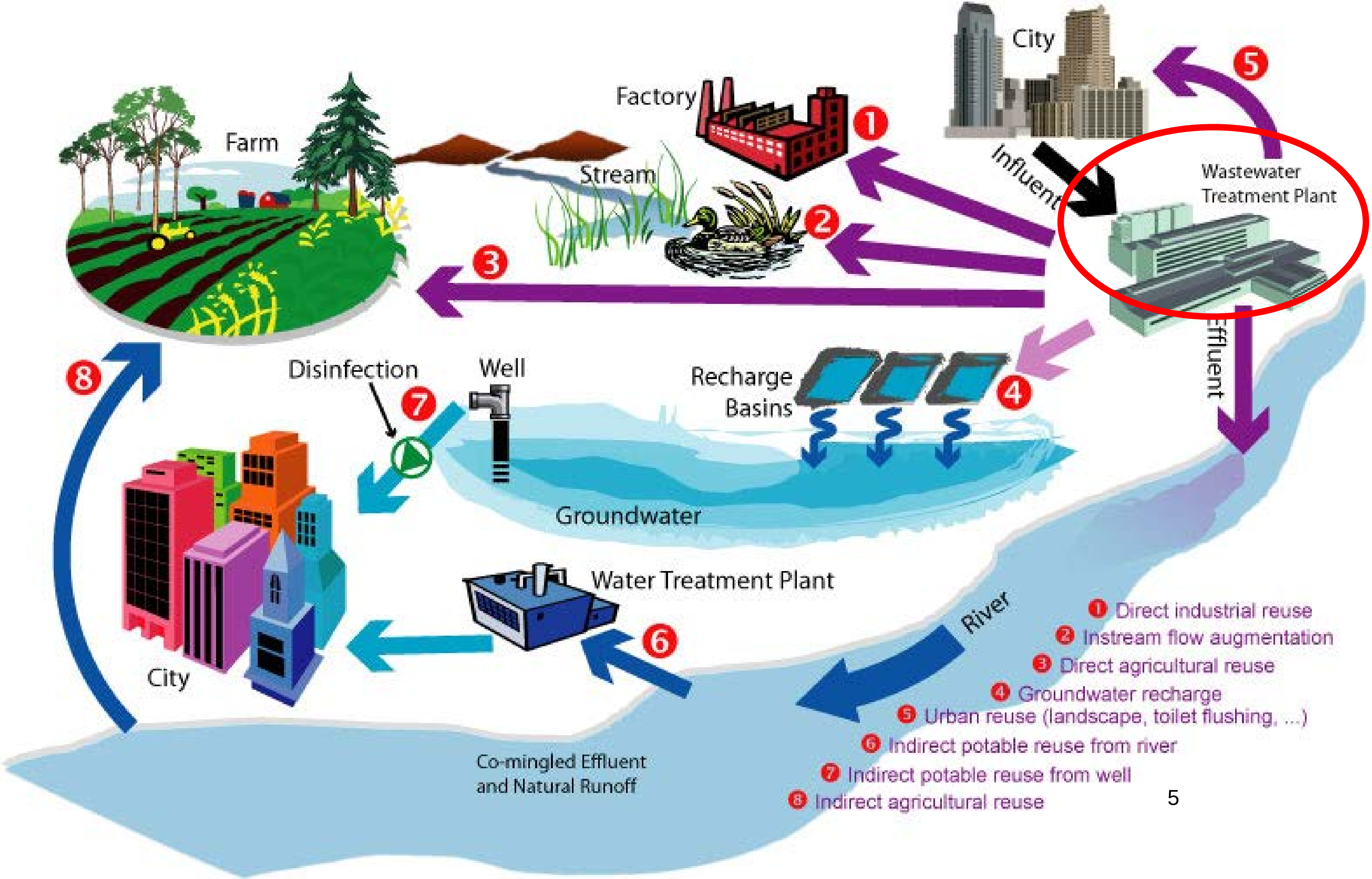
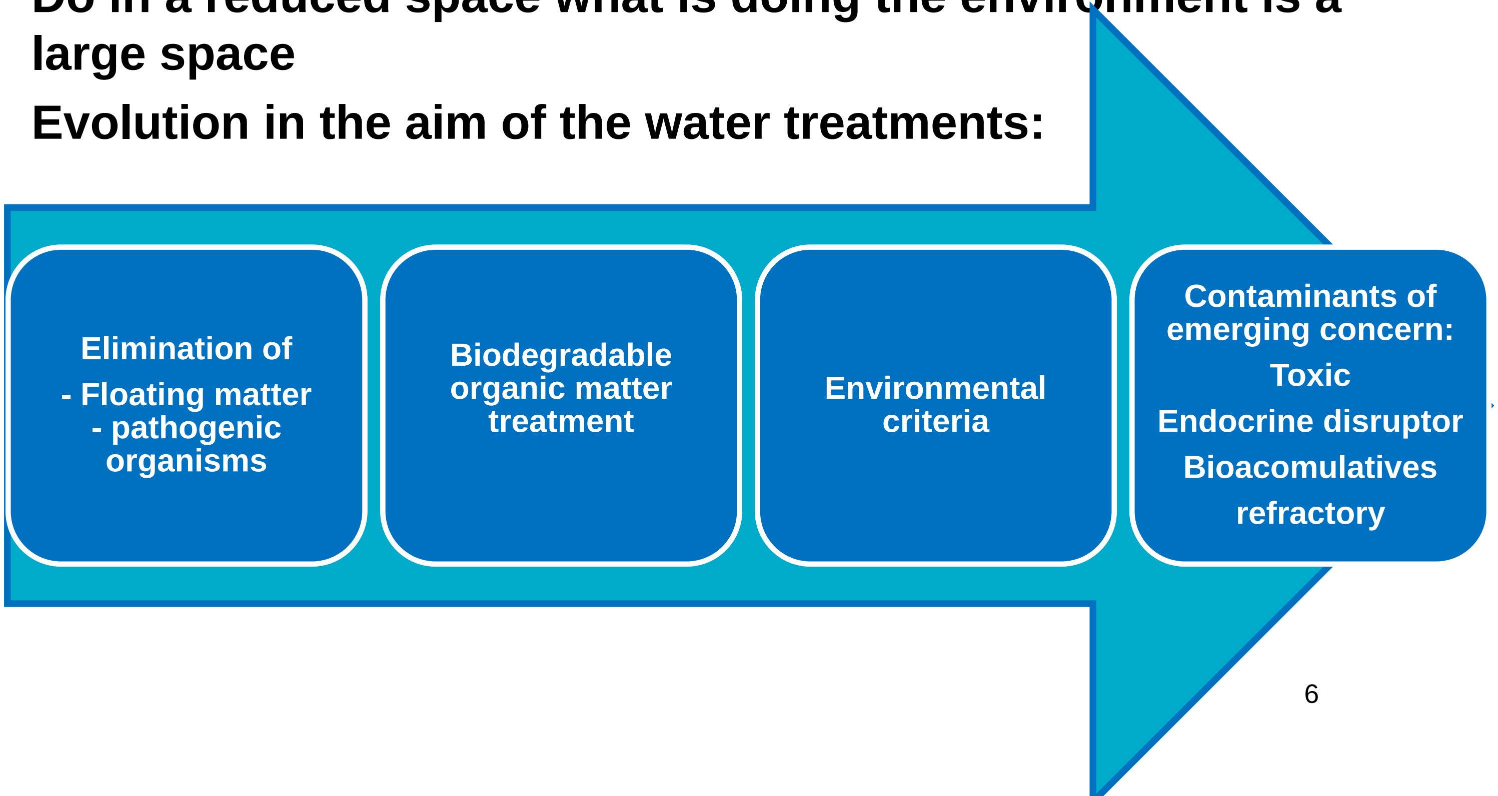


1. Direct industrial reuse
2. Instream flow augmentation
3. Direct agricultural reuse
4. Groundwater recharge
5. Urban reuse (landscape, toilet flushing, ...)
6. Indirect potable reuse from river
7. Indirect potable reuse from well
8. Indirect agricultural reuse

WHAT'S THE AIM OF THE WATER TREATMENTS?

- **Public health**
- **Environmental care**
- **Do in a reduced space what is doing the environment is a large space**
- **Evolution in the aim of the water treatments:**



Elimination of
- Floating matter
- pathogenic organisms

Biodegradable organic matter treatment

Environmental criteria

Contaminants of emerging concern:
Toxic
Endocrine disruptor
Bioacomulatives
refractory

Contaminants of emerging concern (CEC)

Before 90s - Hazardous, non-polar and persistent compounds

→ Drastic reduction of discharges

“New” contaminants (Contaminants of emerging concern) →

- Non-regulated
- Low concentration (ng L^{-1} to μg L^{-1})
- Continuous introduction into the environment

- Endocrine disrupting compunds (EDC)
- Pharmaceuticals and personal care products (PPCP)
- Pesticides
- Dyes

CEC - Pharmaceuticals

Therapeutic classes	Pharmaceutical	Source
Analgesic	Naproxen, paracetamol, salicylic acid	▪ Mainly human excretion (partial absorption) ▪ Inefficiency of sewage treatment plants (STP) for pharmaceutical residues elimination ▪ Livestock ▪ Veterinary medicine ▪ Effluent from drug manufacture
Anti-inflammatory	Diclofenac, ibuprofen	
Antihypertensive	Atenolol, celiprolol, metoprolol, propranolol, sotalol	
Lipid regulator	Bezafibrate, clofibric acid, fenofibric acid, gemfibrozil	
Antiepileptic	Carbamazepine, diazepam, primidone	
Antibiotics	Amoxicillin, ofloxacin, sulfamethoxazole, sulfathiazole, erythromycin	
Contraceptive	17β-Estradiol, estrone, 17μ-ethinylestradiol, diethylstilbestro	

Removal rates of pharmaceuticals in sewage streams

	Verlicchi et al, 2012	Petrie et al, 2014	Gurke et al., 2015
Amitriptiline	-	M-H	L (15%)
Atenolol	L-M	M-H	L (23%)
Bezafibrate	L-M	L-M	L (49%)
Carbamazepine	L	l	L (-7%)
Gabapentin	H	L-H	L (6%)
Metoprolol	L	L-M	L (-9%)
Propranolol	L-M	-	L (-4%)
Sulfamethoxazole	L-H	L-M	L (43%)
Trimethoprim	L-H	L-M	L (-11%)
Valsartan	-	L	L (24%)

Removal rates
L: < 50%
M: 50-80%
H: > 80%

Sewage treatment plants have not been designed to remove pharmaceutical residues from wastewaters

Gurke et al., 2015, Sci. Total Environm., 532, 762.

Effects of CEC

- Few data available about the toxicity of these emerging contaminants and effects to humans and aquatic organisms
  - feminization of male fish (endocrine disruptors)
  - bacterial resistance (antibiotics)

- Chronic effects?
- Synergistic effects?

Lack of Information

Jobling et al., Environ. Sci. Technol. 1998, 32, 2498-2506

Tamtam et al., Sci. Total Environ., 2008, 393, 84-95

WASTEWATER QUALITY PARAMETERS

- Suspension solids
- Evaporation solids
- Calcination solids
- Turbidity
- Hardness
- Color
- CO_2 free
- Cl^-, SiO_2, SO_4^{2-}
- On-line parameters:
  - Temperature
  - Alkalinity, pH
  - O_2 dissolve
  - Conductivity, [soluble salts]
  - Redox Potential

- Organic Matter:
  - TOC (Total Organic Carbon)
  - COD (Chemical Oxygen Demand)
  - BOD (Biological Oxygen Demand)
- Toxicity
- AOX (Absorbable Organics Halogens)
- Specific contaminant monitoring (HPLC, GC_MS,...)

Which parameters are usually check in legislation?

