



***Destrucción de
Contaminantes Orgánicos Por Fotocatálisis Heterogénea***

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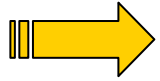


FOTO- Catálisis Heterogénea



1) Transferencia de los reactantes en la fase fluída



2) Adsorción de los reactantes en la superficie del catalizador



3) Reacción en la fase adsorbida

3.1 Adsorción de los fotones por el sólido (no fotoquímica)

3.2 Creación de electrones y huecos foto-inducidos

3.3 Reacciones de transferencia de electrones (ionosorción, neutralización de cargas eléctricas, formación de radicales, reacciones químicas en fase adsorbidas)

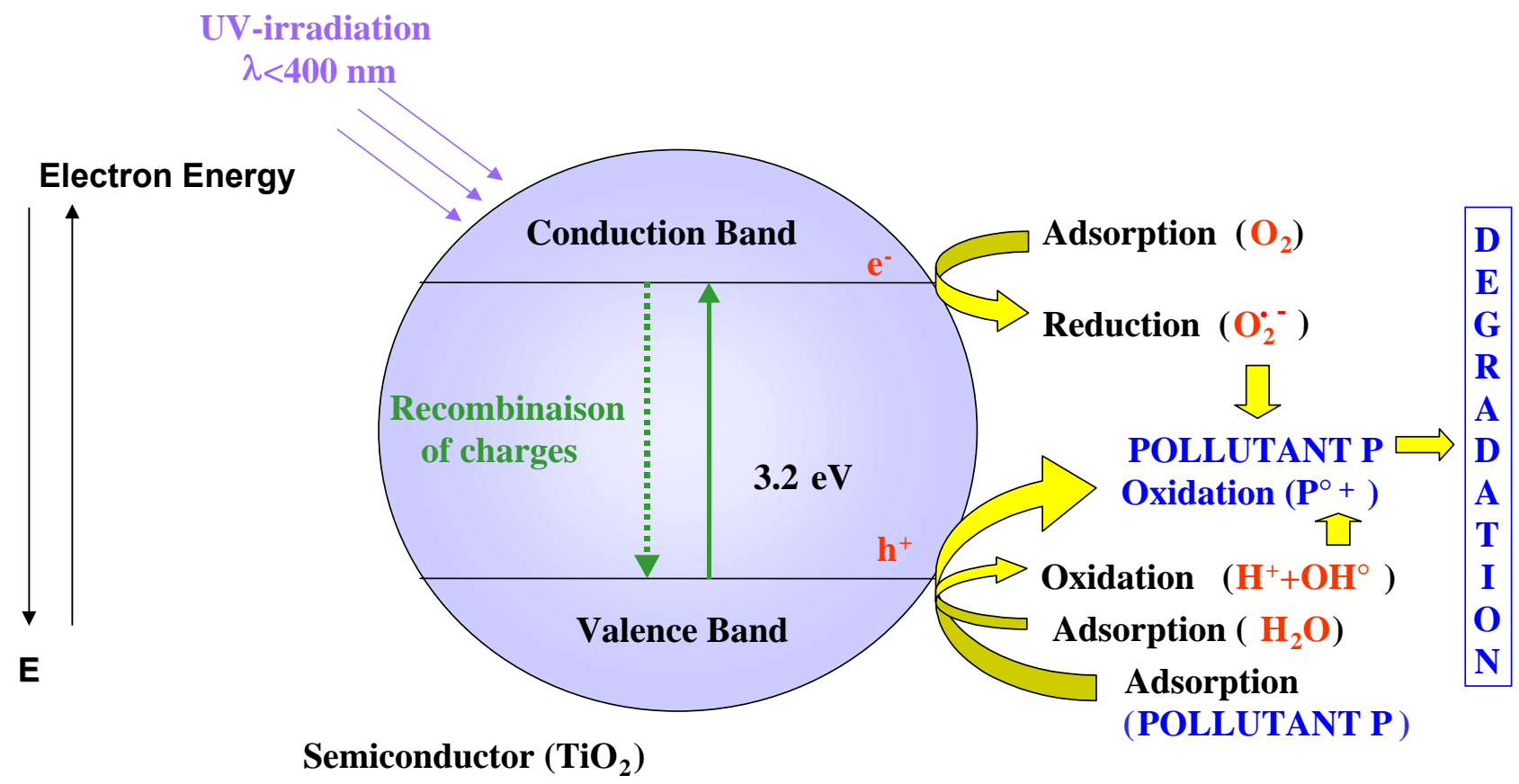


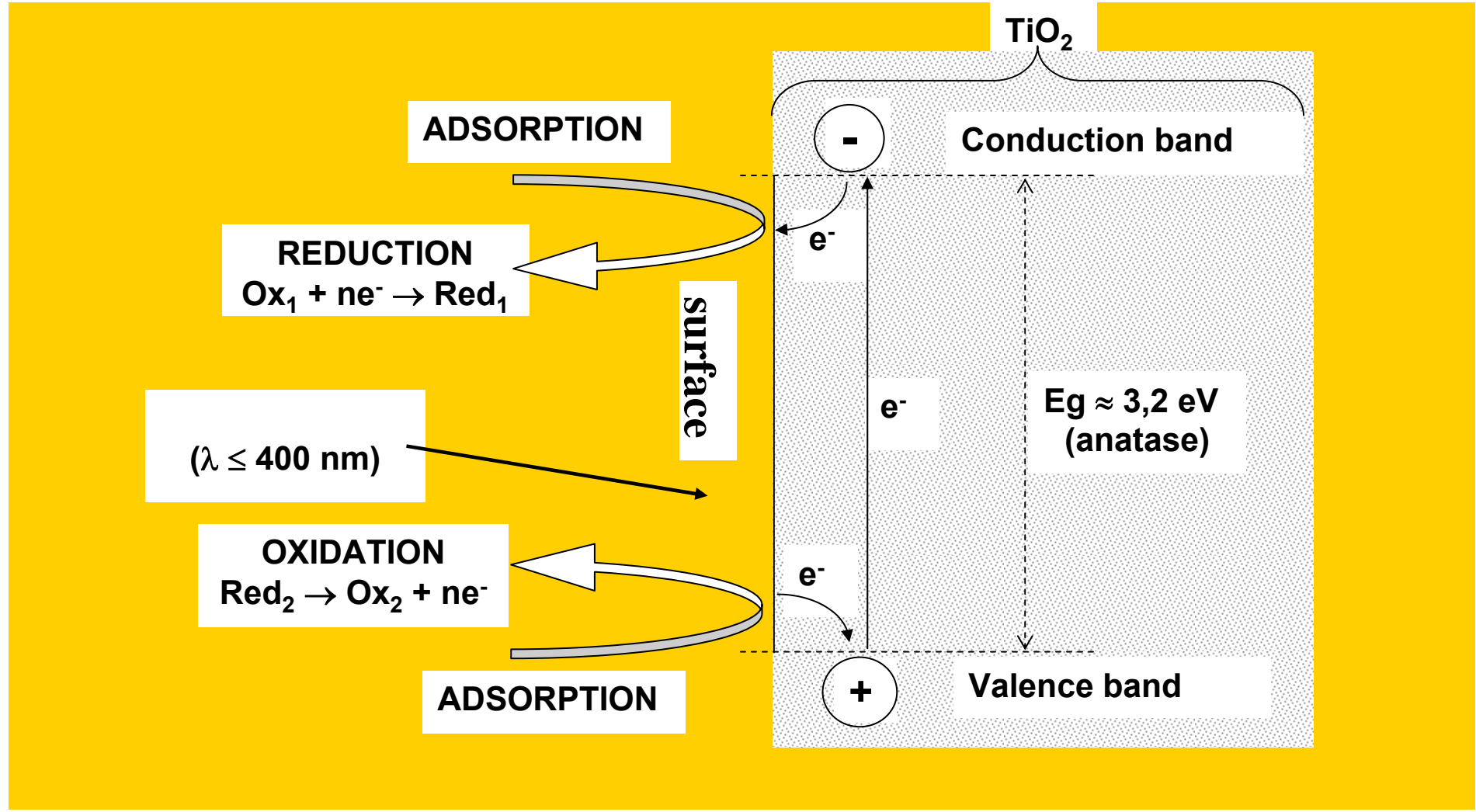
4) Desorción de los productos finales

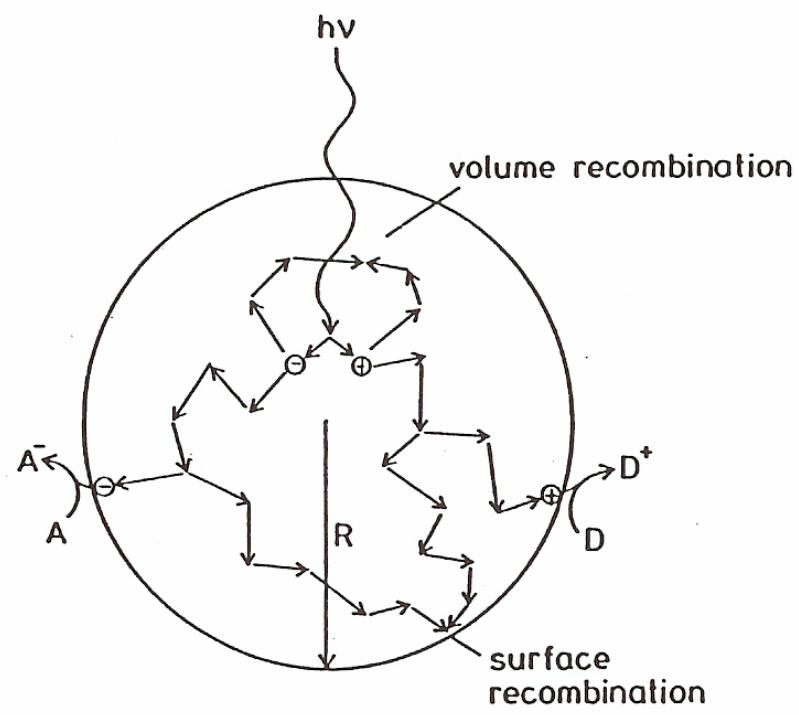


5) Evacuación de los productos finales en/por la fase fluída

