PLATAFORMA SOLAR DE ALMERÍA

PLATA

MINISTERIO DE EDUCACION Y CIENCIA

Ciemat Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas

PSA

LA … O THE TECHNOLOGICAL
DE … CATIONS.

1. Central Receiver Technology
2. Parabolic-Trough Technology
3. Direct steam generation
4. Parabolic dishes + Stirling system
5. Solar Furnace (materials testing)
6. SOLAR PHOTOCATALYSIS
7. Solar desalination
8. Solar hydrogen & fuel production
9. Edifice materials testing

1 8 5 7 6 2 4 9

Optimizing AOPs treatment strategy

Sixto Malato

(sixto.malato@psa.es)

Plataforma Solar de Almería , TABERNAS-Almería

SPAIN

Outlook

- Introduction
  - Photocatalysis
  - Photo-Fenton
- Applications
- AOPs evaluation
- AOPs optimisation

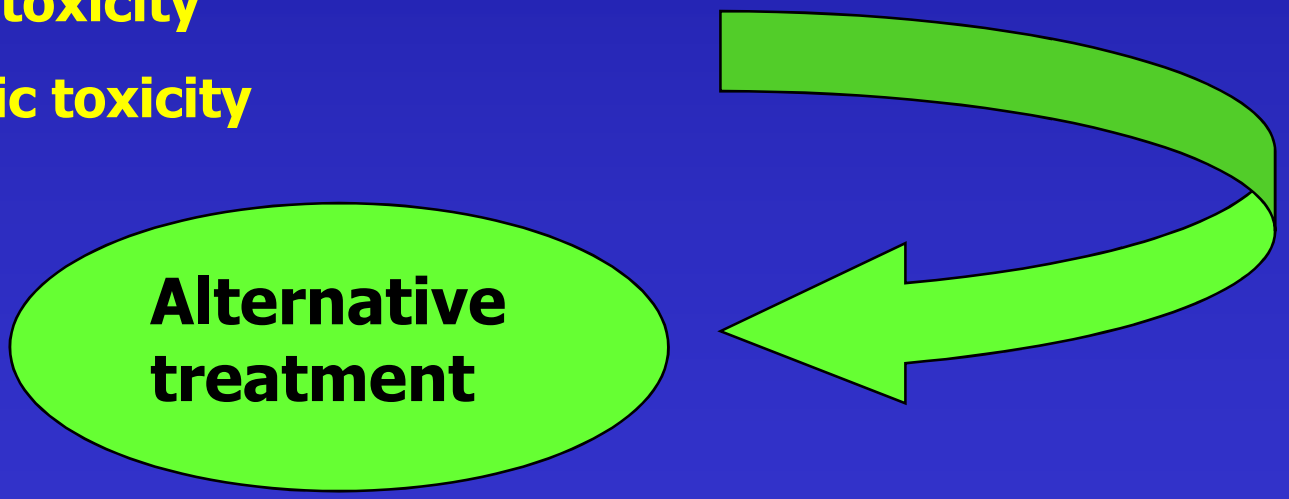
Introduction

Biodegradable substances:

- Biofilter treatment/ activated sludge treatment

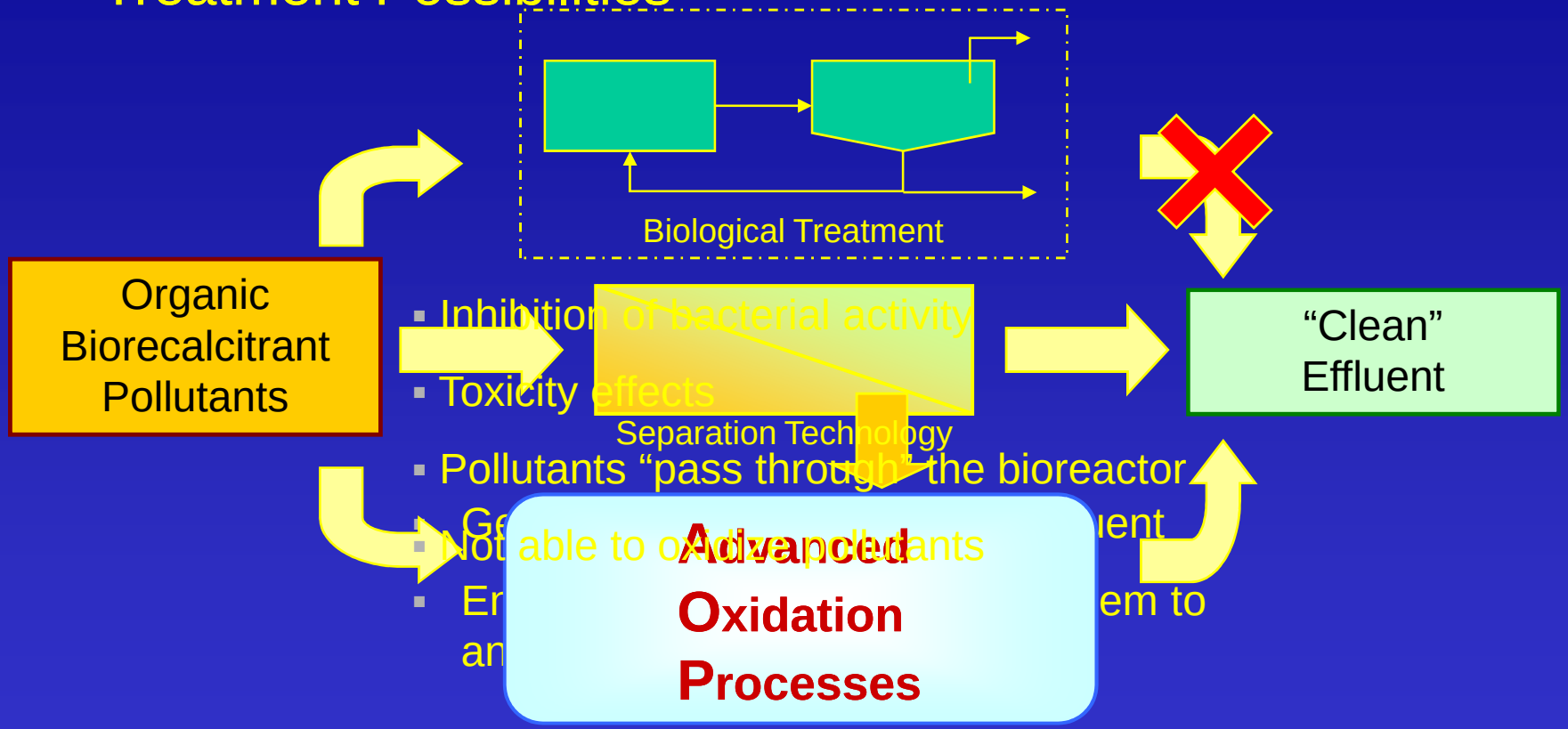
Non-biodegradable substances can show

- Non-toxic / inert behaviour
- Acute toxicity
- Chronic toxicity



Introduction

Treatment Possibilities



Feasible for accelerating the oxidation and destruction of a wide range of organic contaminants in polluted water

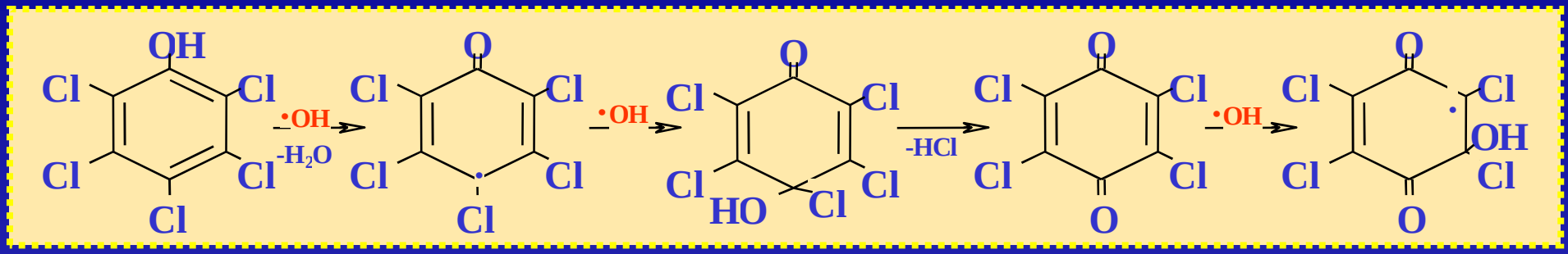
Introduction

Advanced Oxidation Processes are a source of hydroxyl radicals (•OH).

Especie	Oxidation Potential
Fluorine	*2.23*
Hydroxyl radical	*2.06*
Atomic Oxygen	*1.78*
Hydrogen Peroxide	*1.31*
Peroxyradical	*1.25*
Permanganate	*1.24*
Chlorine dioxide	*1.15*
Chlorine	*1.00*
Bromine	*0.80*
Iodine	*0.54*

"near ambient temperature and pressure water treatment processes which involve the generation of hydroxyl radicals in sufficient quantity to effective water purification"

Introduction



•OH

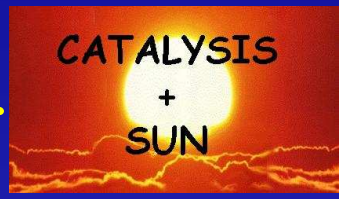
CO_2
Inorganic acids
Water

$$C_nH_mO_pCl_q + \left(\frac{(m-2p)}{4} + n\right)O_2 \rightarrow nCO_2 + \frac{m-q}{2}H_2O + qHCl$$

Introduction

- H_2O_2/Fe^{2+} (Fenton): $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^{\bullet}$
- H_2O_2/Fe^{2+} (Fe^{3+})/UV (photo-Fenton) $Fe^{3+} \xrightarrow{h\nu} Fe^{2+} + OH^{\bullet}$
- $TiO_2/h\nu/O_2$ (Photocatalysis) $TiO_2 \xrightarrow{h\nu} e^- + h^+$

$h^+ + H_2O \rightarrow {}^{\bullet}OH + H^+$



- O_3/ H_2O_2:

$H_2O_2 \xleftrightarrow{H^+} HO^- + O_3 \rightarrow O_2 + HO_2^-$ $\quad HO_2^- + O_3 \rightarrow HO_2^{\bullet} + O_3^{\bullet -}$

$HO_2^{\bullet} \Leftrightarrow H^+ + O_2^{\bullet -}$ $\quad O_2^{\bullet -} + O_3 \rightarrow O_2 + O_3^{\bullet -}$ $\quad O_3^{\bullet -} + H^+ \rightarrow HO_3^{\bullet}$

$HO_3^{\bullet} \rightarrow OH^{\bullet} + O_2$ $\quad HO^{\bullet} + O_3 \rightarrow HO_2^{\bullet} + O_2$