WASTEWATER QUALITY PARAMETERS

- **Suspension solids**
- **Evaporation solids**
- **Calcination solids**
- **Turbidity**
- **Hardness**
- **Color**
- **CO_2 free**
- **Cl^-, SiO_2, SO_4^{2-}**
- **On-line parameters:**
  - **Temperature**
  - **Alkalinity, pH**
  - **O_2 dissolve**
  - **Conductivity, [soluble salts]**
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  - **TOC (Total Organic Carbon)**
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- **Toxicity**
- **AOX (Absorbable Organics Halogens)**
- **Specific contaminant monitoring (HPLC, GC_MS,...)**

CONVENTIONAL TREATMENTS CLASSIFICATION

Pretreatments

- Aim: To remove whatever that could interfere in the next treatments and/or the maintenance of the operations

Primary

- Aim: To remove the organic matter which is easily removed

Secondary

- Aim: To remove biodegradable organic matter, sometimes even disinfection

Tertiary

- Aim: To remove specific compounds as N or P, sometimes even disinfection

Regeneration

- Aim: To remove toxic compounds, inorganic and organic matter, disinfection.

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WHAT’S WRONG WITH CONVENTIONAL WATER TREATMENT?

- **THERE ARE INSUFFICIENT IN MANY CASES**
- **CONTAMINANT IS NOT ALWAYS**
  - ✓ **REMOVED**
  - ✓ **DEGRADATED (turn into biodegradable matter)**
  - ✓ **MINERALIZED**

Advanced Oxidation Processes (AOPs) presents and interesting alternative or complement

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WHAT'S AN ADVANCED OXIDATION PROCESS?

Technologies based on the generation of an active and non selective oxidants

↓

HO• radical

("activated oxygen species")

↓

Oxidative degradation of pollutants (organic and inorganic) in aqueous or air media.

ADVANCED OXIDATION PROCESS

·OH generation achieved by a combination of oxidizing agents (ozone, hydrogen peroxide), ultraviolet (UV), visible or ultrasound radiation and catalysts (metallic ions or semicondutors).

Main advantages:

- The contaminant is chemically transformed not only transported from a phase to another
- It is possible to reach complete mineralization
- It is possible to transform refractory contaminants into biologically treatable substances

Main disadvantages:

- Cost
- Modeling/ Prediction/ Automation

RADICALS REACTS IN A WELL-KNOWN WAYS WITH ORGANIC COMPOUNDS

✓**Abstracting H from C-H, N-H or O-H bonds**

$$HO\bullet \quad + \quad R-H \quad \rightarrow \quad H_2O \; + \; R\bullet$$

✓**Adding to C = C bonds**

$$HO\bullet \; + \; RR'C{=}\,CR''R''' \rightarrow \; RR'C(OH){-}\,C\bullet\, R''R'''$$

✓**Adding to aromatic rings**

OXIDATION / MINERALIZATION

OXIDATION

HO• + Contaminant → Oxidized Intermediate

In the presence of molecular oxygen

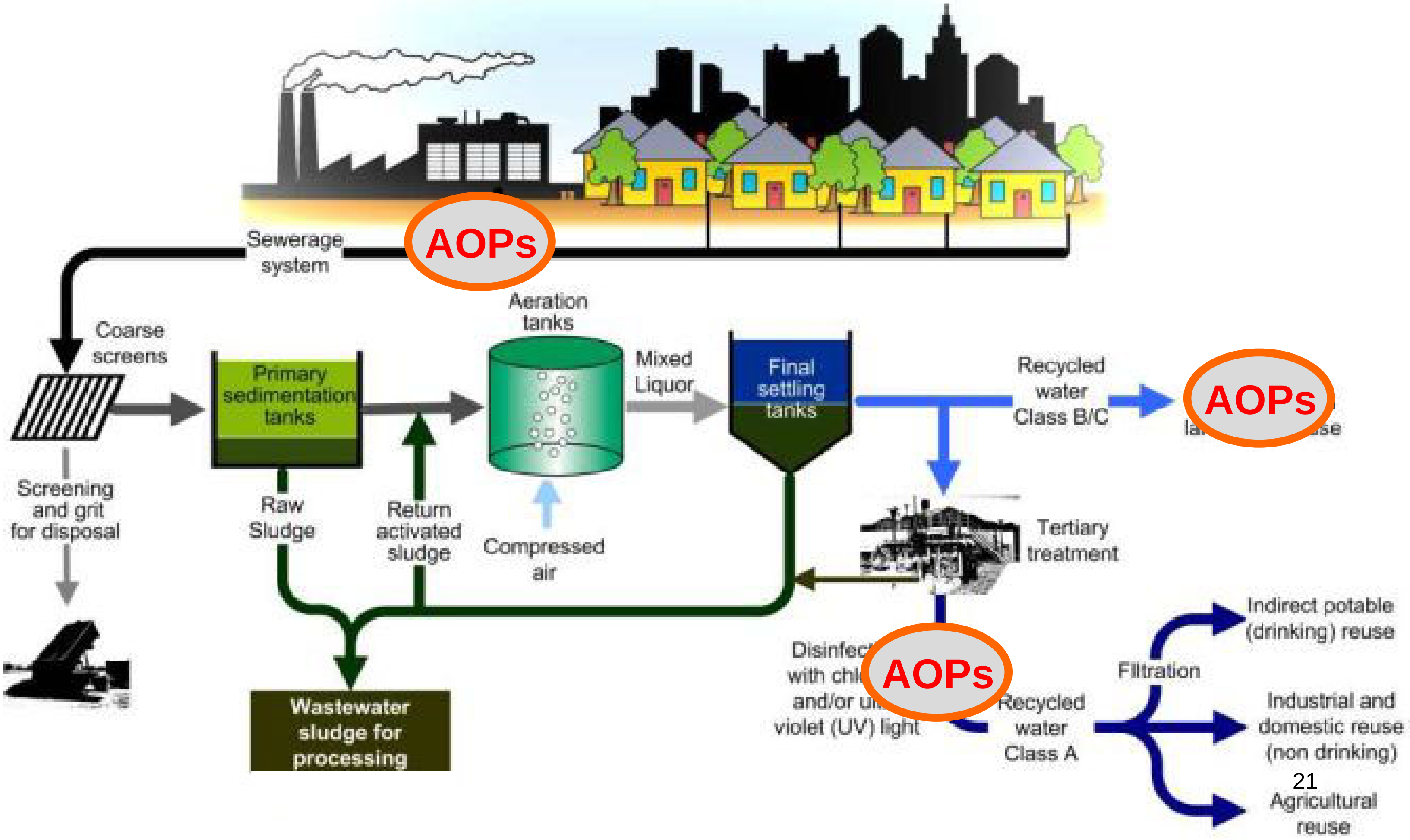
$R\bullet + O_2 \rightarrow RO_2\bullet$ **(diffusion controlled reaction)**

$RO_2\bullet \rightarrow$ Oxidized Intermediate

MINERALIZATION

HO• + Oxidized Intermediate → $H_2O + CO_2$

WHEN / WHERE TO USE AN AOP?



Wastewater → **Biological treatment** → **Treated water**

Wastewater containing:
Recalcitrant species
Endocrine disruptors
Antibiotics
Antiseptics
High TOC
⇨ ***High toxicity and persistent nature***
Low biodegradability

→ **AOP's** → **Biological treatment** → **Treated water**

Low toxicity
High biodegradability

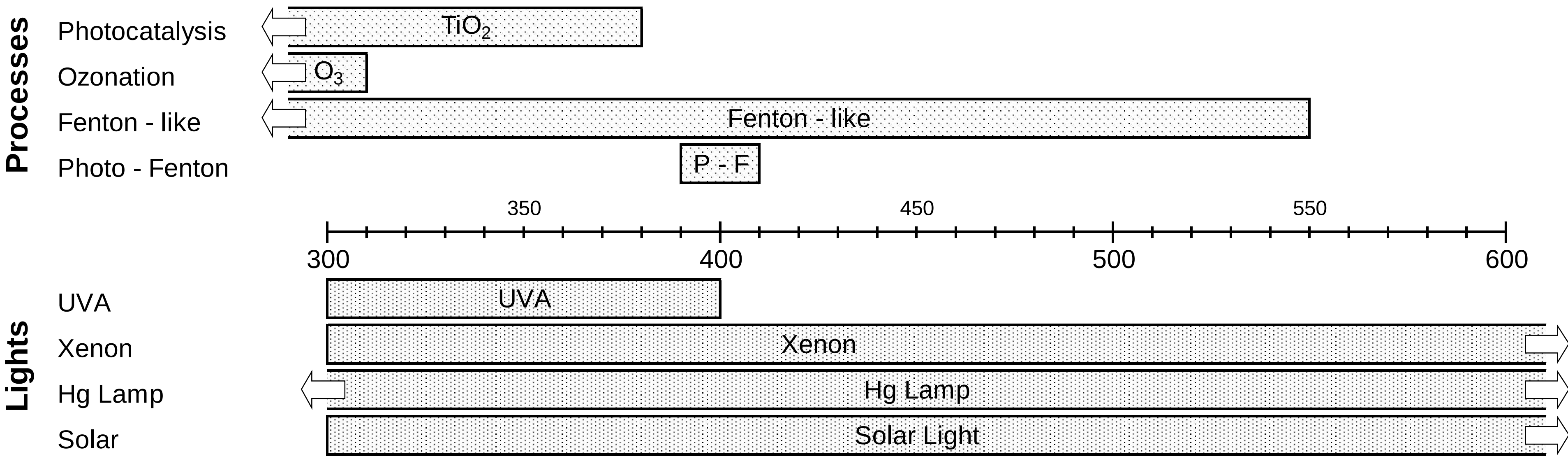
Process	λ (nm)	Solar light
Photolysis	< 290	NO
Photo catalysis $TiO_2 + h\nu$	< 380	YES
H_2O_2 $H_2O_2 + h\nu$	----- < 290	NO
H_2O_2 + catalyst H_2O_2 + catalyst + $h\nu$	----- < 400	YES
O_3 $O_3 + h\nu$	----- < 290	NO
$H_2O_2 + O_3$ $H_2O_2 + O_3 + h\nu$	----- < 290	NO
Fenton ($Fe^{+2}+H_2O_2$) Photo -Fenton ($Fe^{+2}+H_2O_2 + h\nu$)	UV + Visible (<550 nm)	YES

Infrared > 700 nm

Visible – low energy photons (400 - 700 nm)

UV (40 – 400 nm / 30 – 3 eV):

> **UVA (320 - 400 nm), UVB (290 – 320 nm), UVC (220 – 290 nm), Far UV (190 – 220 nm), VUV (40 – 190 nm)**



Photolysis, hν ≤ 290 nm

$$H_2O + h\nu \rightarrow H\bullet + HO\bullet$$ *(VUV – Xe-excimer, λ_{max}= 172 nm)*

$$H\bullet + O_2 \rightarrow HO_2\bullet$$

$$HO\bullet + RH \rightarrow H_2O + R\bullet$$

$$R\bullet + O_2 \rightarrow RO_2\bullet$$

Limited penetration of V-UV radiation

$H_2O_2 + h\nu \leq 290$ nm

$$H_2O_2 + h\nu \rightarrow 2\ HO\bullet$$

$$H_2O_2 + HO\bullet \rightarrow HO_2\bullet + H_2O$$

$$\textit{Contaminant} + h\nu \rightarrow \text{Intermediate}$$

$$\textit{Contaminant} + HO\bullet \rightarrow \text{Intermediate}$$

Lopez, J.; García Einschlag, F.; Gonzalez, M.; Capparelli, A. L.; Oliveros, E.; Hashem, T.; Braun, A. M.