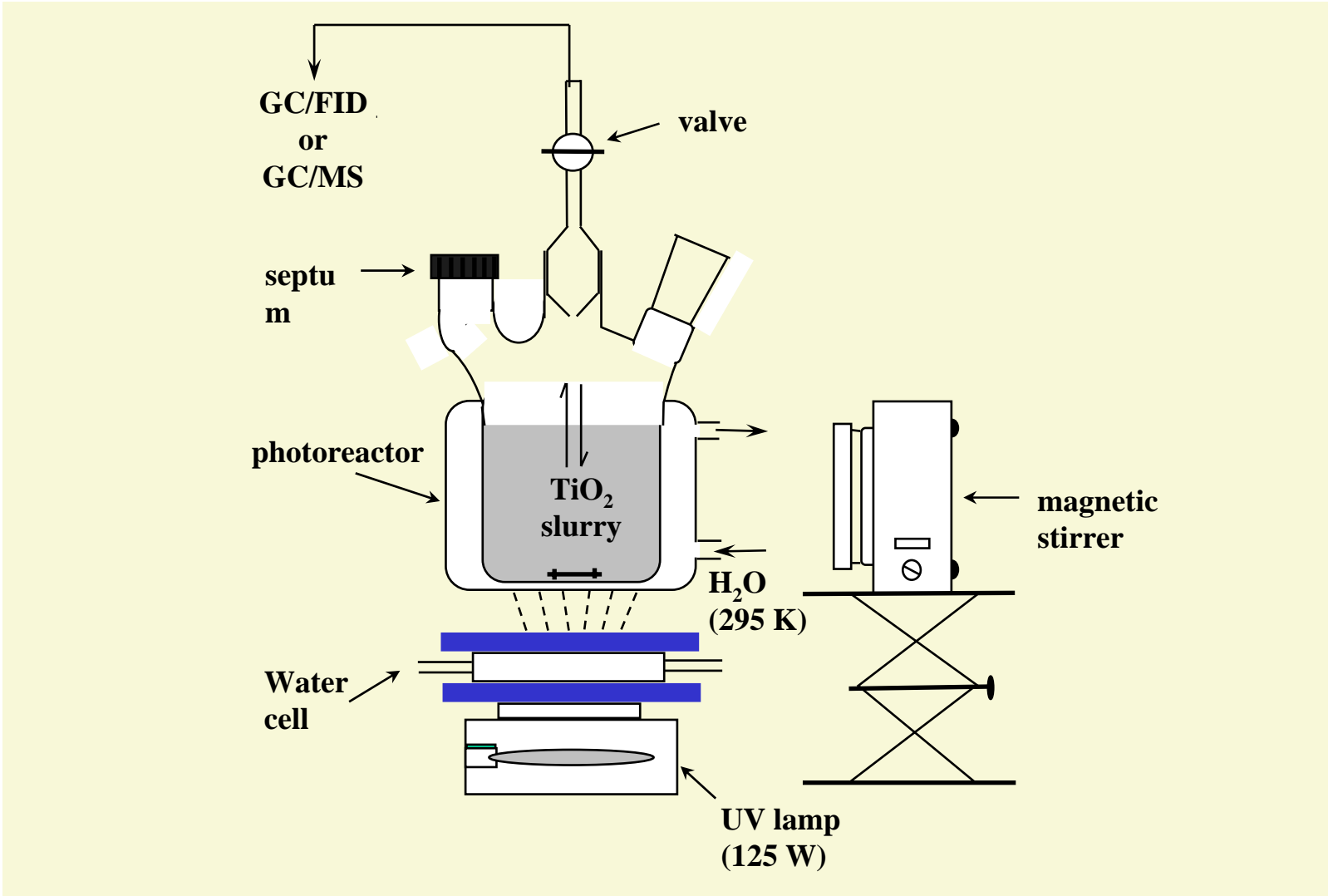
Energy band diagram of titania



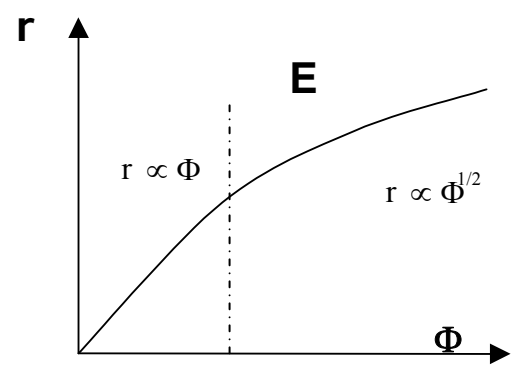
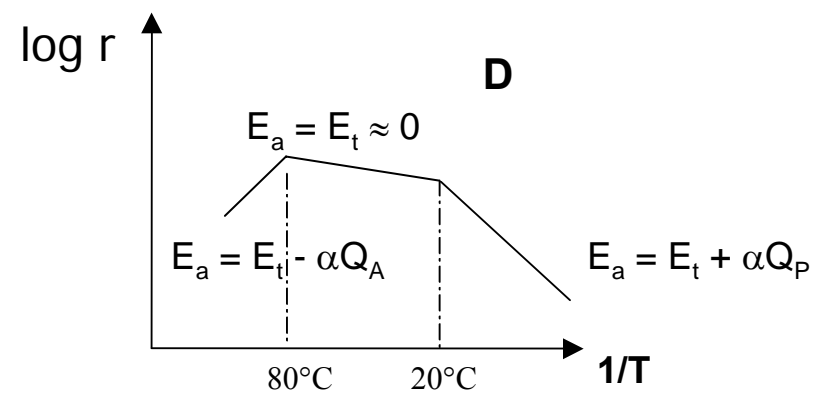
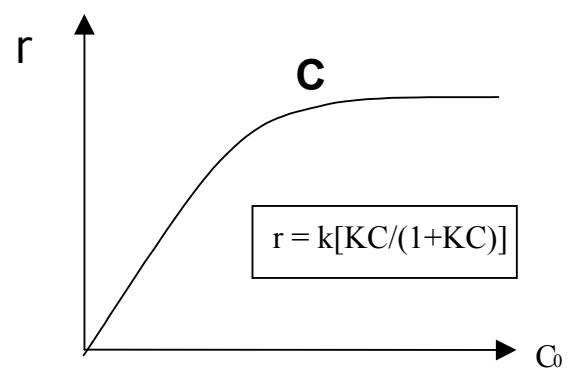
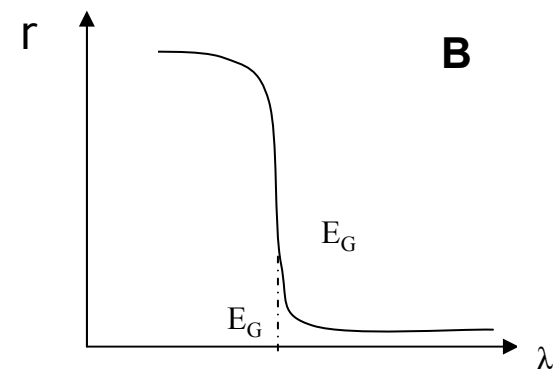
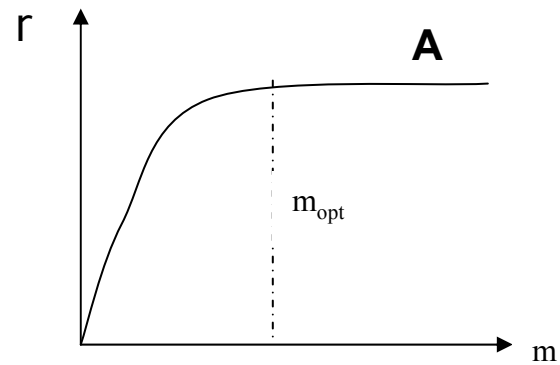