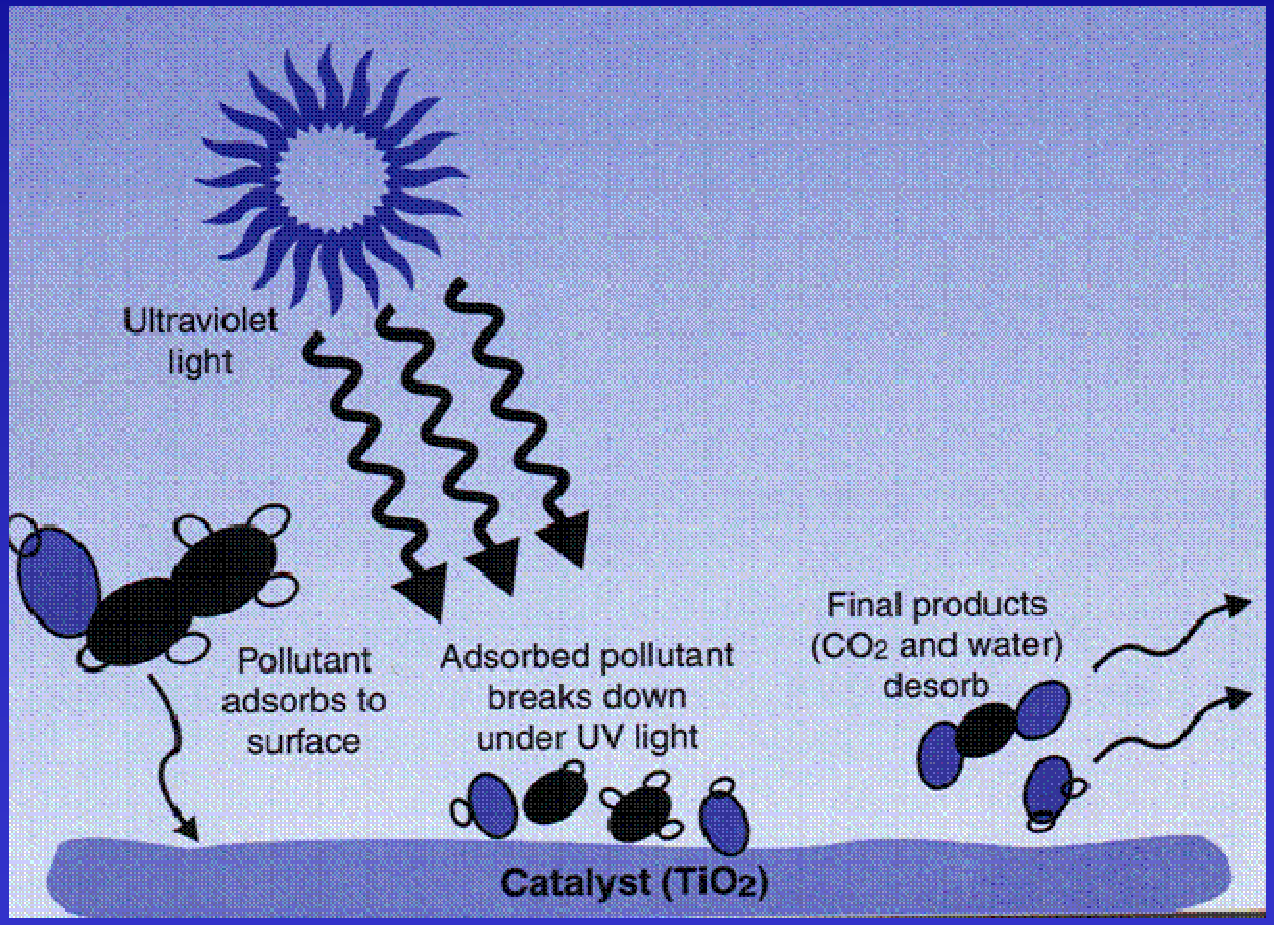
- O_3/ UV: $O_3 \xrightarrow{h\nu} O^1(D) + O_2$ $\quad O^1(D) + H_2O \longrightarrow H_2O_2$ $\quad H_2O_2 \xrightarrow{h\nu} 2OH^{\bullet}$
- H_2O_2/UV: $H_2O_2 \xrightarrow{h\nu} 2OH^{\bullet}$

Introduction

Photochemical AOPs

AOP	key reactions	wavelength
UV/ H_2O_2	$H_2O_2 + h\nu \rightarrow 2\ OH^{\bullet}$	$\lambda < 300$ nm
UV/ O_3	$O_3 + h\nu \rightarrow O_2 + O\ (^1D)$ $O\ (^1D) + H_2O \rightarrow 2\ OH^{\bullet}$	$\lambda < 310$ nm
UV/H_2O_2/ O_3	$O_3 + H_2O_2 + h\nu \rightarrow O_2 + OH^{\bullet} + OH_2^{\bullet}$	$\lambda < 310$ nm
UV/ TiO_2	$TiO_2 + h\nu \rightarrow TiO_2\ (e^- + h^+)$ $TiO_2(h^+) + OH^-_{ad} \rightarrow TiO_2 + OH_{ad}^{\bullet}$	$\lambda < 390$ nm
photo-Fenton	$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^{\bullet} + OH^-$ $Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + H^+ + OH^{\bullet}$	$\lambda < 580$ nm

Photocatalysis



- The process takes place at ambient temperature.
- Oxidation of the substances into CO_2 is complete.
- The oxygen necessary for the reaction is obtained from the atmosphere.
- The catalyst is cheap, innocuous and can be reused.
- The catalyst can be attached to different types of inert matrices.

Photo-Fenton

Photo-Fenton method

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH$$

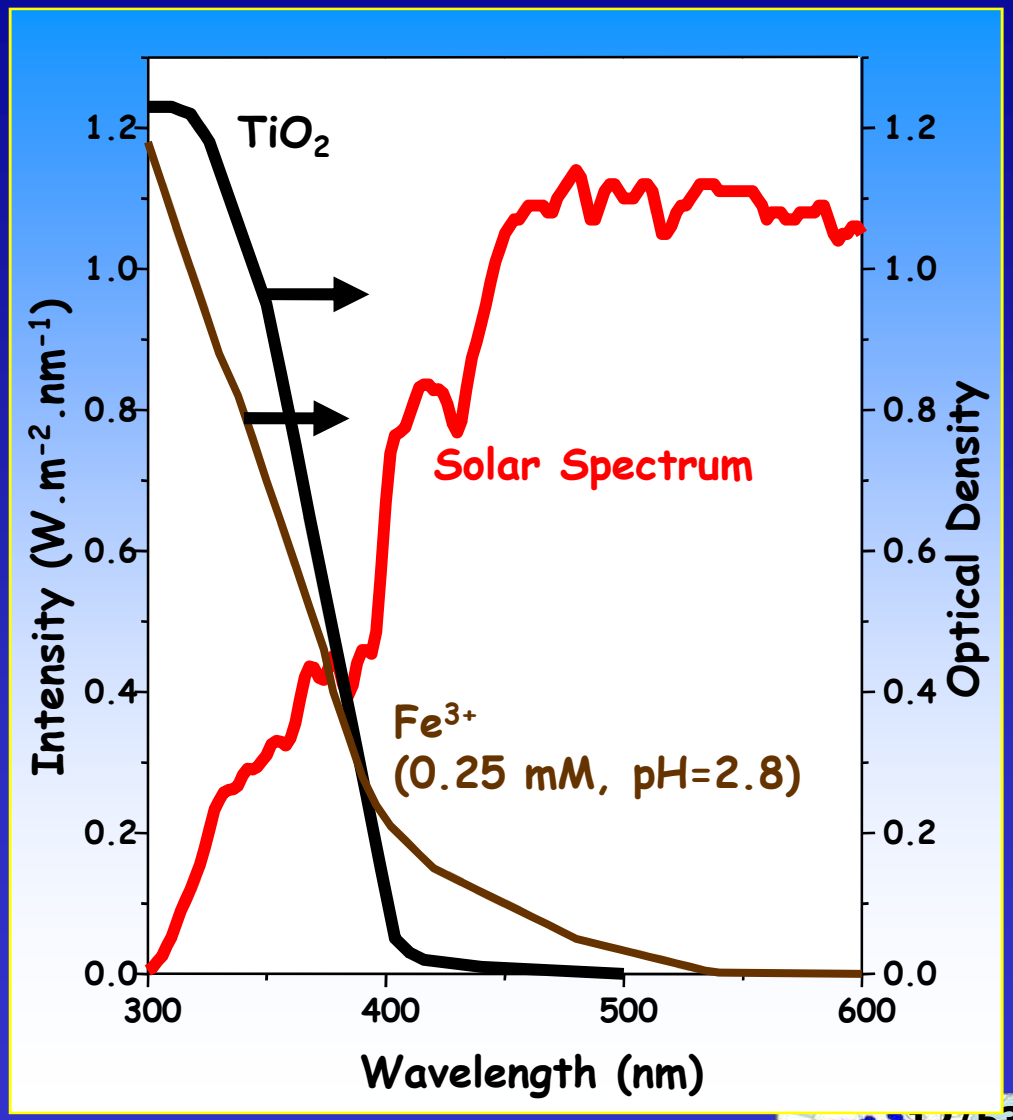
$$Fe^{3+} + H_2O \xrightarrow{h\nu} Fe^{2+} + H^+ + {}^{\bullet}OH$$

Advantages

- High reaction rates
- Cheap, non-toxic reagents (Fe, H_2O_2, acid, base)

Disadvantages

- pH adjustment necessary
- Iron removal necessary



Outlook

Introduction

Photocatalysis

Photo-Fenton

Applications

AOPs evaluation

AOPs optimisation

Applications

The SOLARDETOX Consortium (Brite-Euram III Program, Contract No. BRPR-CT97-0424) has installed during 1999 the **first European Solar Detoxification Plant.** Main plant characteristics are:

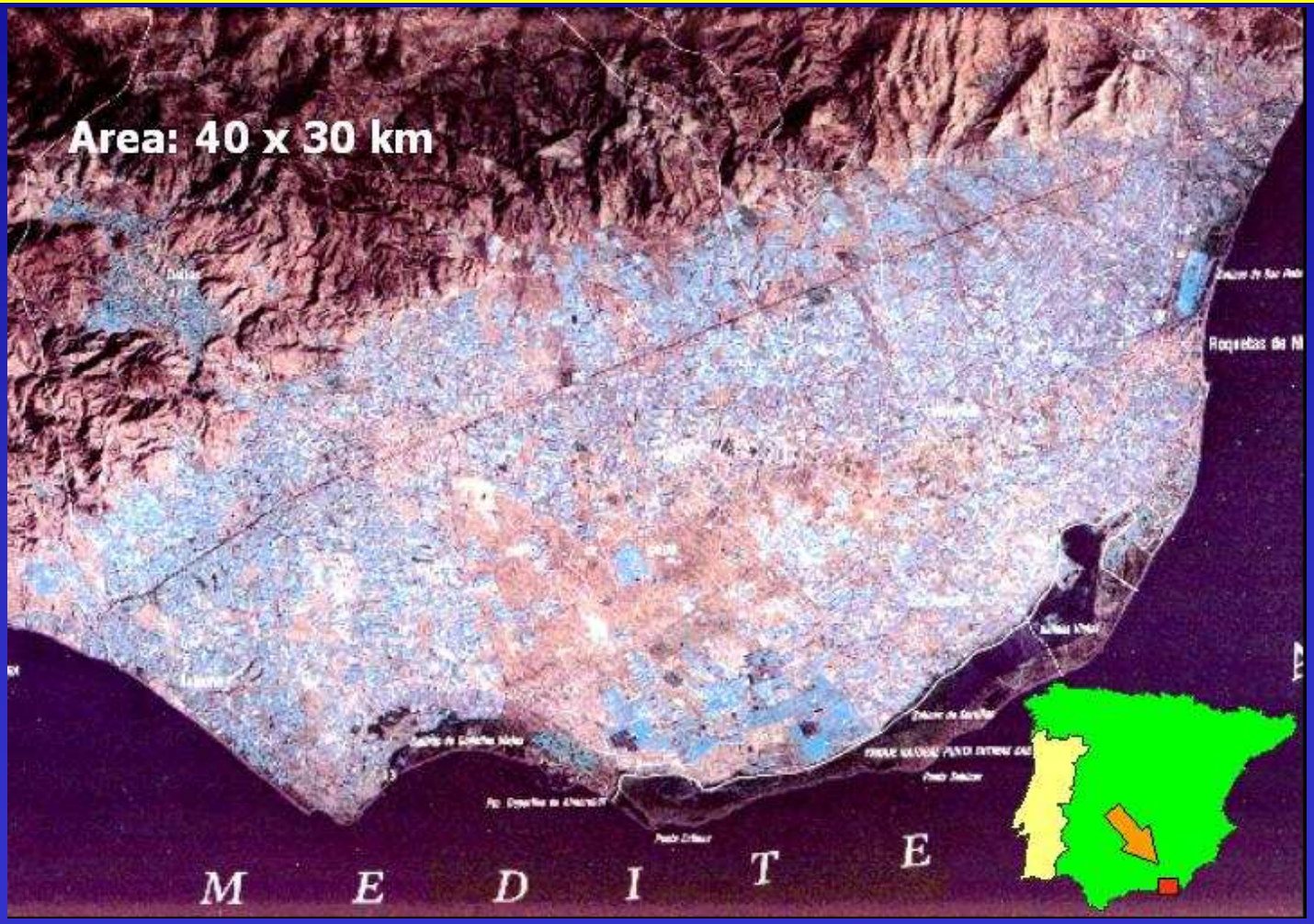
- CPC surface: 100 m^2
- Treatment volume: 800 L.
- Batch Operation
- Automatic operation
- cost of the plant: 100000 €

Applications

- Phenols, nitrophenols and halophenols.
- Pharmaceutical compounds (antibiotics, disinfectants...).
- Water disinfection.
- Gasoline additives (MTBE, ETBE,..).
- Chlorinated hydrocarbons (solvents, VOCs, etc).
- Residues from textile industry (dyes).
- Agrochemical wastes (pesticides).

Applications

The intensive agriculture activity is a very important economical sector in Almería. There are more than 350 km² of greenhouses.

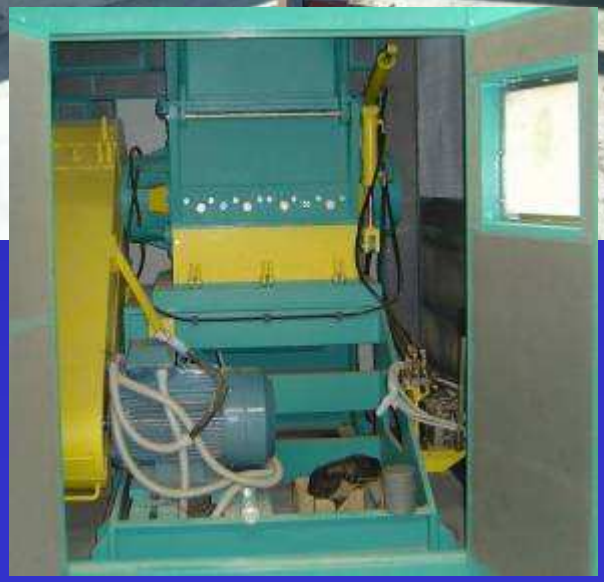


Applications

These greenhouses yearly consume 5.200 tons of phytosanitary products (1.5 million of bottles; 1.9 L average volume).
A process has been designed to recycle the plastic of these bottles. The recycling process needs a washing of the plastic. This produces a water with hundreds of mg/L of persistent toxic compounds.

Proposed Solution : *Solar Photocatalytic Treatment*

Applications



Applications

Solar field figures:

a) Individual CPC modules formed by **20 parallel tubes** (surface: **2.7** m^2/module)

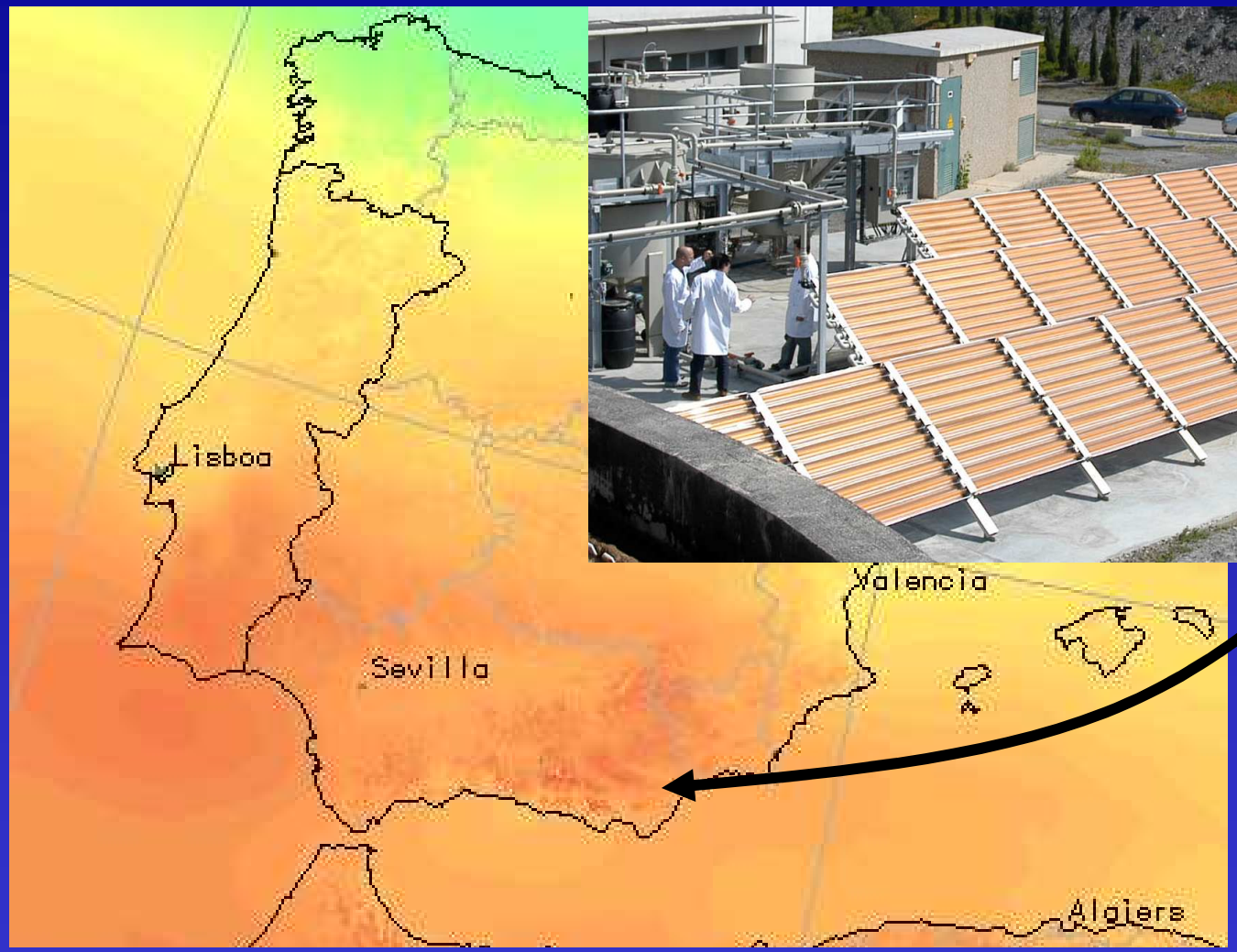
b) 4 parallel rows with **14 modules** each mounted on a 37º-tilted platform (local latitude)

c) total collectors surface: **150 m^2**

d) Total photoreactor volume: **1061 L**

e) Total volume per batch: **1500** to **2000 L**

Applications



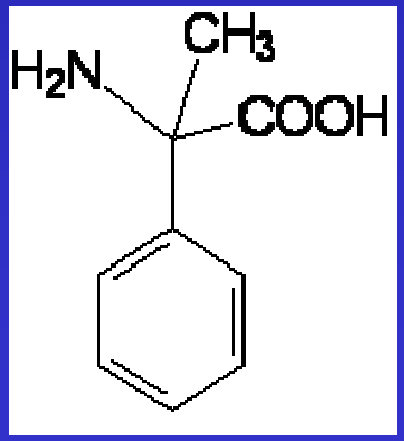
Installed at DSM-DERETIL

Villaricos (ALMERIA)