J. Photochem. Photobiol., A: Chem. 2000, 137,177-184

H_2O_2 + hν ≤ 290 nm

H_2O_2 + hν → 2 HO•

H_2O + hν' → H• + HO• (hν'<190) – Low pressure Hg lamp*

H_2O_2 + HO• → HO_2• + H_2O

Contaminant + hν → Intermediate

Contaminant + HO• → Intermediate

***Suprasil envelope**

Lopez, J.; García Einschlag, F.; Gonzalez, M.; Capparelli, A. L.; Oliveros, E.; Hashem, T.; Braun, A. M.

J. Photochem. Photobiol., A: Chem. 2000, 137,177-184

Photolysis / H_2O_2 + hν ≤ 290 nm

Recent Studies

- **New lamp technology - enhancement of H_2O_2 excitation (UVC) (λ = 185, 222 nm,…)**
- **partial / total substitution of H_2O_2 by the use of VUV radiation**
- **Improvements in reactor design**

PHOTOCATALYSIS PROCESS

It is a heterogenic process which combine:

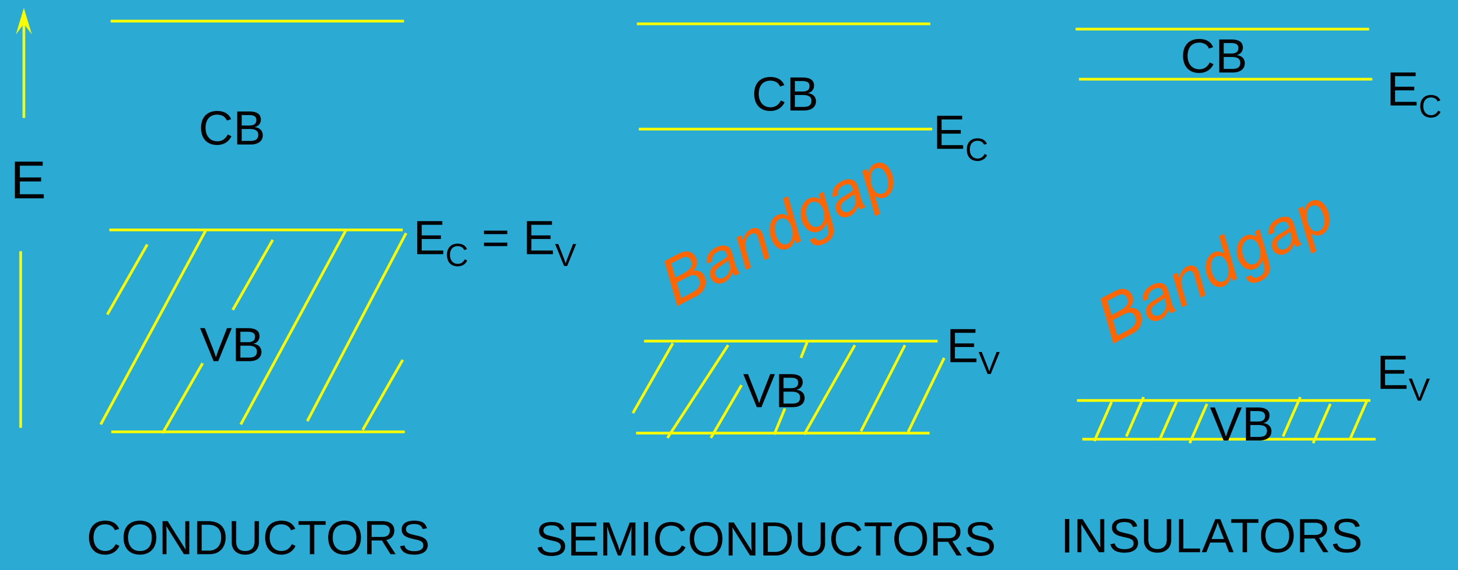
PHOTOCHEMISTRY → **Light (h$\nu \leq$ 380 nm)**

CATALYSIS → **Semiconductor**

Hoffmann et al., 1995

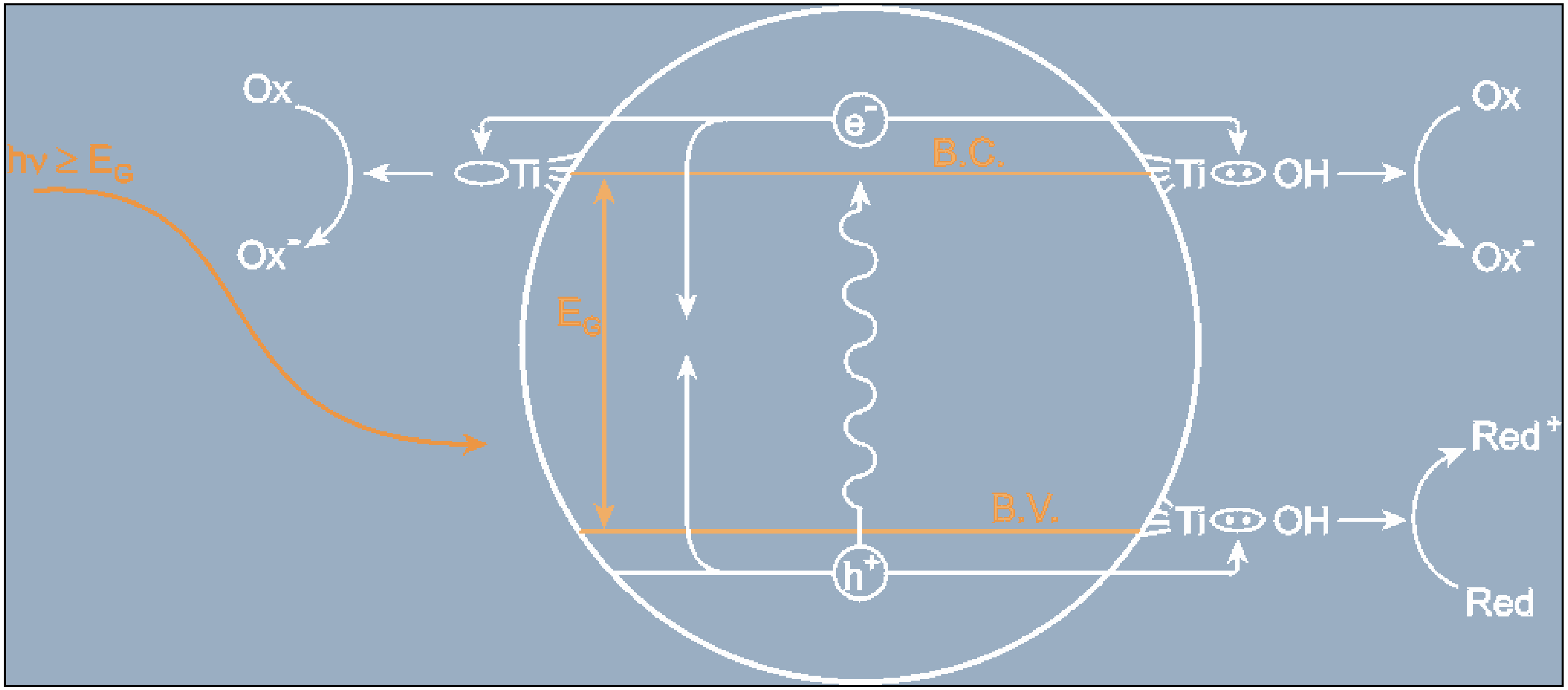
Energetic structures

VB: Valence Band CB: Conduction Band



TiO_2 + $h\nu \leq 380$ nm

It is necessary to avoid h+ and e- recombination in the catalyst (inside /superficially)



Hoffmann et al., 1995

PHOTOCATALYSIS PROCESS

Recent Studies

- **Improvement by the use of doped TiO_2 or TiO_2 / sensitizer / co-catalyst combinations**
- **Doped TiO_2 or TiO_2/ sensitizer / co-catalyst-combinations suitable for Vis- (solar) radiation**
- **Large, mechanically stable TiO_2 particles or mechanically stable TiO_2 on particulate inert support for simple photocatalyst recycling**

Hoffmann et al., 1995

Ozone, O_3

Ozone is a well-known oxidant agent (Reduction potential 2.08 V)

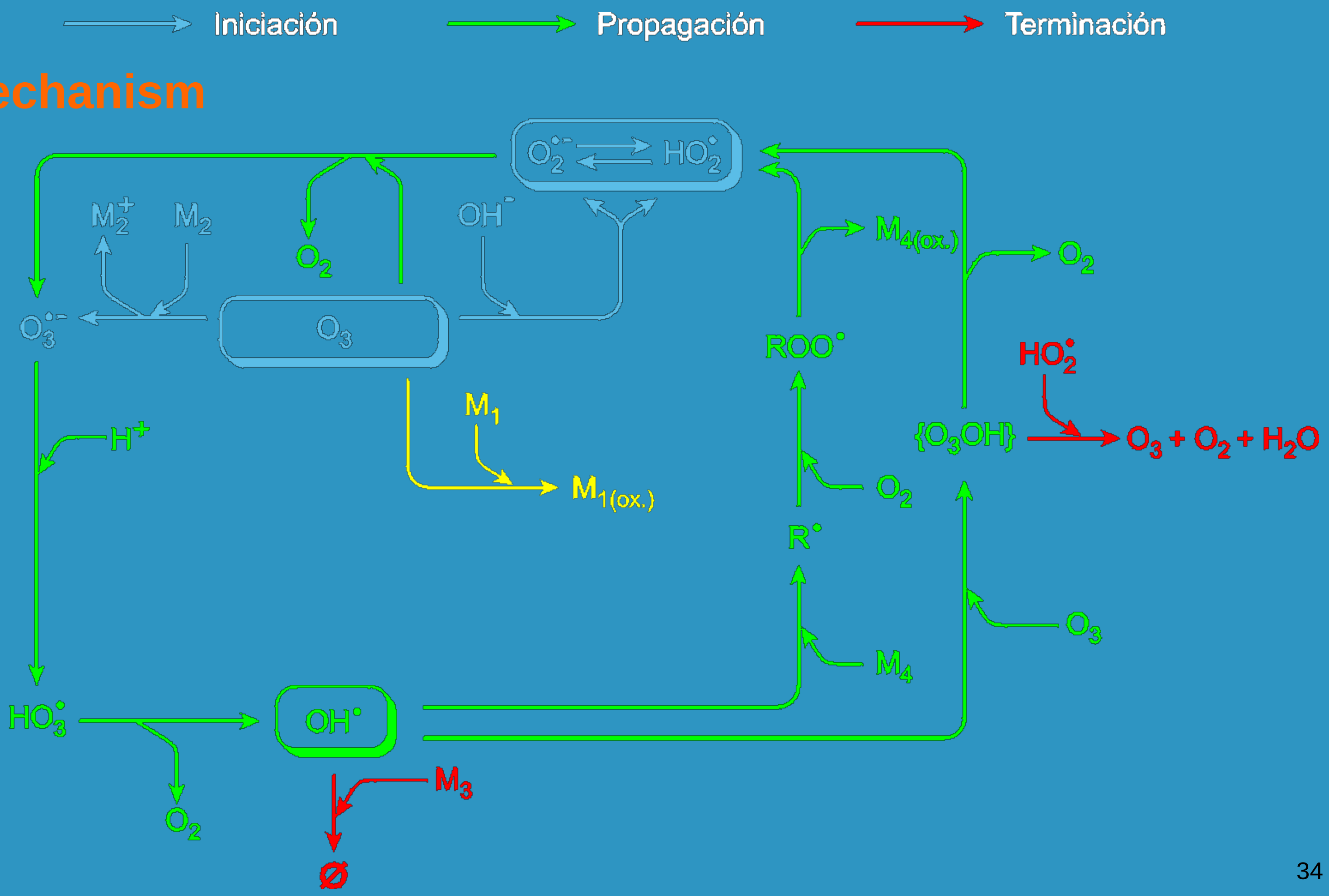
Poor solubility in water

Unfortunately, to generate ozone is required:

- **High energetic demand**
- **Significant reagent consume**

Larson and Weber, 1994 Bauer and Fallmann, 1997

Dark mechanism

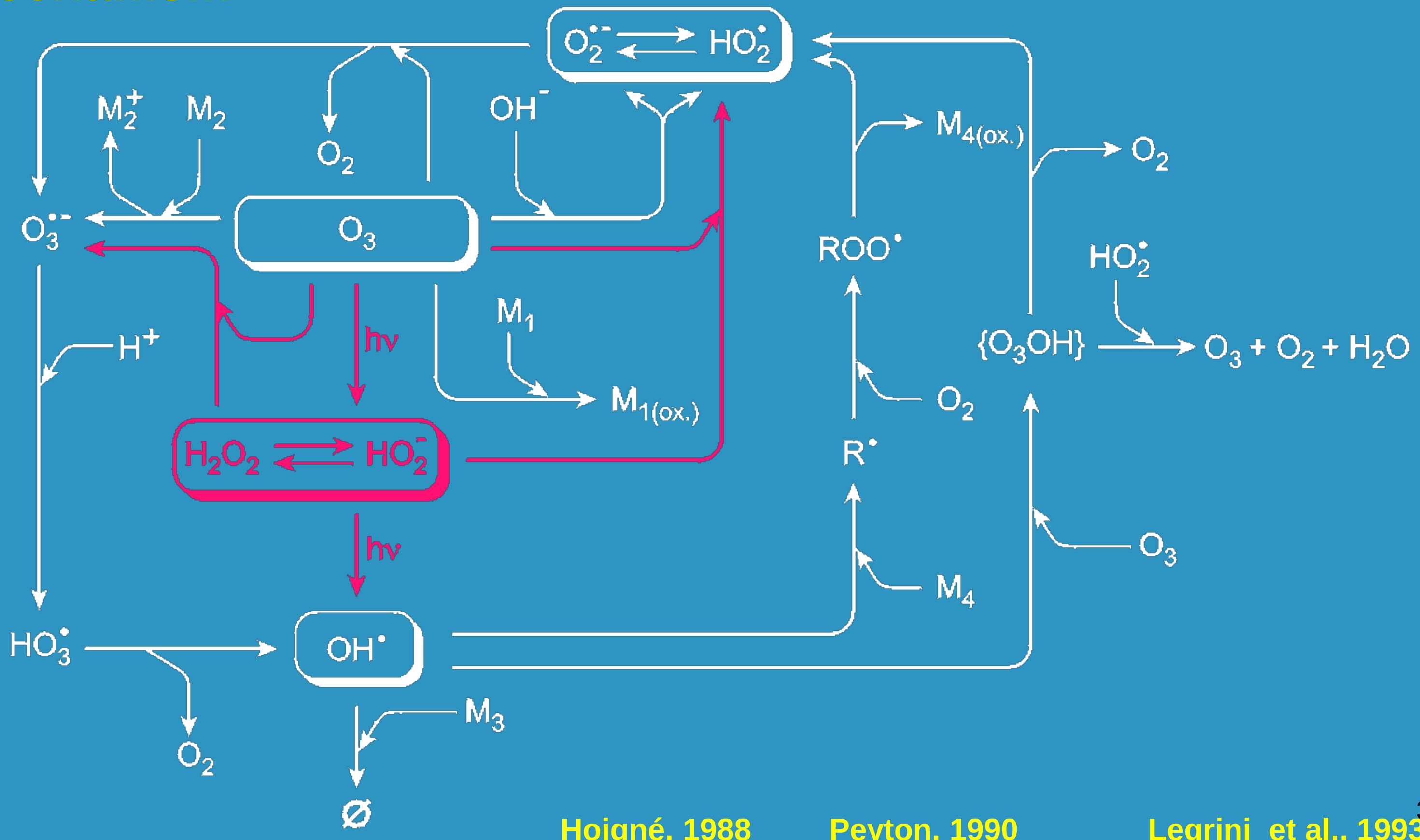


Hoigné, 1985 Staehelin and Hoigné, 1985 Hoigné, 1988

→ O_3 Mecanismo en oscuridad

→ Mecanismo bajo radiación

Light mechanism



Hoigné, 1988 **Peyton, 1990** **Legrini et al., 1993**

Ozone, O_3

Recent Studies

- **partial / total substitution of O_3 by the use of VUV radiation**
- **Improvements in reactor design**

Larson and Weber, 1994 Bauer and Fallmann, 1997

FENTON AND FENTON-LIKE REACTIONS

Fenton Reagents

Hydrogen peroxide

- ✓ relative cheap and easy to handle oxidant (environmentally benign)
- ✓ infinite solubility in water

Iron

- ✓ abundant in the earth + non toxic, (iron(II), iron(III))

Applications

Large variety of organic compounds has been oxidized by this process:

Acids, alcohols, aldehydes, ketones, ethers, amines, aromatics, dyes,…

Fenton, 1894   Barb et al., 1949,1951   Haber and Weiss, 1934   Pignatello,1992   Pignatello,2006

FENTON AND FENTON-LIKE REACTIONS

Accepted mechanism

Fenton ($Fe^{+2} + H_2O_2$)

$Fe(II) + H_2O_2 \rightarrow Fe(III) + HO^- + HO^\bullet$ *k = 40 - 80 $M^{-1}s^{-1}$* **(very fast)**

Fenton-like reaction - Fe^{+2} regeneration

$Fe(III) + H_2O_2 \rightleftarrows [Fe(III)\text{-}OOH]^{+2} + H^+$

$[Fe(III)\text{-}OOH]^{+2} \rightarrow Fe(II) + HO_2^\bullet + H^+$ *k = 0.01 – 0.02 $M^{-1}s^{-1}$* **(very slow)**

Much lower rate ⇨ Fe(III) accumulates in reaction medium

$^\bullet$**OH** + organic contaminants → → → oxidation products

Fenton, 1894 Barb et al., 1949,1951 Haber and Weiss, 1934 Pignatello,1992

FENTON REACTIONS - **Limitations**

- pH = 2.8 – 4
- Only partial mineralization when

Formation of ferrioxalate and other stable Fe^{3+} complexes (prevent recycling of Fe^{3+} to Fe^{2+})

To improve the overall degradation process

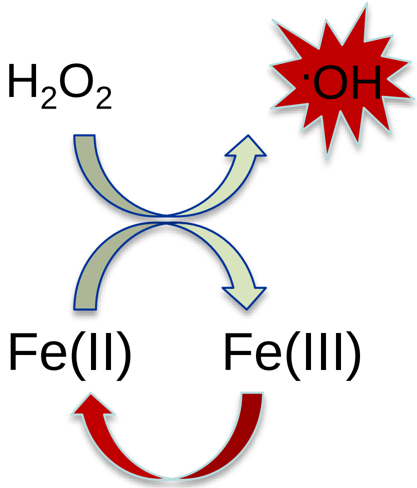
- Relatively high concentrations of Fe(II) ⇨ stoichiometric amounts
  - Generation of high amount of iron sludge due to separation before discharge
  - Limits for iron discharge in effluents in Europe: 10 mg L^{-1} (0.18 mmol L^{-1})
- Concentrations of H_2O_2 ⇨ above stoichiometric amounts

Too high concentrations must be avoided: $\cdot OH + H_2O_2 \rightarrow H_2O + HO_2\cdot$

Einsenhauer, 1964 *Pignatello,1992* *Pignatello,2006*

Reduction of Fe(III) ⇨ limiting step of the process

Iron cycle

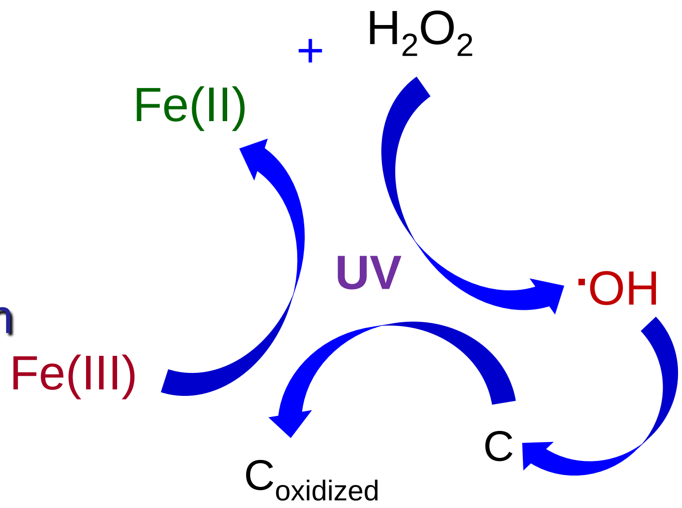


H_2O_2

$\cdot OH$

Fe(II) Fe(III)

Other reactions under irradiation



+ H_2O_2

Fe(II)

UV

$\cdot OH$

Fe(III)

C

$C_{oxidized}$

- **UV-Vis irradiation**
- **Iron reducing species**

C: contaminant

LIGHT SOURCE

Increases the oxidant production rate

- Reaction given by low-energy photons
- **Photo-Fenton** reactions (photon absorption close to 400 nm)

$$Fe^{+3} + H_2O + \lambda \rightarrow Fe^{+2} + HO^{\bullet} + H^{+}$$

- Fenton like reactions **(photon absorption up to 550 nm)**
  - ✓ Formation of high valence Fe-based oxidants
  - ✓ Direct attack on organic matter

Limitations ⇨
- **pH restrictions as in dark Fenton**
- **need of transparent solution**

Pignatello,1992 Sun and Pignatello, 1993 Pignatello et al., 1999 Bossmann, et al. 1998

COMPETITIVE REACTIONS

Fenton reagent excess decreases the oxidation rate

- Experimental conditions should be established to avoid the competitive reactions for HO• radical:

$$\mathrm{HO\bullet} + \mathrm{Fe}^{+2} \rightarrow \mathrm{Fe}^{+3} + \mathrm{HO}^{-}$$

$$\mathrm{HO\bullet} + \mathrm{H_2O_2} \rightarrow \mathrm{HO^{\bullet}_2} + \mathrm{H_2O}$$

$$\mathrm{HO\bullet} + \mathrm{HO\bullet} \rightarrow \mathrm{H_2O_2}$$

Pignatello et al., 2006

FENTON AND PHOTO-FENTON REACTIONS

Recent Studies

- Replacement of Fe(II) or Fe(III) salts by
  - Immobilize Fe (Heterogeneous Fenton Process)
  - Non dependable pH Fe
- Catalyst or process design to enable Fe(III) recycling
- Development of
  - large scale solar applications
  - combinations of solar and artificial light reactors

Fenton, 1894 Barb et al., 1949,1951 Haber and Weiss, 1934 Pignatello,1992 Pignatello,2006

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WHAT IS REQUIRED TO INDUSTRIALLY APPLY AOPs?