Fate of electrons and holes within a spherical particle of titania in the presence of an acceptor (A) and of a donor (D) molecule (after the late Dr. H. Gerisher (1993))



Scheme of a laboratory-scale slurry photoreactor



Influence of the different physical parameters which govern the reaction rate. (A): mass of catalyst; (B): wavelength; (C): initial concentration of reactant; (D): temperature; (E): radiant flux.

Los Doce Principios de la Química Verde*

1. Prevención
2. Economía de átomos
3. Síntesis de productos químicos menos peligrosos
4. Diseño de productos más seguros
5. Disolventes y corrientes auxiliares más seguros
6. Diseño para la eficiencia energética
7. Uso de materias primas renovables
8. Reducción de sub-productos
9. Catálisis
10. Diseño para la degradación
11. Análisis en tiempo real para la prevención de la contaminación
12. Química intrínsecamente más segura para la prevención de accidentes

* Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*, Oxford University Press: New York, 1998, p.30. By permission of Oxford University Press.

Fine Chemicals vs Environmental and Green Chemistry in Photocatalysis

Influence of the nature of the related active species

O^* vs OH°

Fine Chemicals in Photocatalysis

Fine Chemicals vs Environmental and Green Chemistry in Photocatalysis

Influence of the nature of the related active species

O^* vs OH°

Fine Chemicals vs Environmental Photocatalysis



Common Features

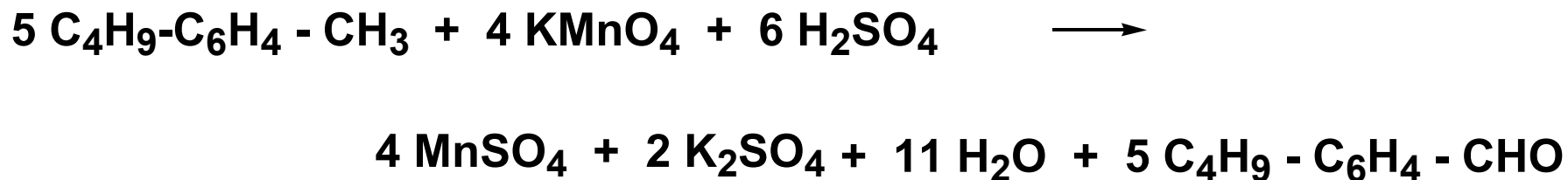
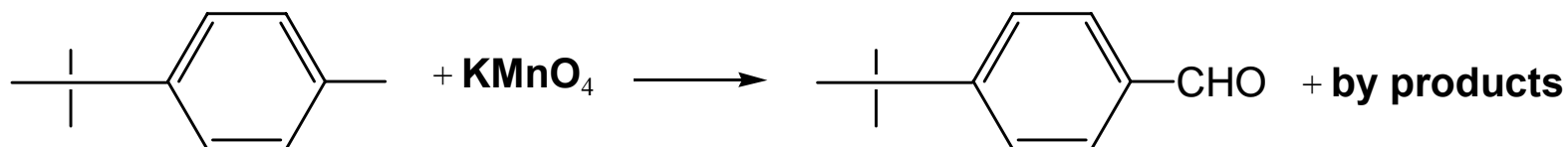
Opposite Features

Parameters	Fine Chemicals	Environmental Catalysis
Catalyst	TiO ₂ , Pt/TiO ₂	TiO ₂
Photoreactors	Batch, plug flow	Batch plug flow
medium	Gas and liquid phase	Gas and liquid phase
Activation Process	Photonic absorption	Photonic absorption
Kinetic laws	Langmuir-Hinshelwood	Langmuir-Hinshelwood
Main reaction	Mild oxidation	Total oxidation
Initial selectivity	100%	No selectivity
Final products for organics	>C=O	CO ₂
Medium	<u>Dry</u> medium	Water, Humid air
Active species	O*	OH°
Reaction of Formation	$\text{O}^- (\text{ads}) + \text{h}^+ \rightarrow \text{O}^* (\text{ads})$	$(\text{TiO}_2) + \text{h}\nu \rightarrow \text{e}^- + \text{h}^+$ $(\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-) + \text{h}^+ \rightarrow \text{H}^+ + \text{OH}^\circ$