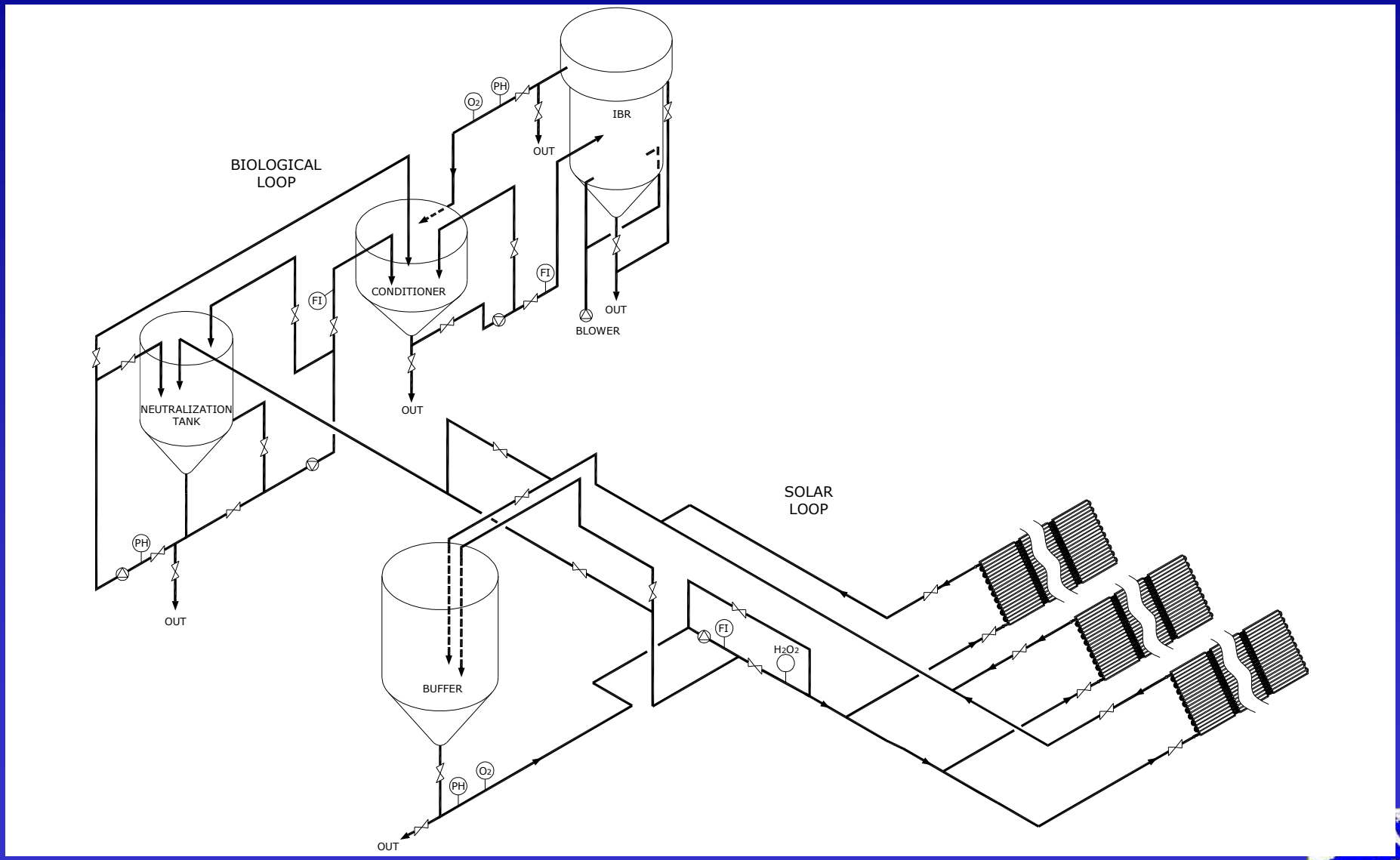
Applications

Pharmaceutical WW

Composition of wastewater (seawater) containing Femac (α-methylphenilglycine, $C_9H_{11}NO_2$)					
	mg L^{-1}		mg L^{-1}		mg L^{-1}
Femac	500-600	Susp. solids	20-100	COD	1500-1800
TOC	400-500	NH_4^+	0-40	NO_3^-	200-600



Applications



Applications

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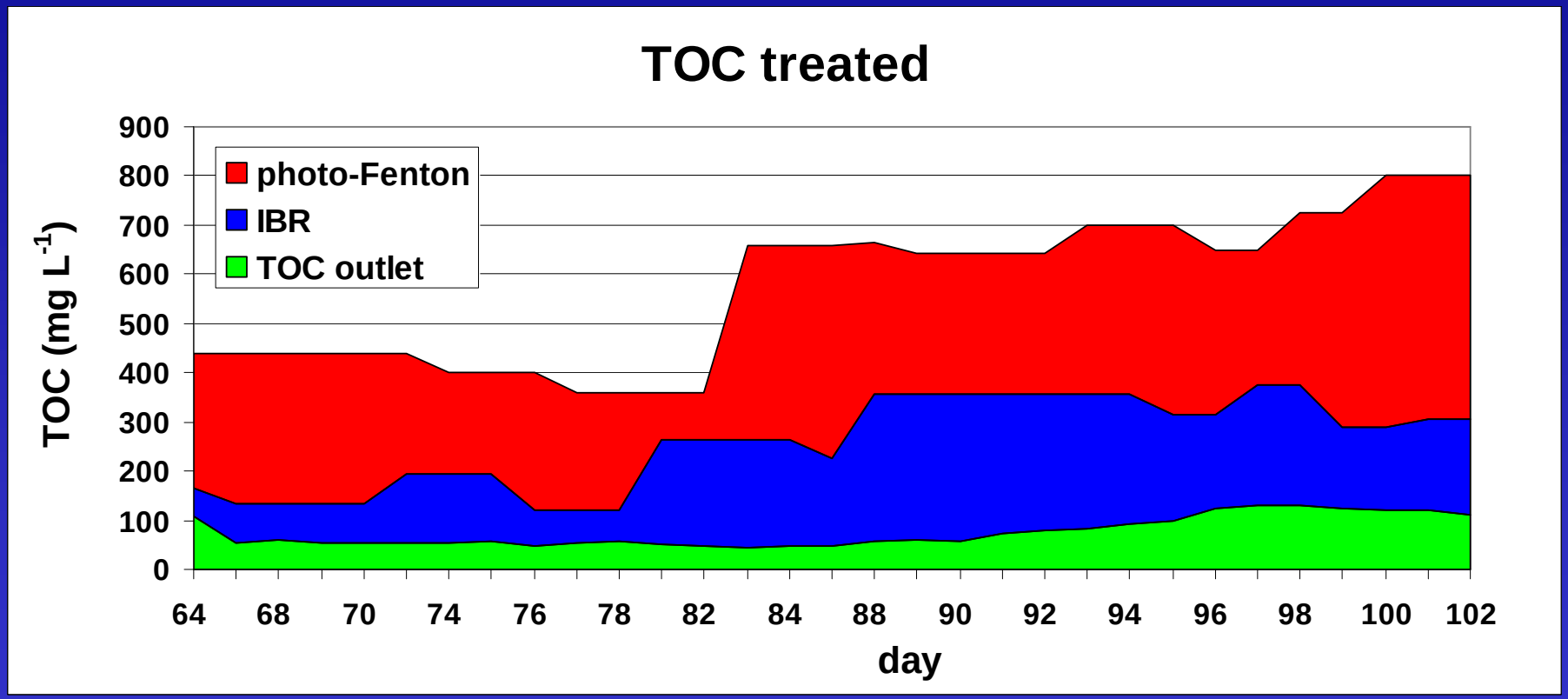
Overview coupling Photo-Fenton/Biotreatment



Innova-Med

Outlook

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PSA

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Photo-Fenton

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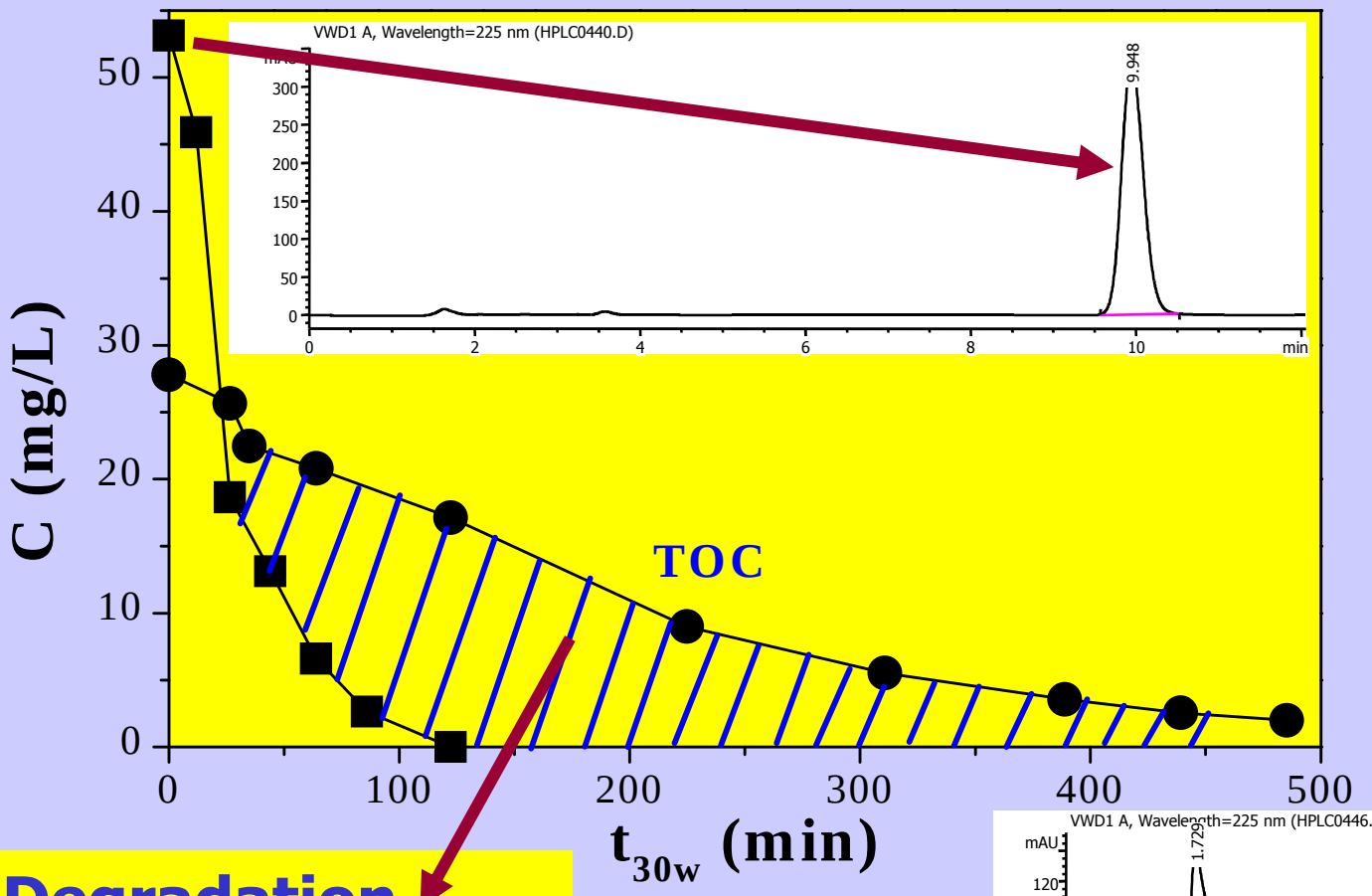
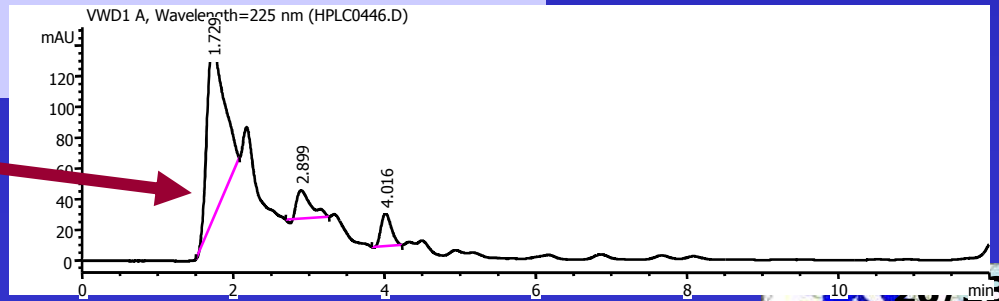
AOPs optimisation

Innova-Med

AOPs evaluation



Degradation products (DPs)



AOPs evaluation

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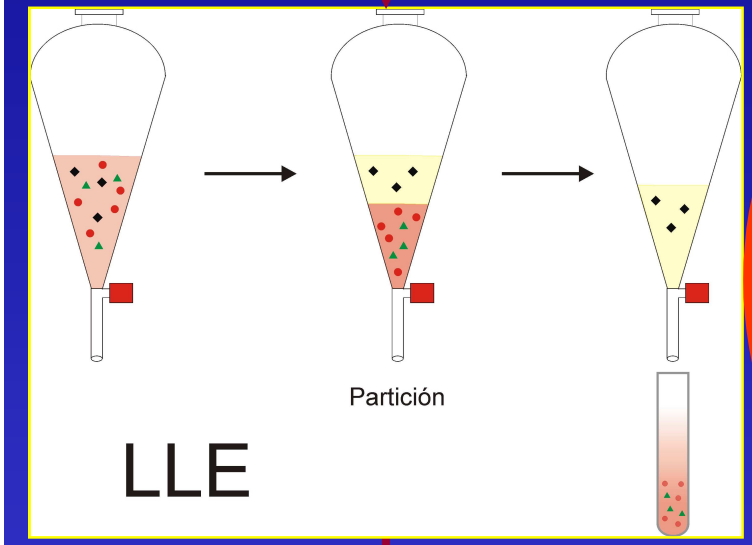
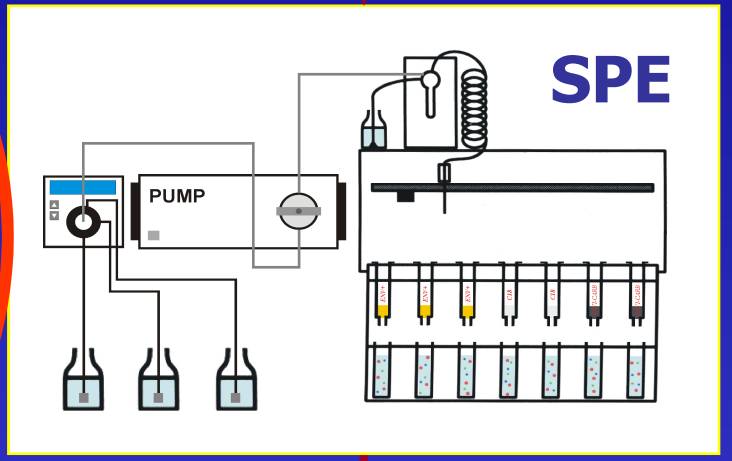
Sample from WW treatment by AOPs

TOC
COD/BOD
TOXICITY
Biodeg.