DECREASE:

» **Energy demand**

» **Reagent demand**

» **pre or post treatment needs**

To minimize cost treatment

Balcioglu and Arslan, 1998 Andreozzi et al., 1999 Chen and Ray, 1999

STRATEGIES TO REDUCE ENERGY DEMAND

- **Use of Solar radiation**
- **Develop catalyst to modify the radiation necessary to activate them**
- **Effective reactors' design to use all the available radiation**
  - Modeling / Simulation
  - Appropriate materials selection

STRATEGIES TO REDUCE REAGENT DEMAND

- **Select appropriate reagent ratios**
    - Contaminant:Reagent ratio, Reagents ratios
- **Dosage of reagents***
- **Work in the better reaction conditions**
- **On-line monitoring***

STRATEGIES TO AVOID PRE- / POST- TREATMENTS

» Wastewater segregation/ management

- **to use natural conditions**
- **avoid specific pretreatments**
- **Reduce treatment cost**
- **Select the better treatment for every wastewater**

STRATEGIES TO AVOID PRE- / POST- TREATMENTS

» **Modified catalyst**

- **Fenton - pH necessary to better usage**
- **Photocatalysis - light radiation in visible**

» **Immobilize catalyst helps to**

- **avoid post- elimination**
- **Reutilization - Reduce catalyst demand**
- **Apply treatment in natural ecosystems (sea, lake, river,…)**

Miller et al., 1999 Chu et al., 1994 Xu et al., 1991 Aguado et al., 1993

STRATEGIES TO REDUCE REAGENT DEMAND

- » Select appropriate reagent ratios
  - » Contaminant : ratio, Reagents : ratios
- » **Dosage of reagents* Exemple: Photo-Fenton**
- » Work in the better reaction conditions
- » On-line monitoring*

DOSAGE PROTOCOLS FOR HYDROGEN PEROXIDE

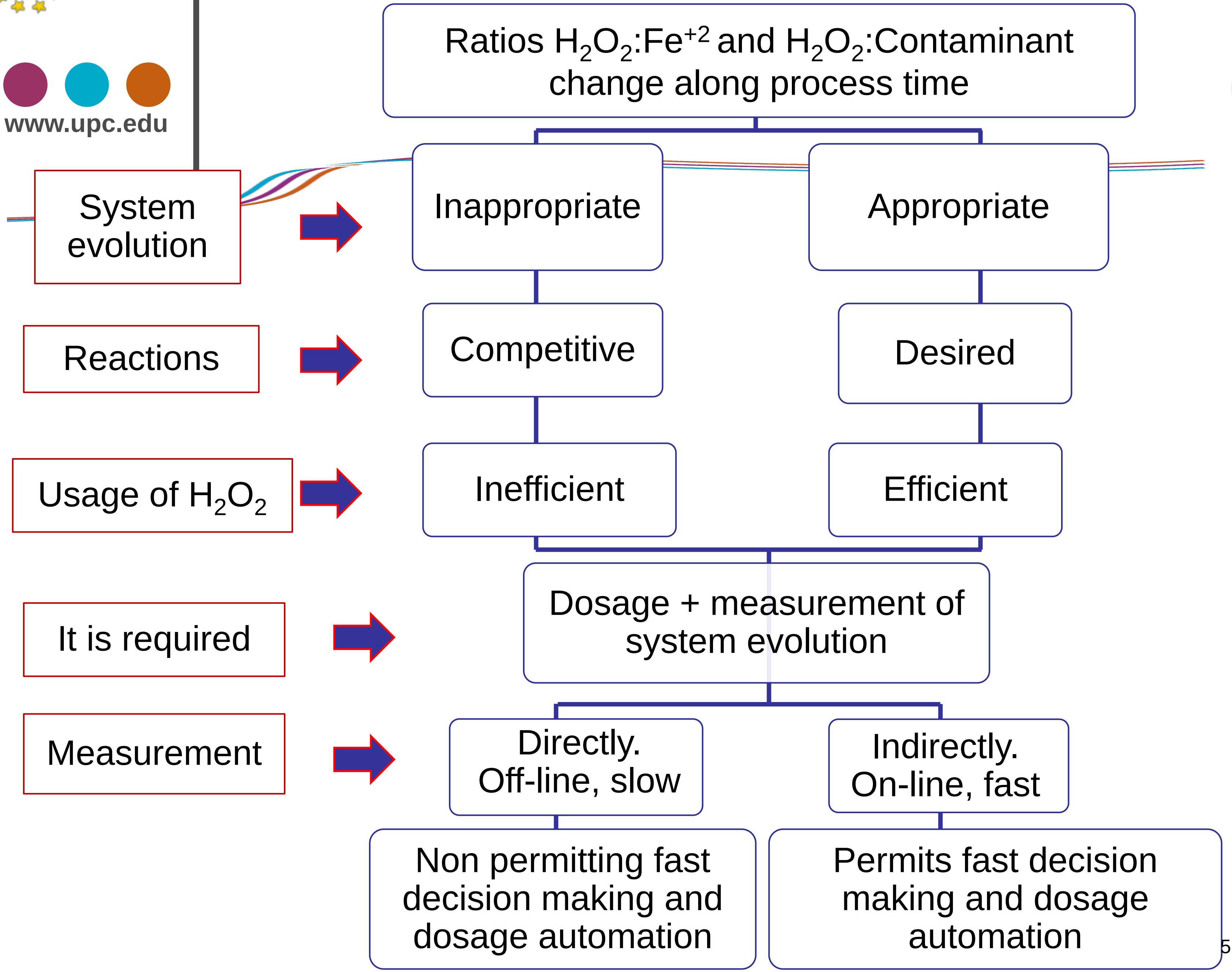
State of the Art

- Dosage has been recently described as a relevant factor
- Batches – addition of load portions along the reaction time
- Continuous dosage
- Continuous automatic dosage

➡ **A new systematic dosage protocol for a two factor analysis:**

- Fixed total load = Initial load + Continuous flow time-span

Nilsun, 1999 *Chu et al., 2007* *Zazo et al., 2009* *Prieto-Rodriguez et al., 2011*



Ratios H_2O_2:Fe^{+2} and H_2O_2:Contaminant change along process time

System evolution → Inappropriate | Appropriate

Reactions → Competitive | Desired

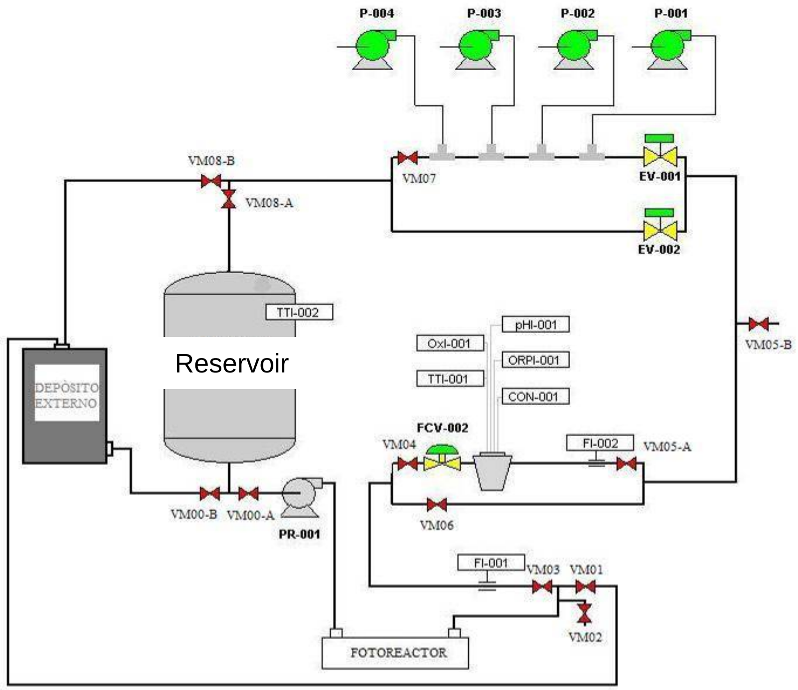
Usage of H_2O_2 → Inefficient | Efficient

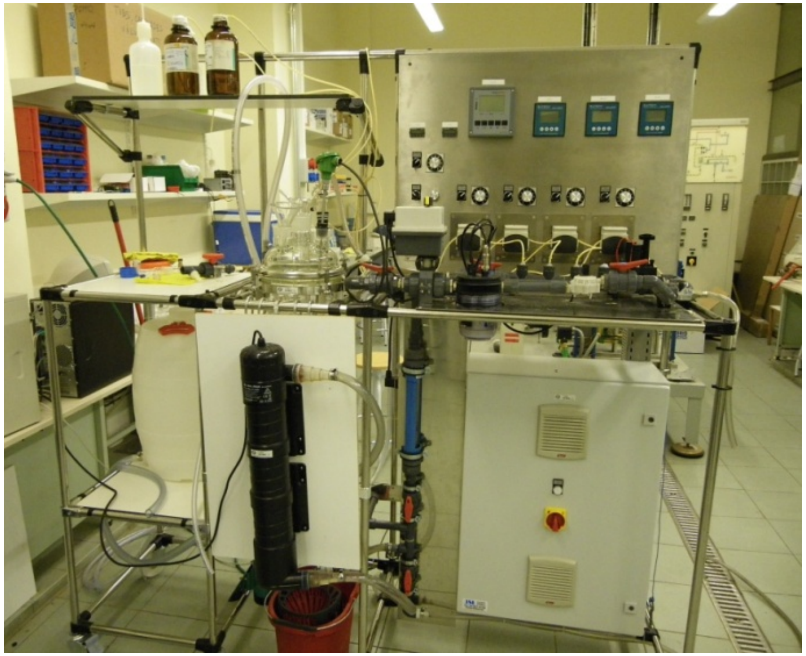
It is required → Dosage + measurement of system evolution

Measurement → Directly. Off-line, slow | Indirectly. On-line, fast

Non permitting fast decision making and dosage automation | Permits fast decision making and dosage automation