Fine Chemicals : Case study of tertio-butyl-tolualdehyde



Perfume Industry

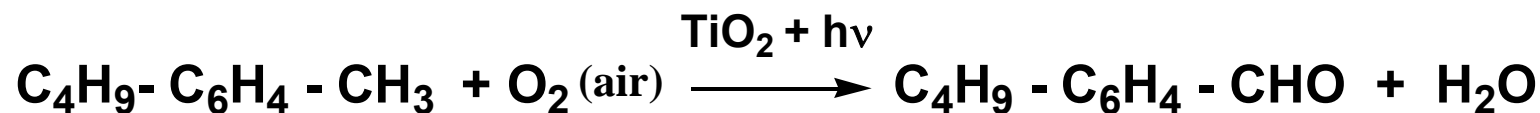


Many by-products as expected in fine chemistry

Fine Chemicals : Case study of tertibutyl-tolualdehyde



The photocatalytic solution

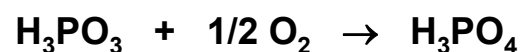
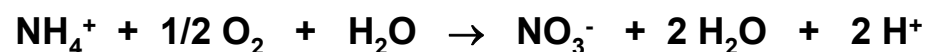
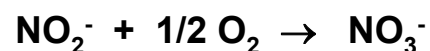
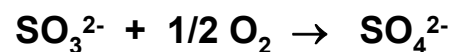
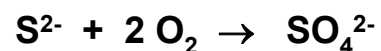
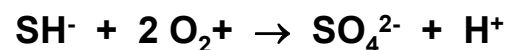
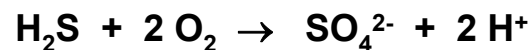


- Selectivity S = 100%
- Reaction is performed in air, at room temperature
- Typical « environmentally friendly reaction » (« Green Chemistry ») which can be carried out in gas and/or pure liquid organic phase

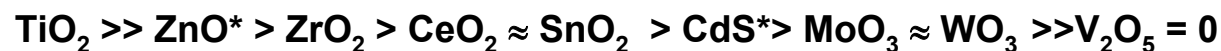
Environmental Photocatalysis in Water

**PHOTOCATALYTIC TOTAL DEGRADATION OF INORGANICS
(CHEMICALS, POLLUTANTS, TOXICS)**

PHOTOCATALYTIC OXIDATION OF AQUEOUS INORGANICS



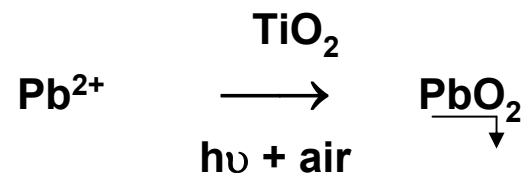
CATALYSTS



(*: photocorrodes)

Heavy metal removal

↪ By photocatalytic oxidation



↪ By photocatalytic reduction



- Toxic metals : Hg^{2+}

- Precious metals :



↪ Recovery of silver from photographic baths

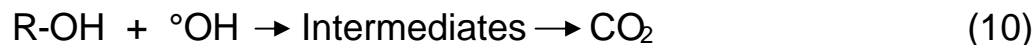
↪ Abatement to less than 0.1 ppm

↪ Separation from common metals

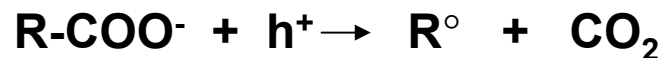
**PHOTOCATALYTIC TOTAL DEGRADATION OF ORGANICS
(POLLUTANTS, PESTICIDES, DYES....)**

Photocatalytic OH° Radicals Generation

In water, UV-irradiated titania is able to generate OH° radicals, known as strongly oxidative (second best after fluorine) but poorly selective agents:

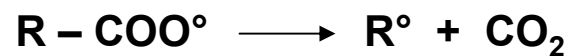
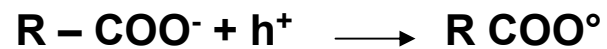
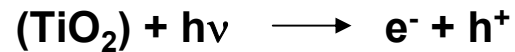