LC-IC
LC-UV



L-L extraction

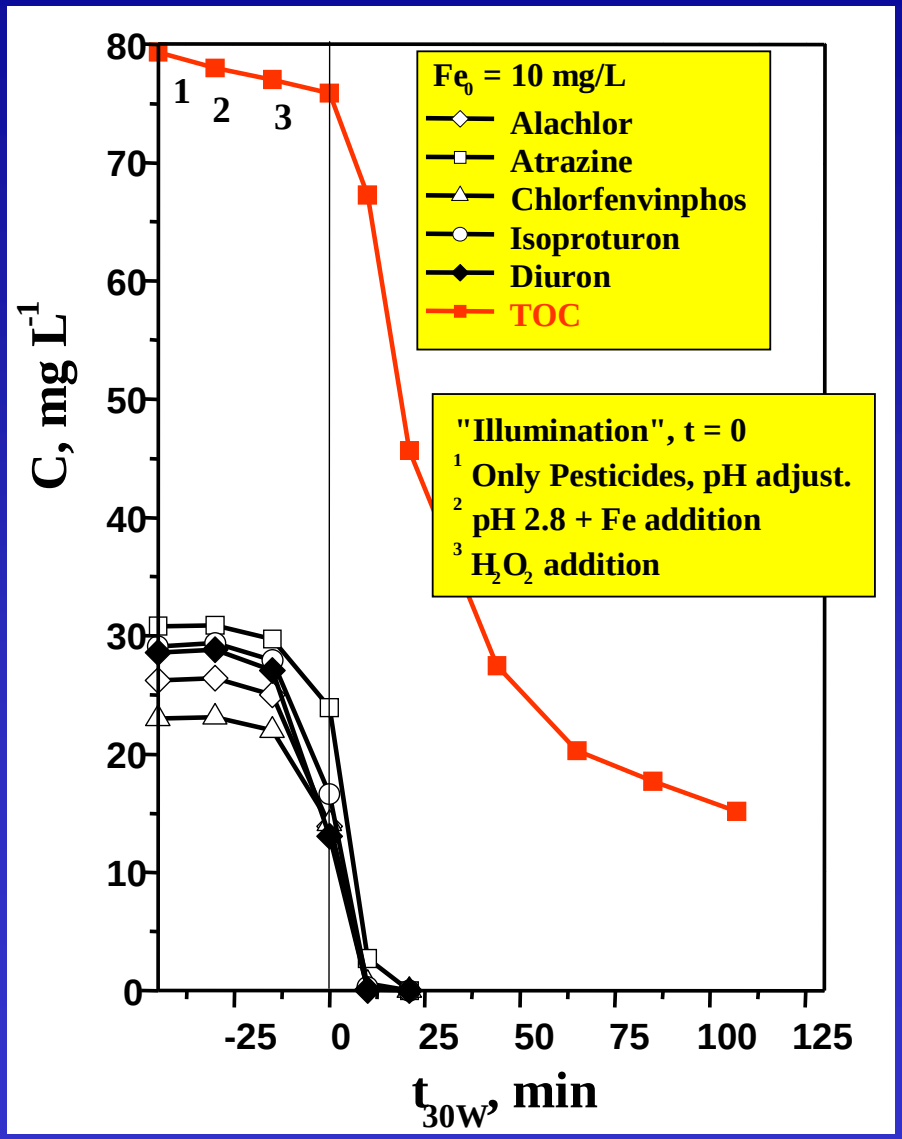


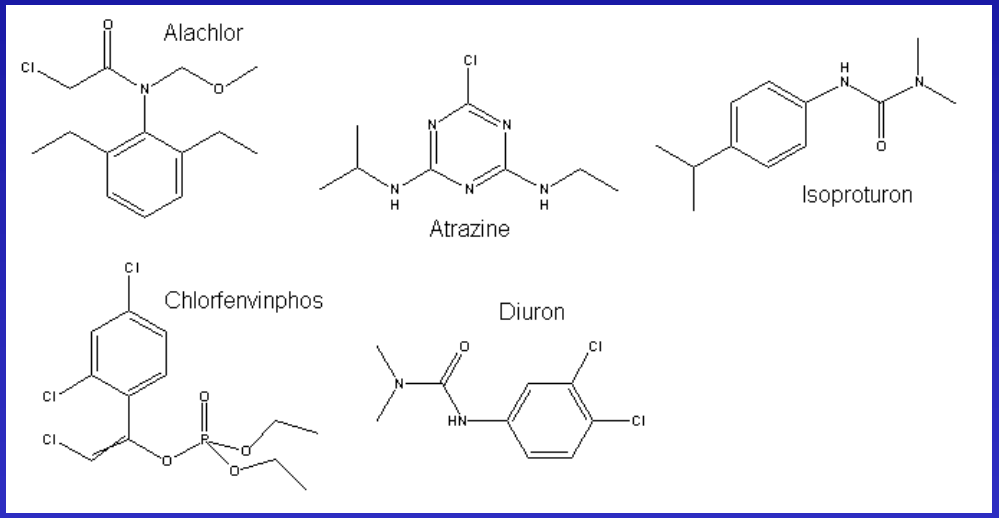
S-L Extraction

GC-MS
LC(API)-MS
GC-AED

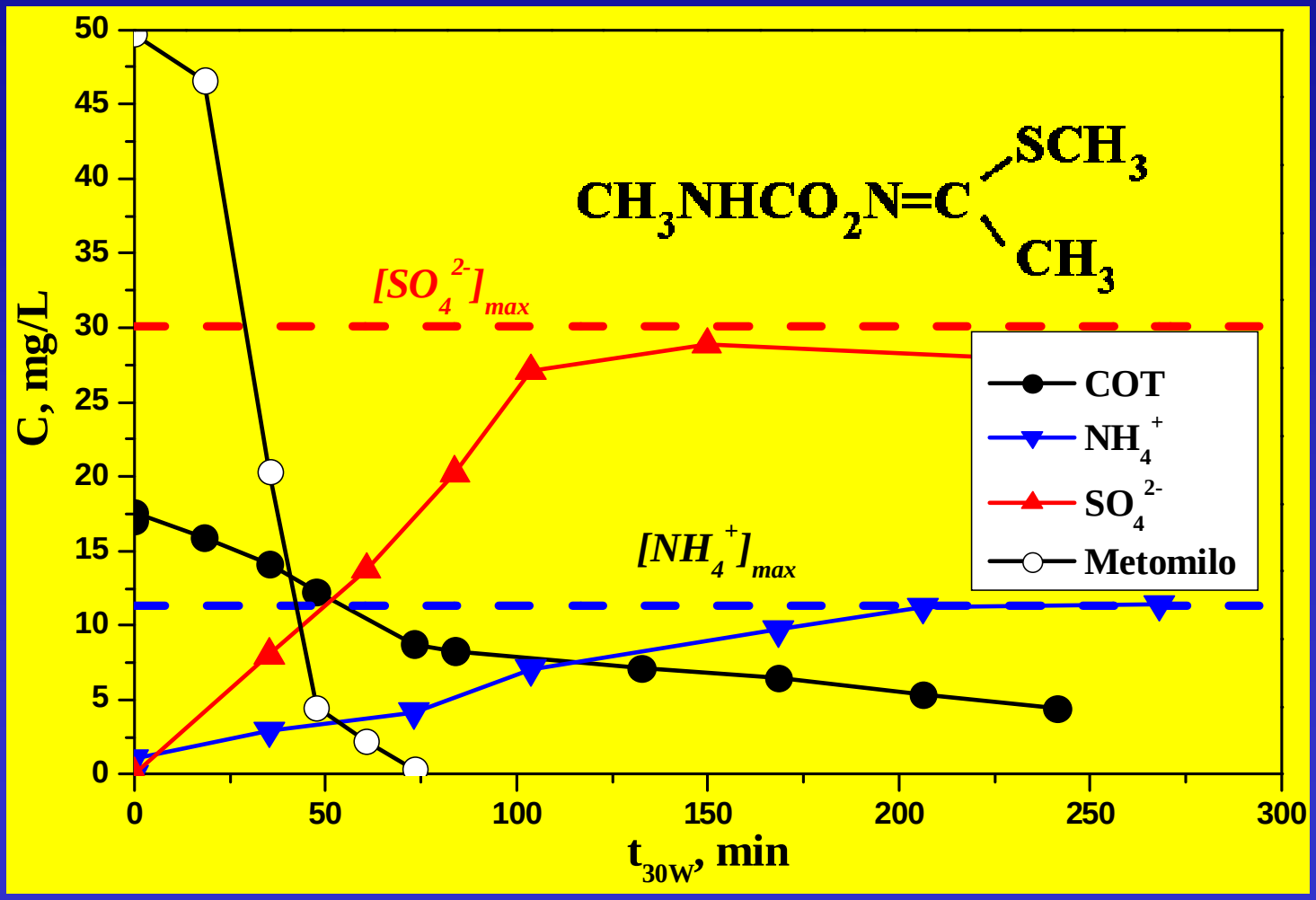
Innova-Med

AOPs evaluation





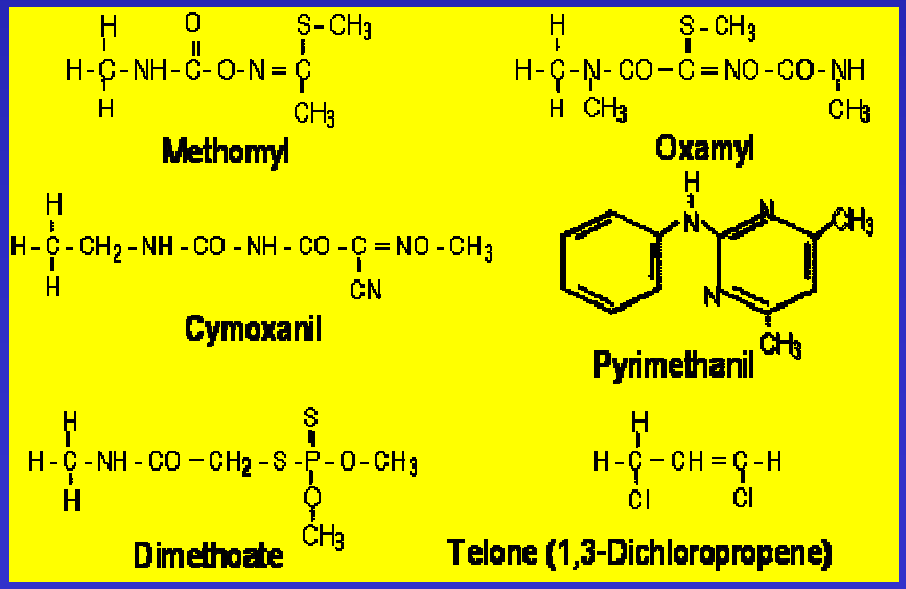
AOPs evaluation



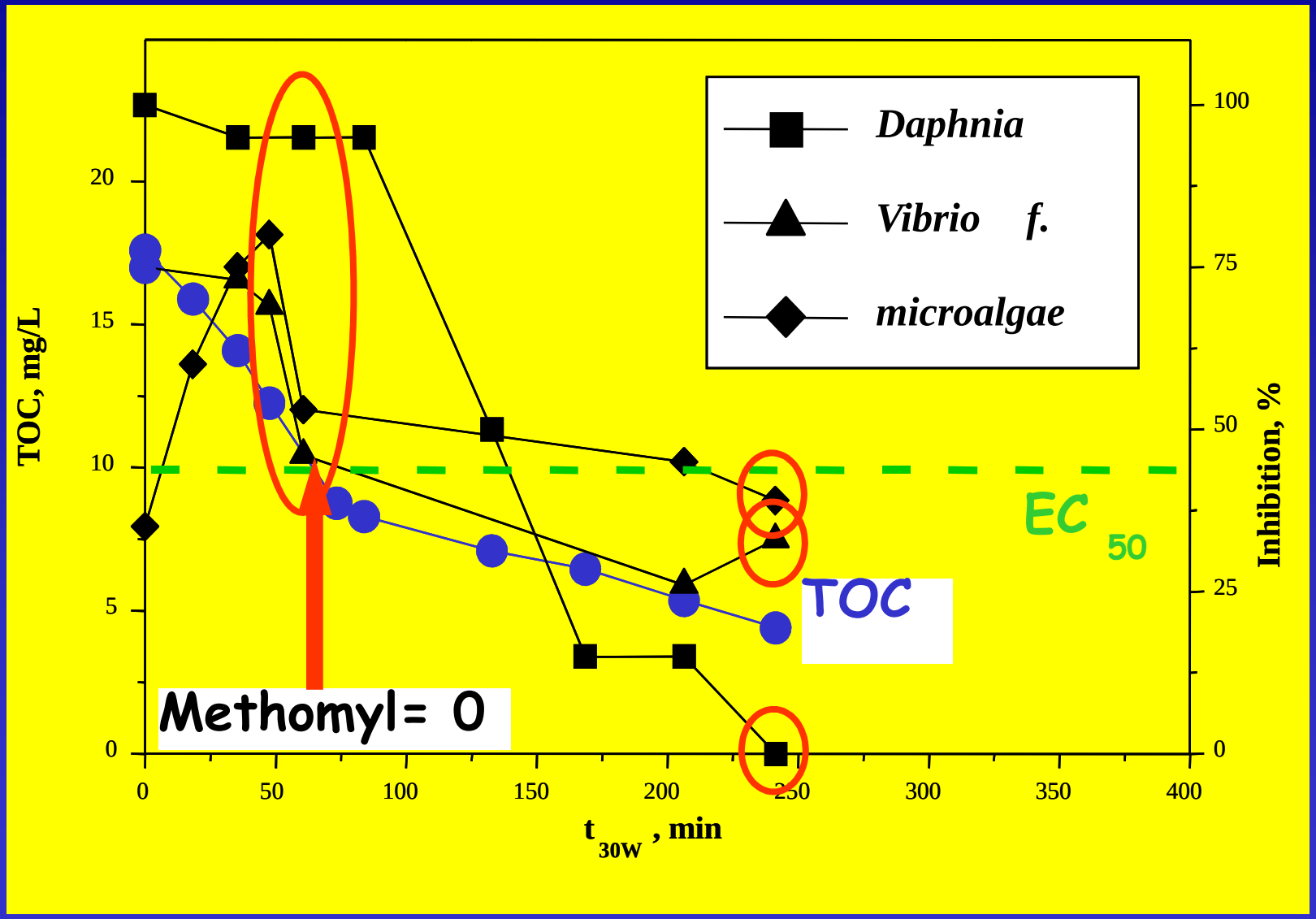
- **Mass balance**

AOPs evaluation

	Methomyl	Dimethoate	Oxamyl[(1)]	Cymoxanil	Pyrimethanil	Telone