EXPERIMENTAL METHODS

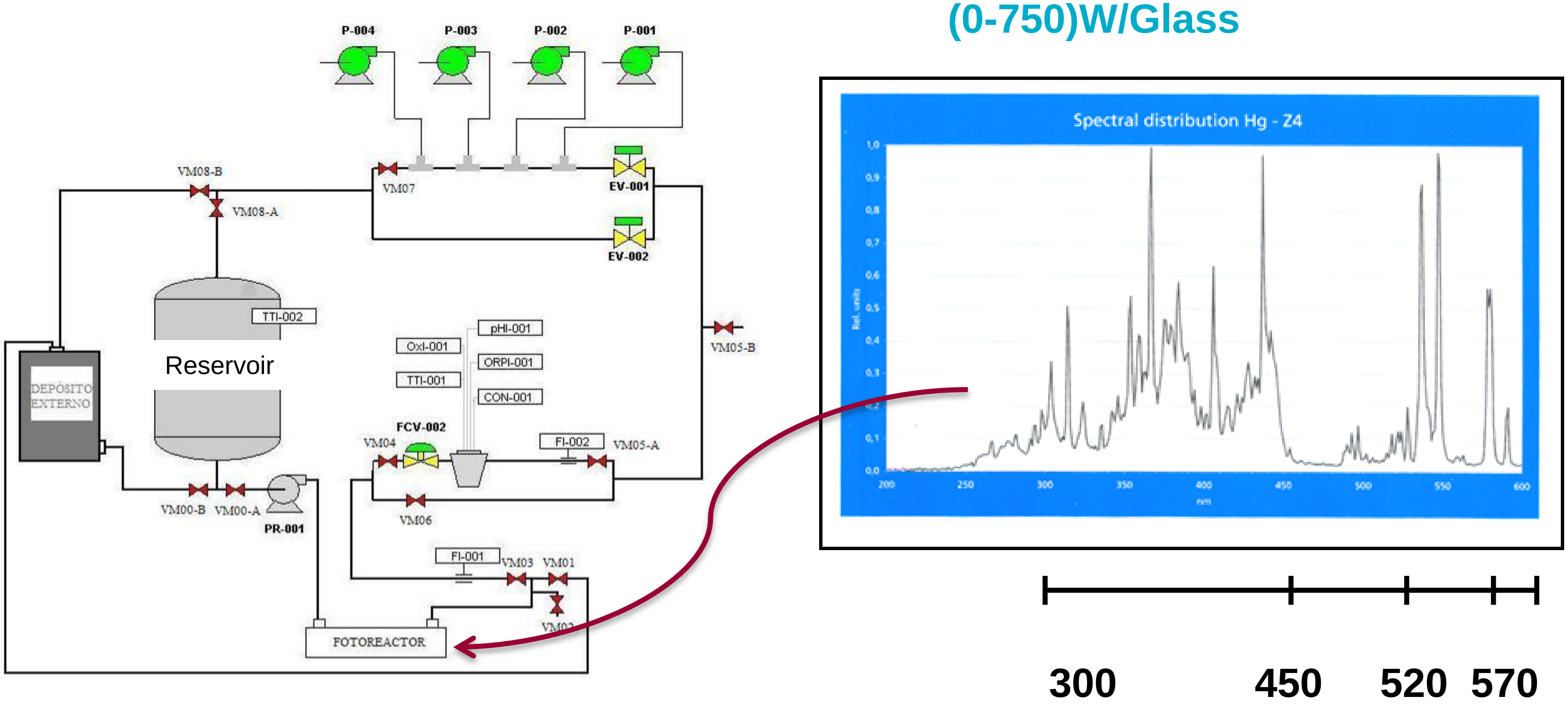




EXPERIMENTAL METHODS

Hg medium pressures

(0-750)W/Glass



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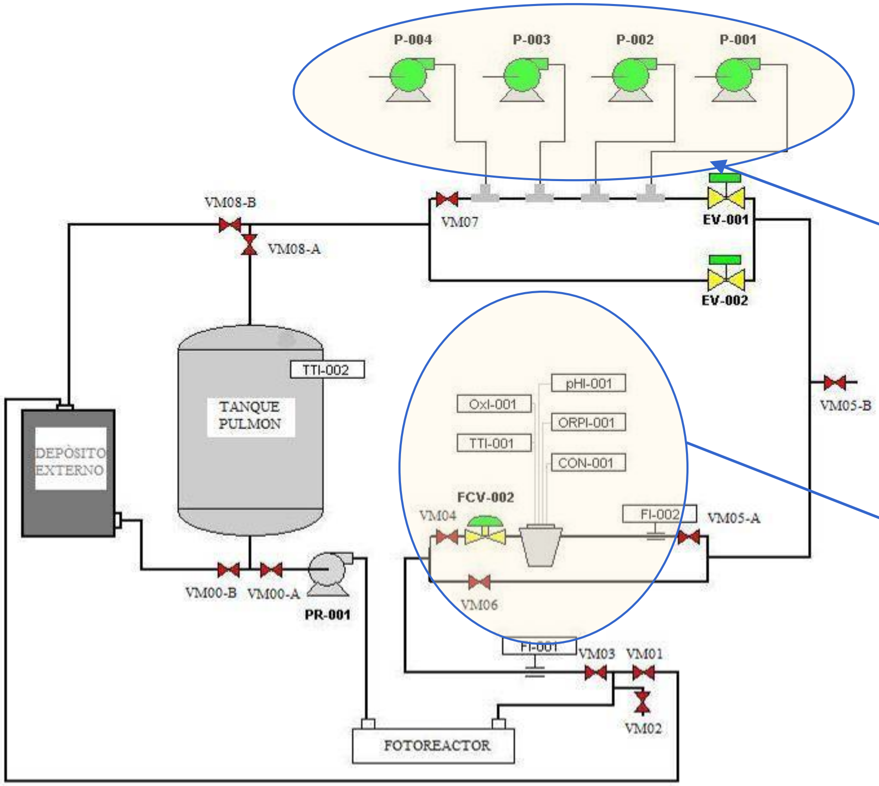
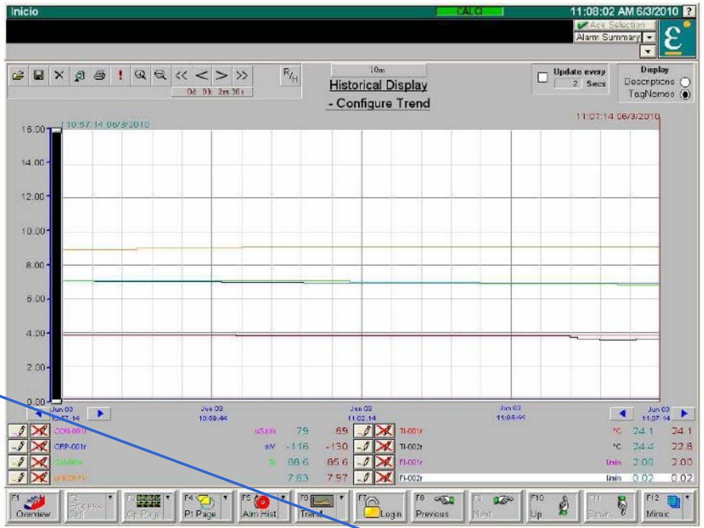
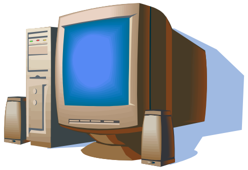






Data on-line:

pH

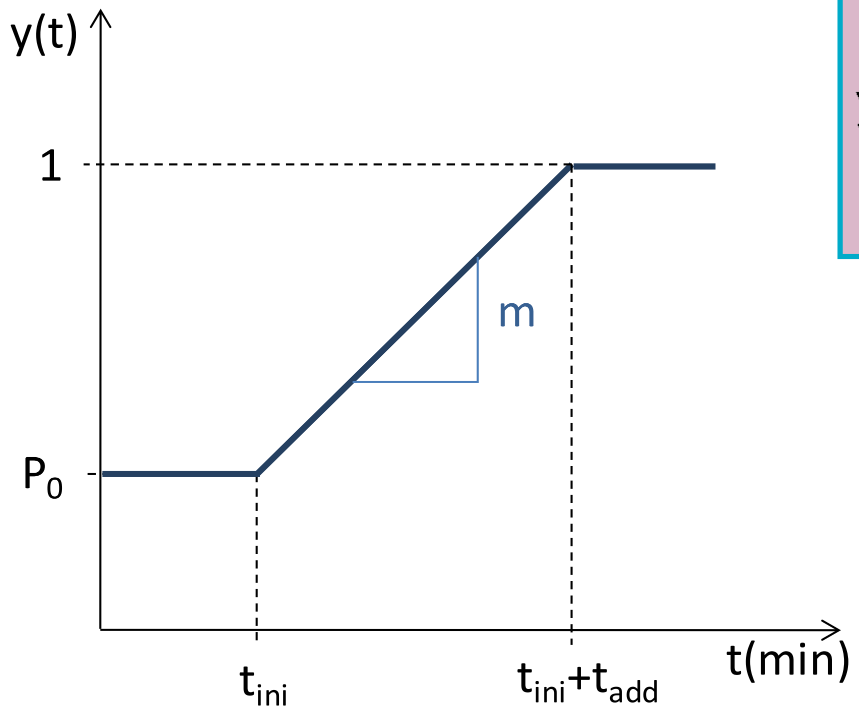
Temperature (ºC)

Conductivity (mS)

Dissolved Oxygen (%)

Oxidation reduction potential (mV)

PROPOSED DOSAGE PROTOCOL



$$y(t)=\begin{cases} 0 & \text{if } t<0 \\ P_0 & \text{if } 0\le t<t_{ini} \\ P_0+m\cdot(t-t_{ini}) & \text{if } t_0\le t\le t_{ini}+t_{add} \\ 1 & \text{if } t>t_{ini}+t_{add} \end{cases}$$

Variables	**min**	**max**	**centre**
t_{ini} (min)	0	30	15
P_0 (%)	10	30	20

Parameters	**Fe(II) (mg·L^{-1})**	**H_2O_2 (mg·L^{-1})**	**TC (mg·L^{-1})**	**t_{add} (min)**
	5	65	40	30

FIXED

RESULTS DOE (2^2)

Variables	min	max	centre
t_{ini} (min)	0	30	15
P_0 (%)	10	30	20

	t_{ini}	P_0	t_{ini}	P_0	ξ^{max}	St.Dev
R	-1	8	0	100%	0,7743	0,0290
A	-1	-1	0	10%	0,9113	0,1254
B	1	-1	30	10%	0,8529	0,2081
C	-1	1	0	30%	0,9410	0,0392
D	1	1	30	30%	0,9033	0,1368
E	0	0	15	20%	1,0000	0,0000
F	0	0	15	20%	0,9355	0,0912
G	0	0	15	20%	1,0000	0,0000
H	-1	0	0	20%	0,8474	0,1206
I	1.414	0	36.21	20%	0,7995	0,0421
J	0	-1.414	15	5.86%	0,9108	0,1123
K	0	1.414	15	34.14%	0,9457	0,2151

“R“ : Reference experiment

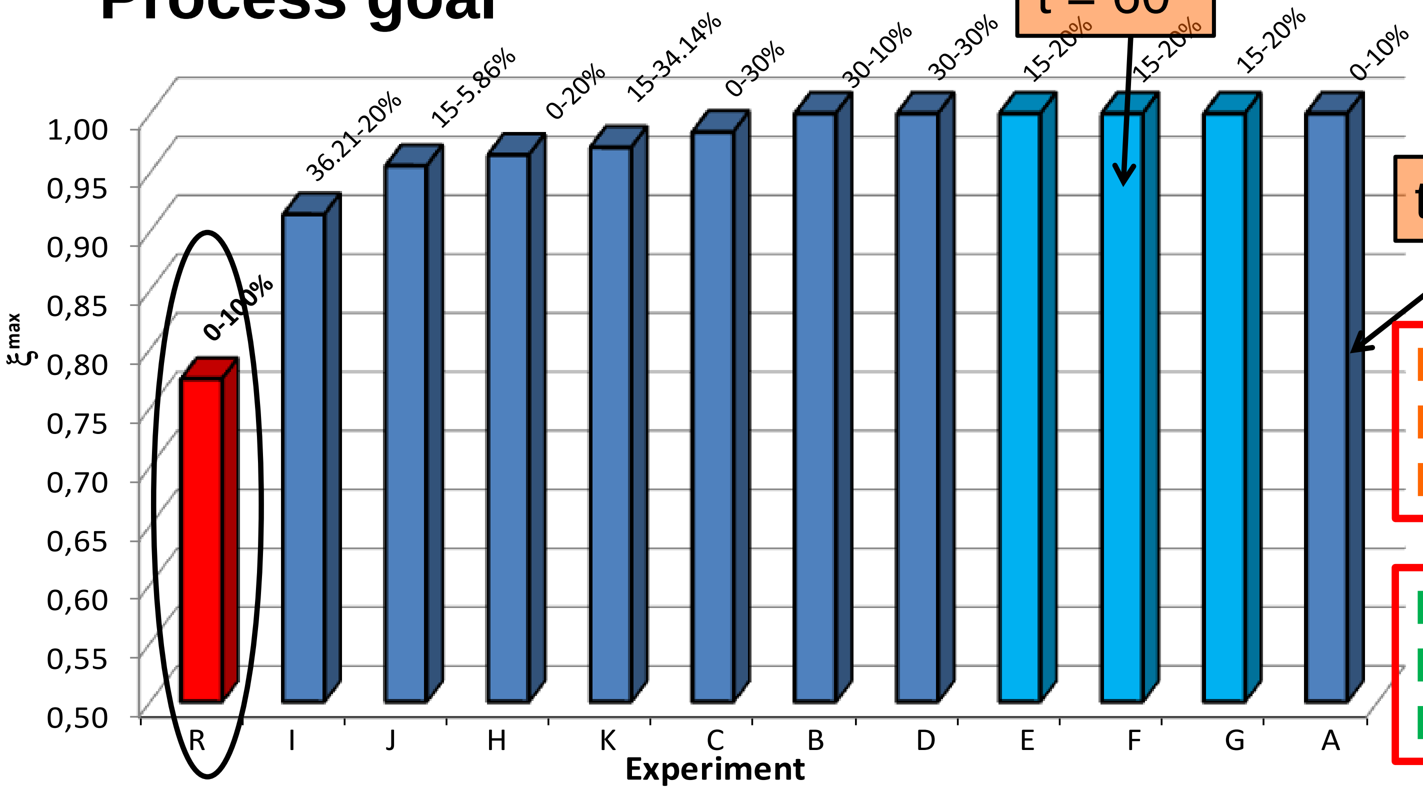
(no dosage protocol)

$$\xi^{màx} = \left(1 - \frac{[TOC]_{\infty}}{[TOC]_0}\right)$$

MAXIMUM CONVERSION ACHIEVED

Process goal

$$\xi^{màx} = \left(1 - \frac{[TOC]_{\infty}}{[TOC]_{0}}\right)$$



t = 60’

t = 90’