Loss of one carbon atom via the “photo-Kolbe” reaction:



Importance of the « Photo-Kolbe »* Reaction

* Firstly described by B. KRAEUTLER and A.J. BARD (1978)



↪ First step of carbon mineralization : $\text{C}_n \longrightarrow \text{C}_{n-1} + \text{CO}_2$

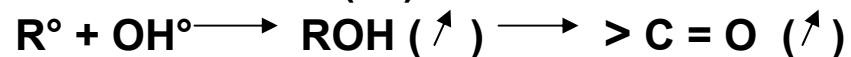
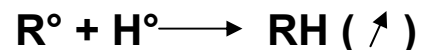
↪ Many carboxylic acids present in Nature (formic, acetic, oxalic, butyric, fatty acids (palmitic, stearic, ...))

↪ Possible subsequent reactions :



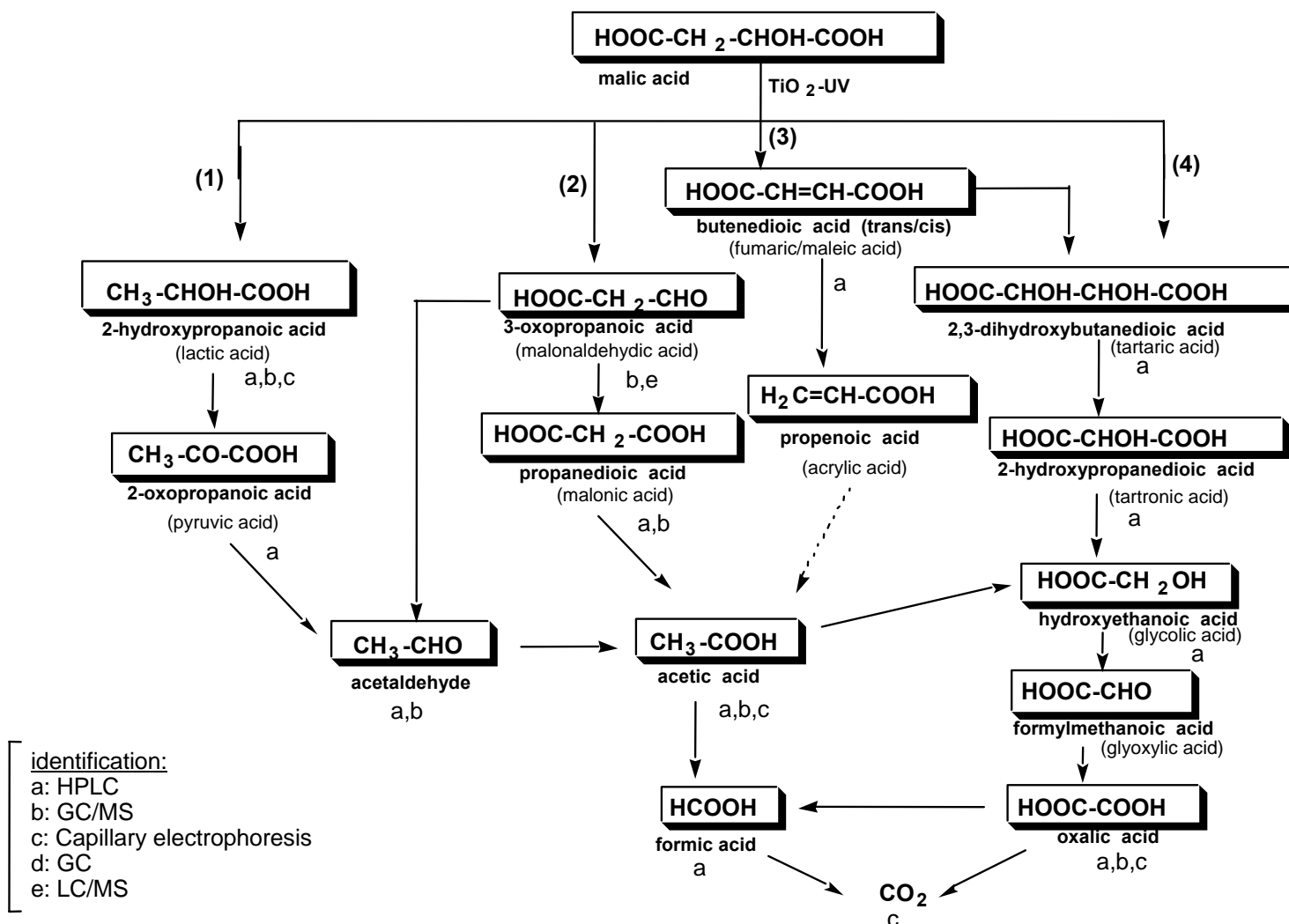
In water : Step-by-step decarboxylations : $\text{C}_n \longrightarrow n \text{CO}_2$