Inhibition (15 min) (beginning photo-Fenton)	73%	80%	98%	60%	73%	24%
Inhibition (15 min) (50% TOC eliminated)	70%	40%	87%[(2)]	85%	60%	32%[(3)]
Inhibition (15 min) (80-90% TOC eliminated)	58%	40%	57%	74%	52%	40%



AOPs evaluation



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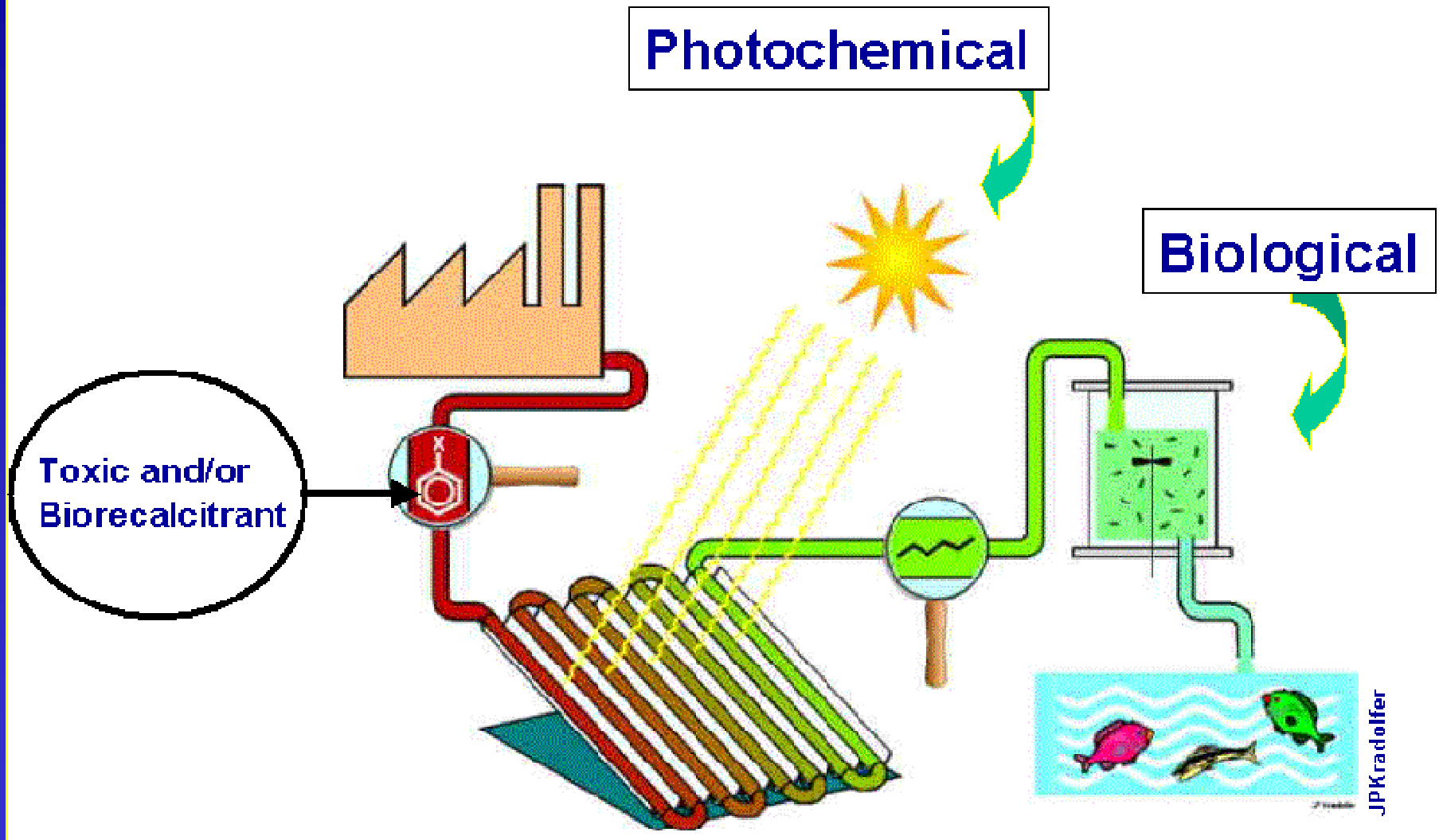
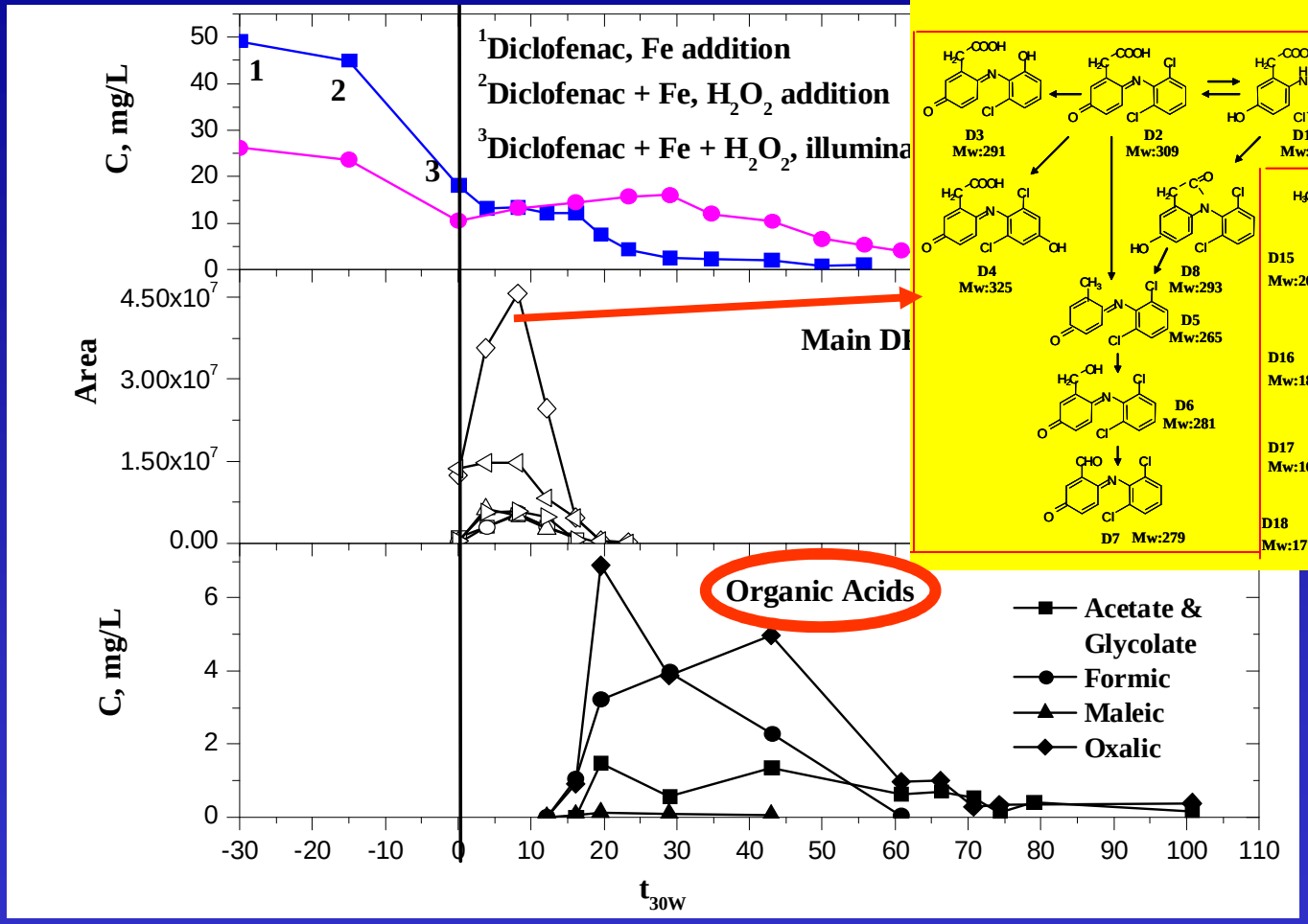
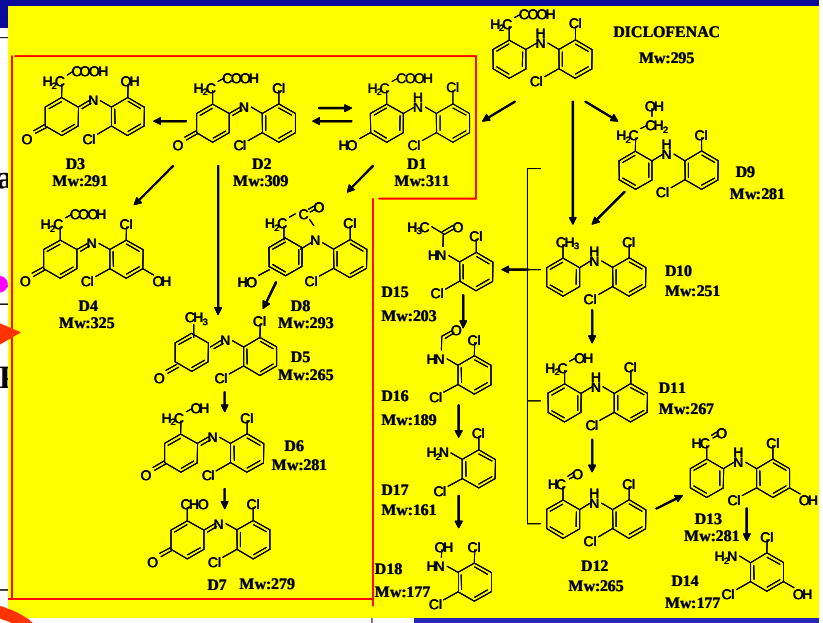