REAGENT DEMAND DECREASE

ENERGY DEMAND DECREASE

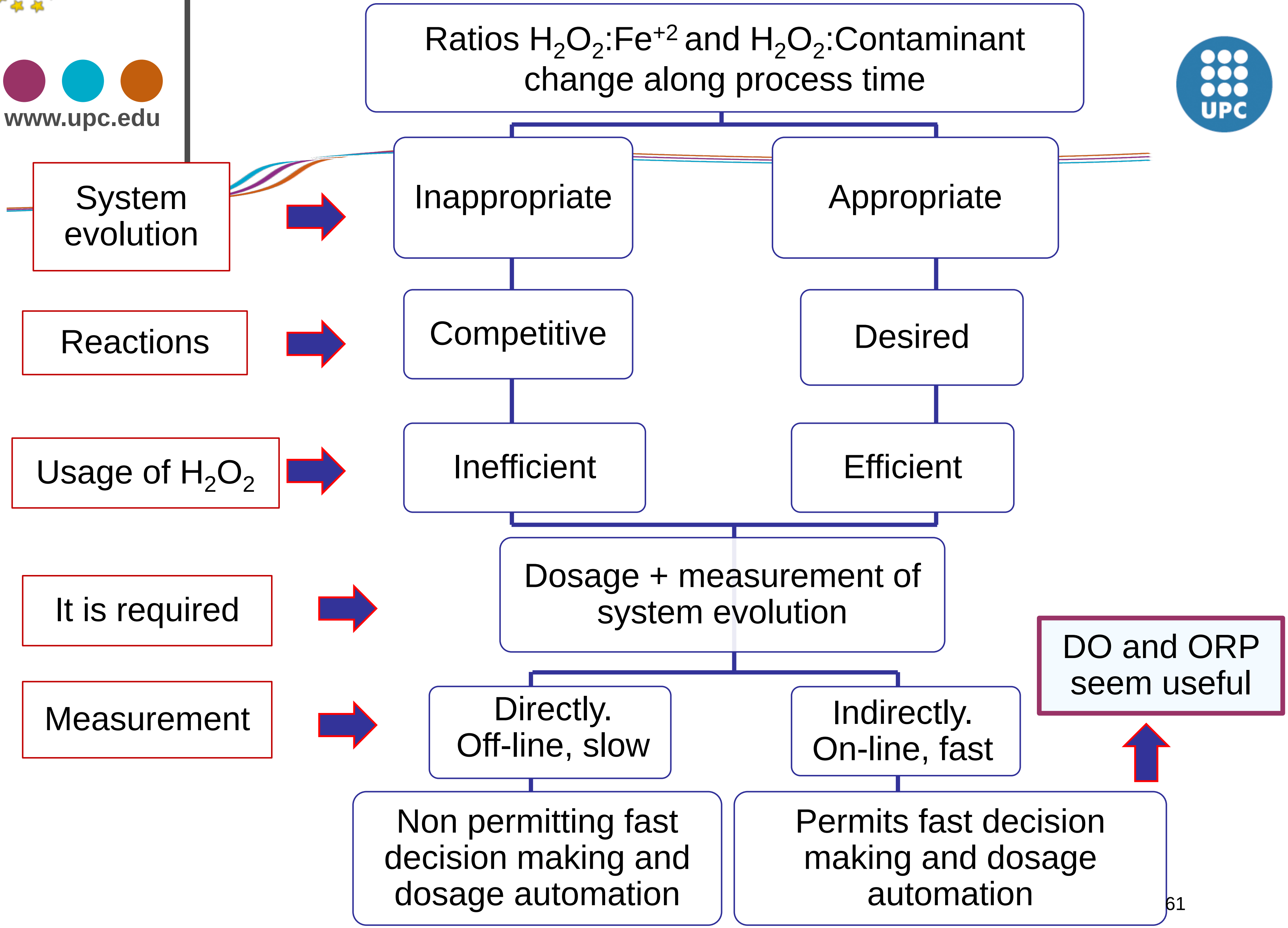
STRATEGIES TO REDUCE REAGENT DEMAND

- Select appropriate reagent ratios
  - Contaminant : ratio, Reagents : ratios
- Dosage of reagents*
- Work in the better reaction conditions
- **On-line monitoring* Exemple: Photo-Fenton**

On-line Monitoring & Dosage

- H_2O_2 is usually measured by off-line methods.
- On-line H_2O_2 monitoring appears to be required for optimal dosage.
- Scarce investigation on the relationship between H_2O_2 evolution during the photo-Fenton process and on-line operational parameters.
- Additionally:
  - ORP, has been one of the first on-line parameters suggested.
  - Recently DO has been related with the H_2O_2 evolution during the photo-Fenton process.

Martinez et al., 2001   Utset et al., 2000   Monteagudo et al, 2009   Santos-Juanes et al., 2011   Prieto-Rodríguez et al, 2011



Ratios H_2O_2:Fe^{+2} and H_2O_2:Contaminant change along process time

System evolution → Inappropriate | Appropriate

Reactions → Competitive | Desired

Usage of H_2O_2 → Inefficient | Efficient

It is required → Dosage + measurement of system evolution

Measurement → Directly. Off-line, slow | Indirectly. On-line, fast

Non permitting fast decision making and dosage automation

Permits fast decision making and dosage automation

DO and ORP seem useful

Oxidation Reduction Potential (E, mV)

Measure the affinity of a substance for electrons, referred to hydrogen (E=0).

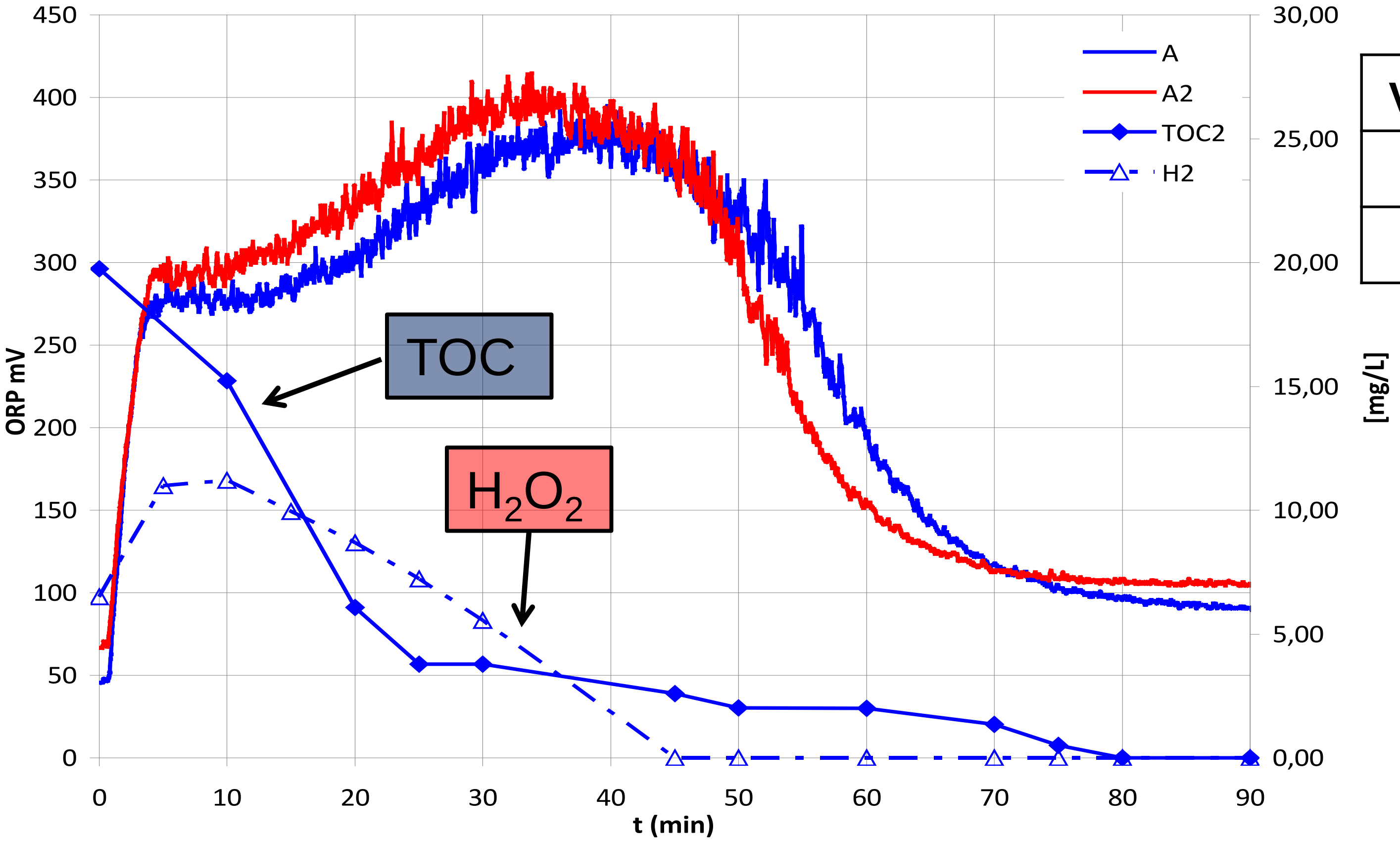
Any substance — atom, ion, or molecule — that

- is more capable of oxidizing than hydrogen is assigned a positive (+) redox potential;
- those less capable than hydrogen has negative (−) redox potential.

When electrons flow "downhill" in a redox reaction, they release free energy. We indicate this with the symbol ΔG (delta G) preceded by a minus sign.