AOPs optimisation

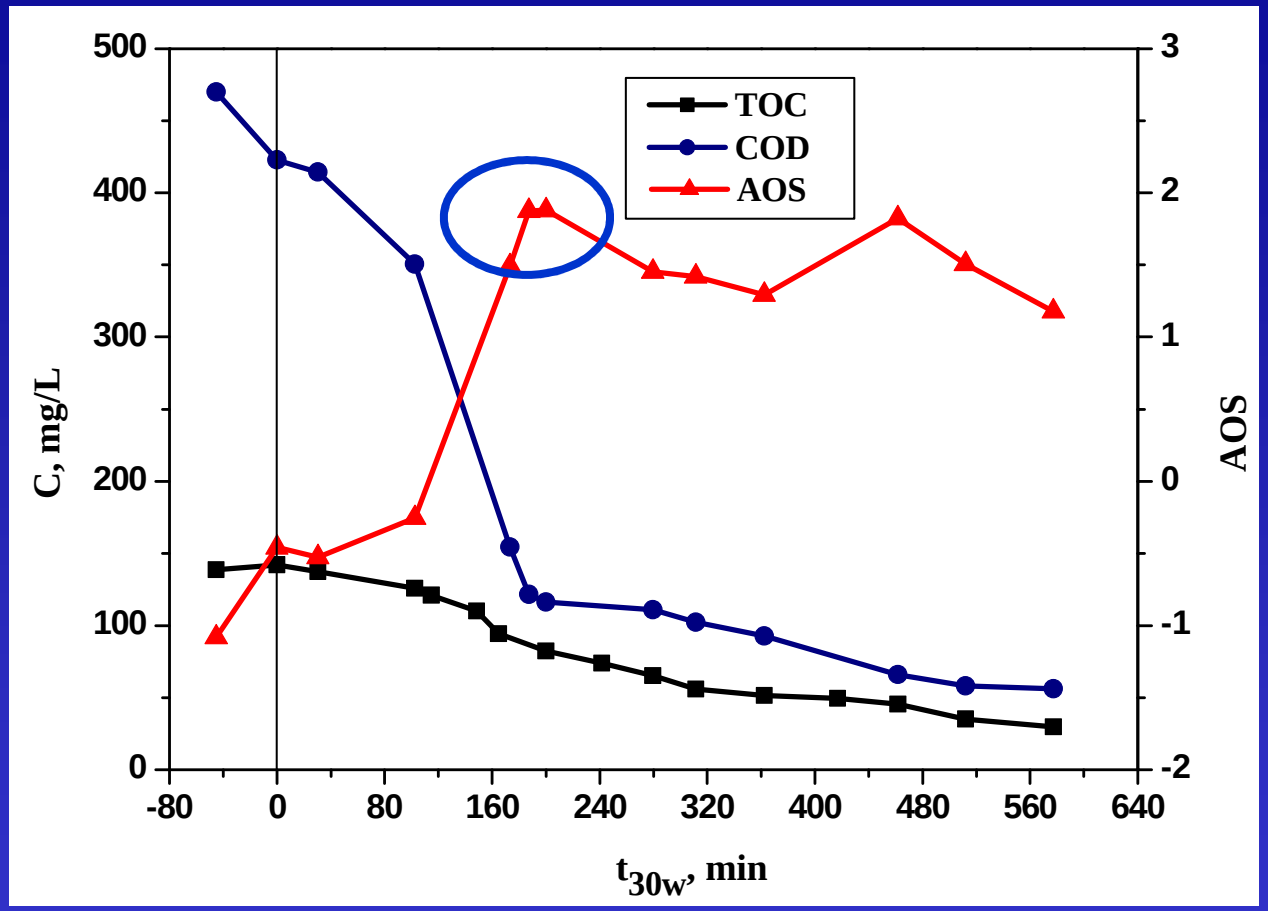




DPs → *R-COOH* → *CO_2 + H_2O +XH*

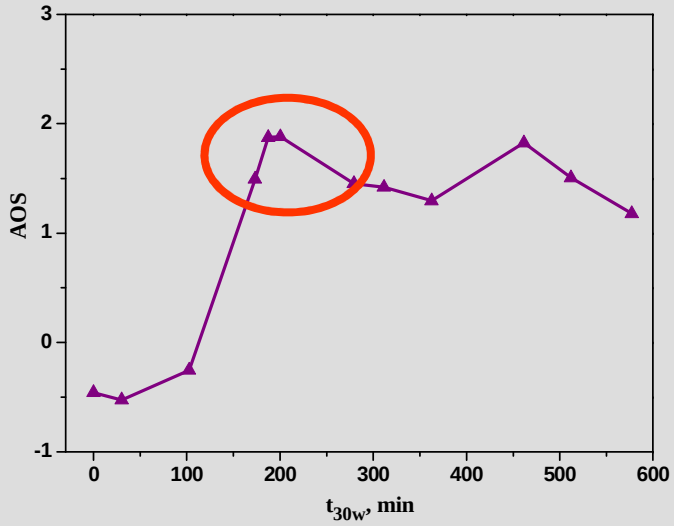
Biodegradability?

AOPs optimisation

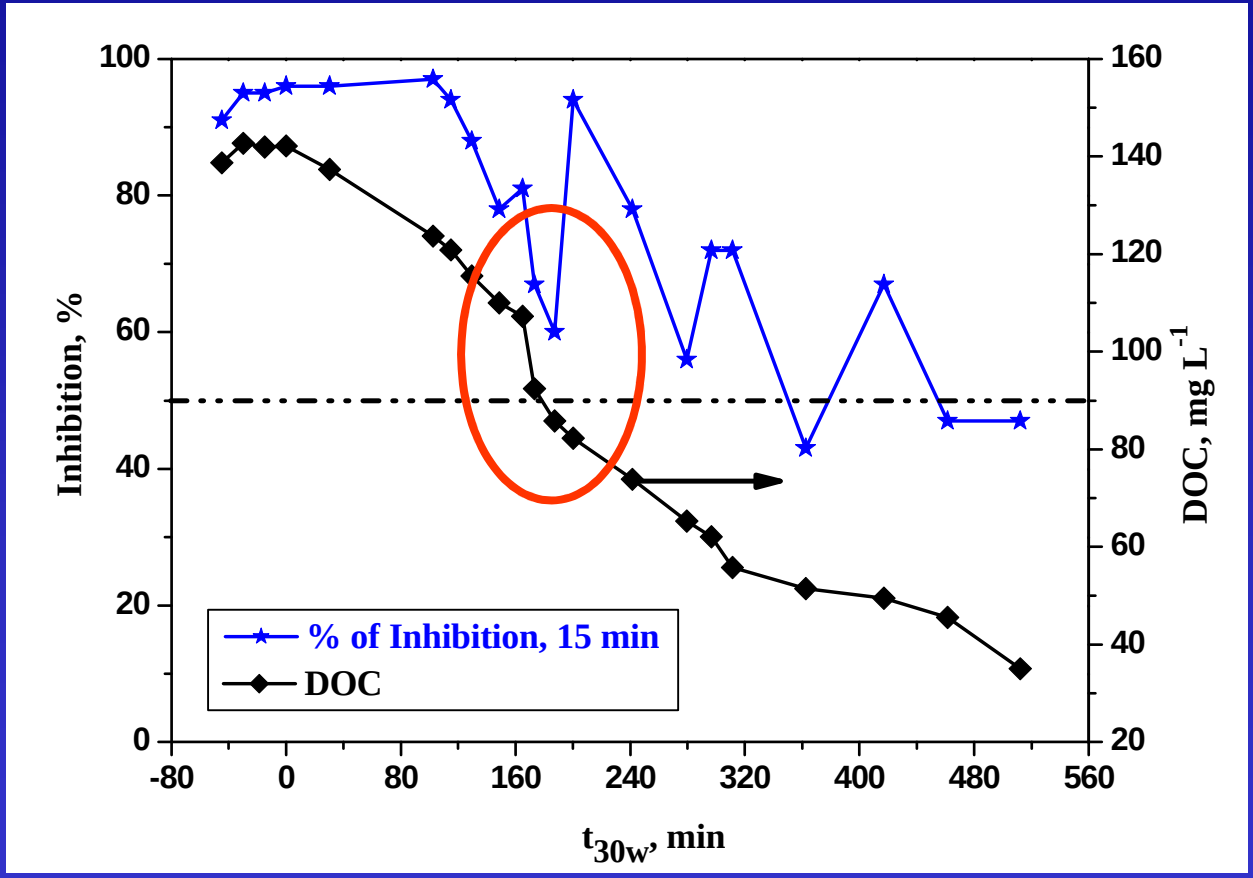


$$AOS = \frac{4(TOC - COD)}{TOC}$$

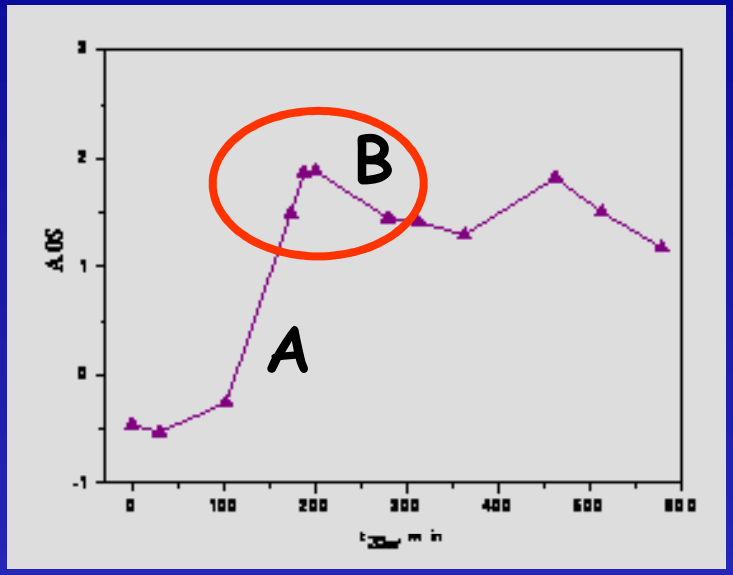
AOPs optimisation

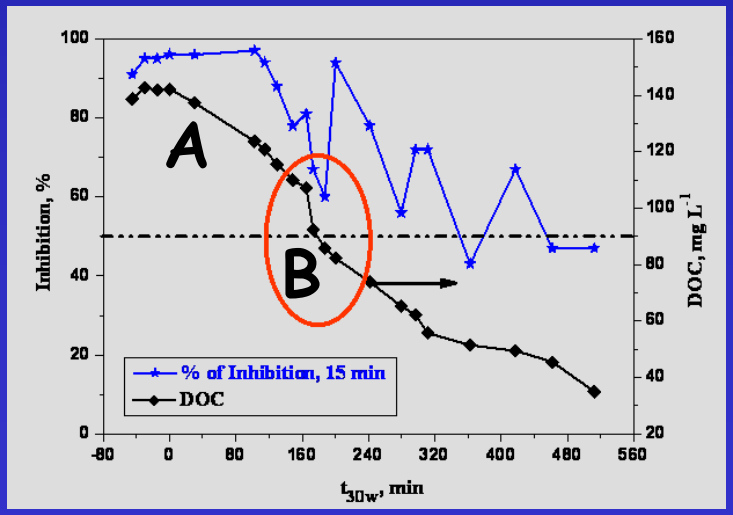


TOXICITY BY *"VIBRIO FISCHERI"*

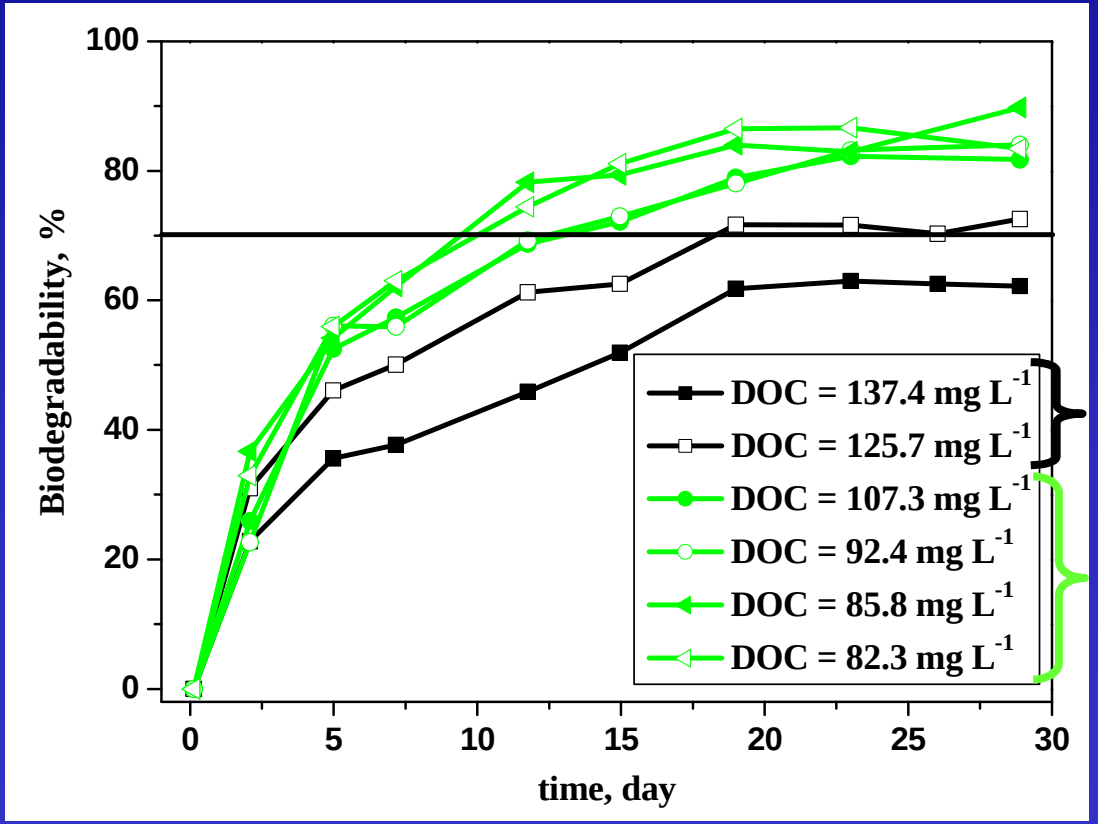


AOPs optimisation

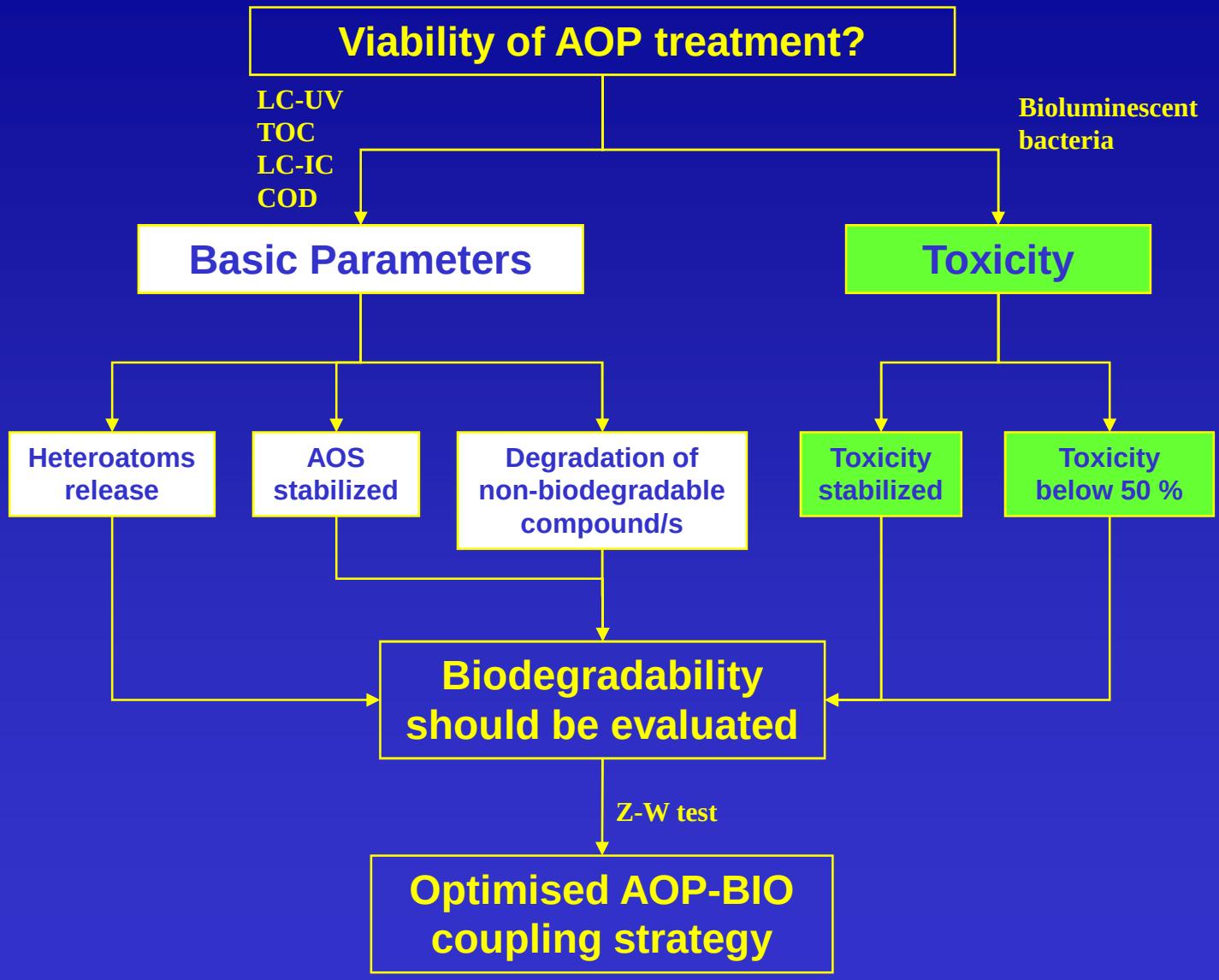




ZAHN-WELLENS TESTS



AOPs optimisation



SPECIAL ISSUES ABOUT SOLAR PHOTOCATALYSIS

Catalysis Today, Vol. 54(2-3), 1999.

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ACKNOWLEDGEMENTS

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INNOVAMED PROJECT

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On-going projects at PSA about waste water treatment

FOTOBIOX. CTQ2006-14743-C03/PPQ.

TRAGUA. CSD2006-00044. Programa "Consolider".

INNOWATECH. EC, FP6, 036882 (GOCE).

PHOTONANOTECH. EC, FP6, 033168 (NMP4).

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