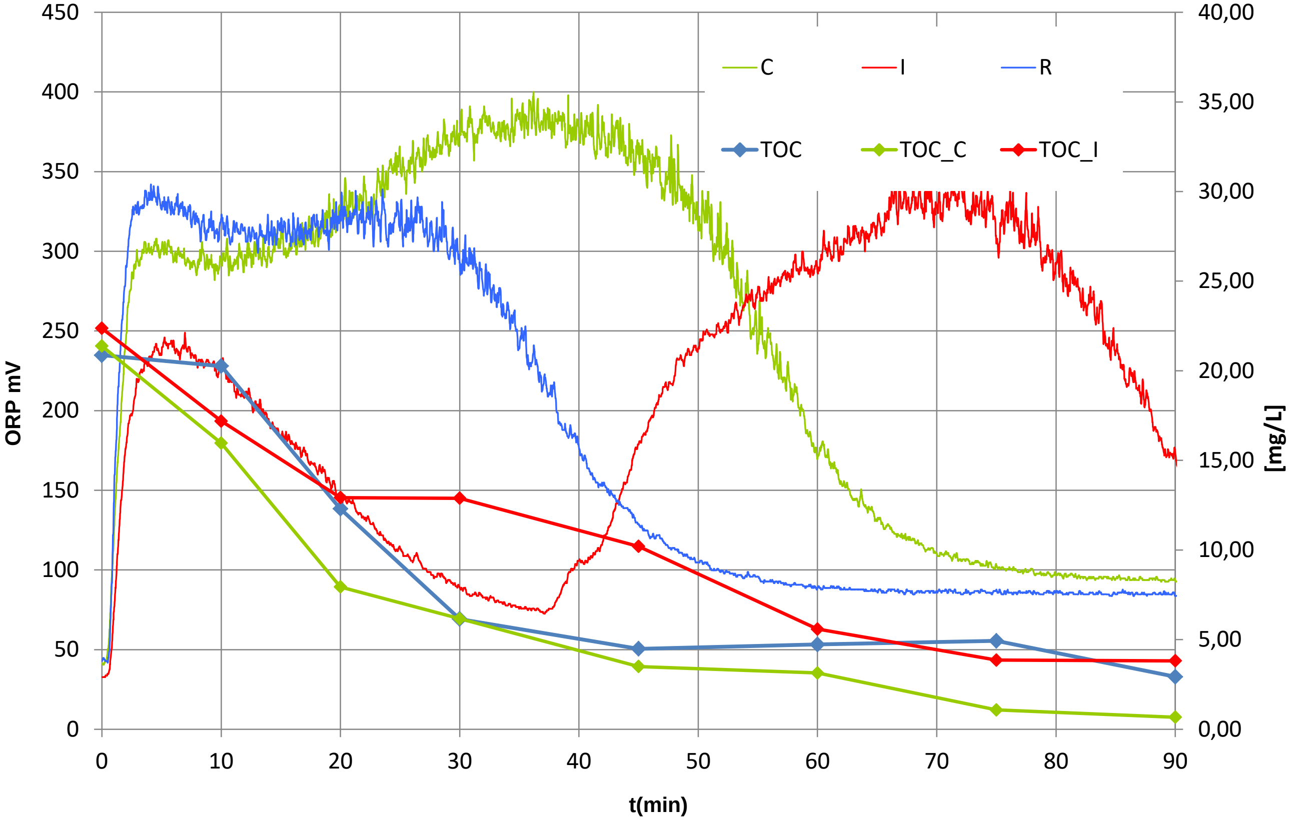
It requires an input of free energy to force electrons to move "uphill" in a redox reaction. We show this with ΔG preceded by a plus sign.

ON-LINE MONITORING & DOSAGE - ORP



Variables	Assay A
t_{ini} (min)	0
P_0 (%)	10

ON-LINE MONITORING & DOSAGE - ORP



Var.	C	I	R
t_{ini} (min)	0	36.2	0
P_0 (%)	30	20	100

O_2 dissolve, DO (mg·L^{-1}, %)

Sensitive electrode determination

Cathode	**Anode**
$\frac{1}{2} O_2 + H_2O + 2\ e^- \rightarrow 2\ OH^-$	**$Pb + 2\ OH^- \rightarrow PbO + H_2O + 2\ e^-$**

Electrode must be calibrated each time it is used:

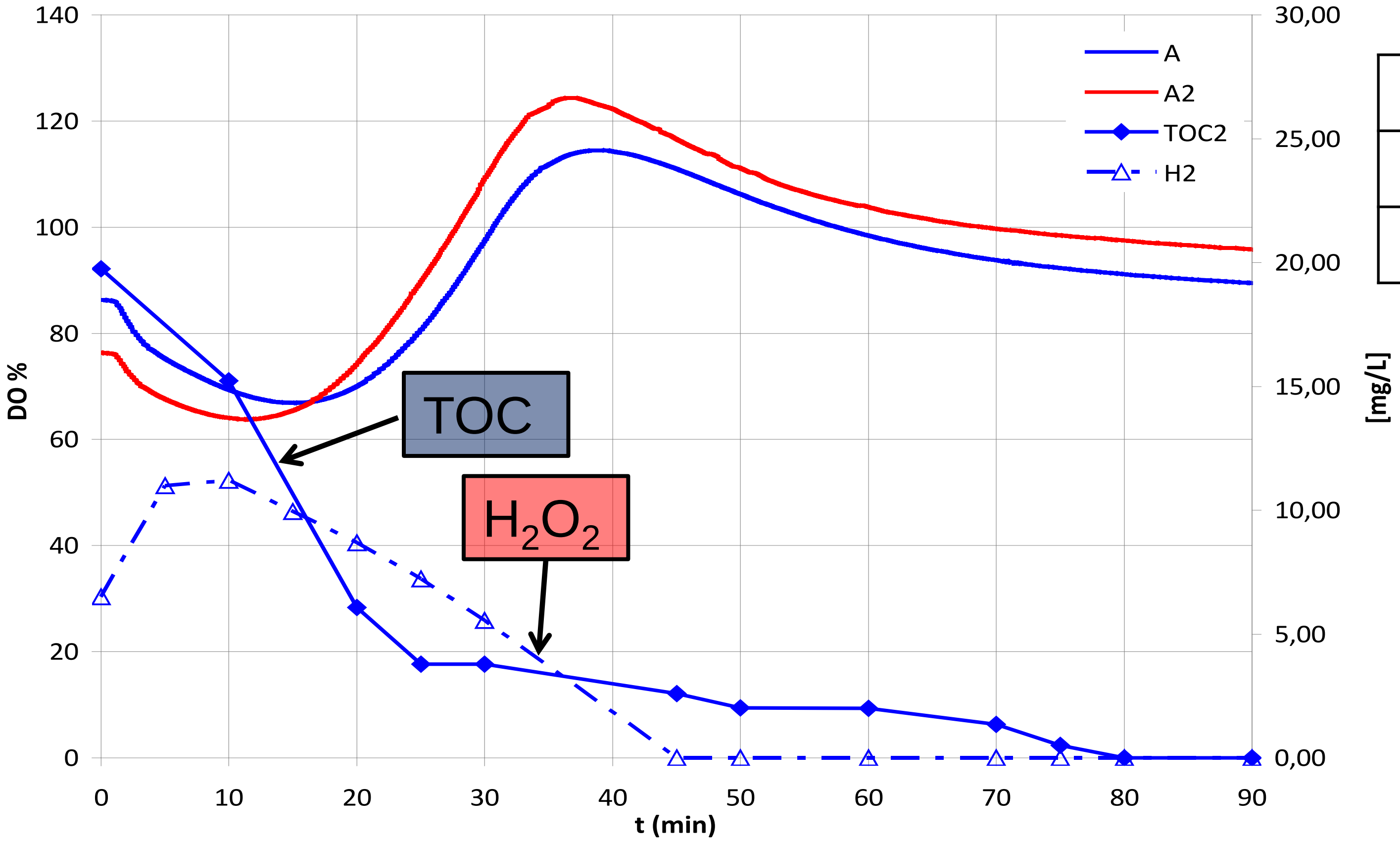
100% O_2 saturation, fully aerated water

0% O_2 (dissolved sodium sulfite is added into water)

The results can be expressed relative percentage to the amount of dissolved oxygen saturated water (at 25 ° C, 8.24 mg L^{-1}O_2).

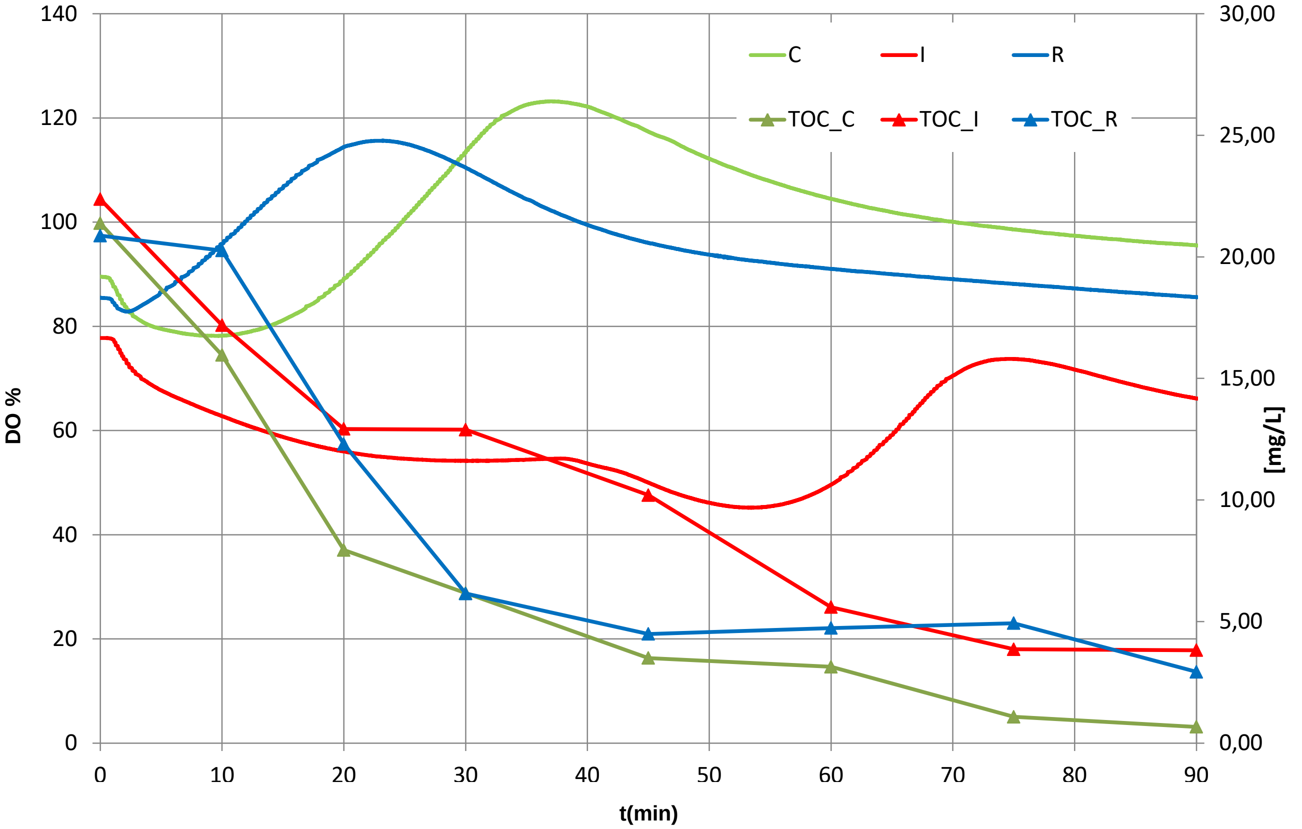
DO value depends on temperature, pressure and water salinity.

ON-LINE MONITORING & DOSAGE - DO



Variables	Assay A
t_{ini} (min)	0
P_0 (%)	10

ON-LINE MONITORING & DOSAGE - DO



Var.	C	I	R
t_{ini} (min)	0	36.2	0
P_0 (%)	30	20	100

On-line Monitoring & Dosage

- Investigation on the relationship between H_2O_2 evolution and on-line operational parameters, ORP and DO is required.
- Preliminary results suggest a dependence. Further work is required to model this dependence.

Martinez et al., 2001 Utset et al., 2000 Monteagudo et al, 2009 Santos-Juanes et al., 2011 Prieto-Rodríguez et al, 2011

OVERVIEW

- INTRODUCTION
  - ✓ Water
  - ✓ Conventional water treatments
  - ✓ Wastewater quality parameters
  - ✓ AOPs
- AOPs
  - ✓ Classification
  - ✓ Process description – Recent Studies
- WHAT IS REQUIRED TO AOPs IMPLEMENTATION?
- STRATEGIES TO IMPROVE AOPs
  - ✓ Dosage of reagents
  - ✓ On-line monitoring
- **CONCLUSIONS**

CONCLUSIONS

- ✓ Advanced Oxidation Processes (AOPs) are and interesting **alternative** or **complement** to conventional wastewater treatment.
- ✓ Select the adequate AOPs and its right operation condition leads to a more effective and inexpensive treatment.
- ✓ It should be clear the goal of the treatment .
- ✓ More research is required in order to improve the existing AOPs
- ✓ Interdisciplinary studies helps faster AOP improvement in order to be applied.
- ✓ pre- and post- AOPs treatment improve the efficient and reduce the cost of the overall process.

OBRIGADA PELA SUA ATENÇÃO

QUESTIONS