In humid air : side reactions



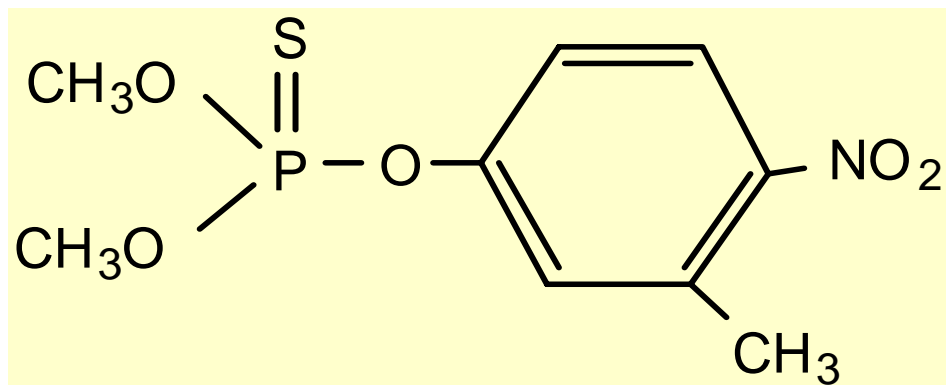
(acceleration of self-cleaning by evolution of gaseous intermediates)

Photocatalytic degradation of Biomass



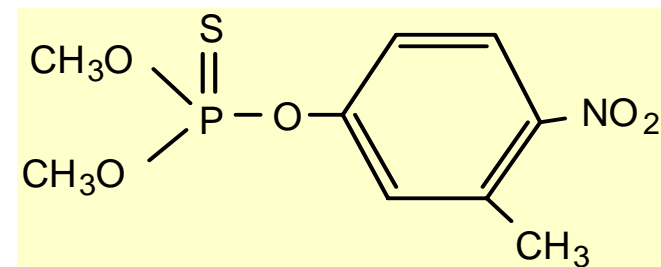
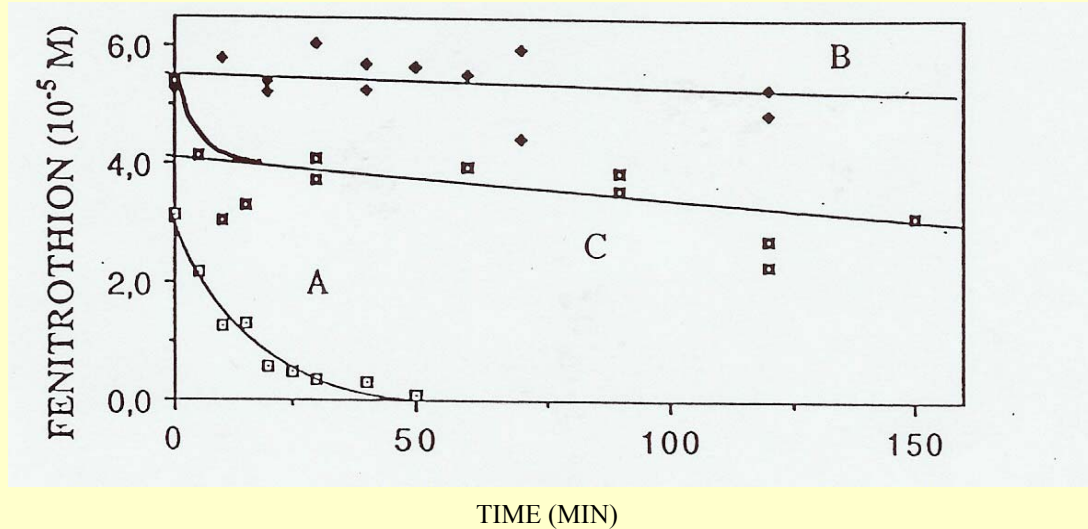
Reaction pathway of the photocatalytic degradation of malic acid in contact with TiO₂ at λ ≥ 290 nm.

Fenitrothion

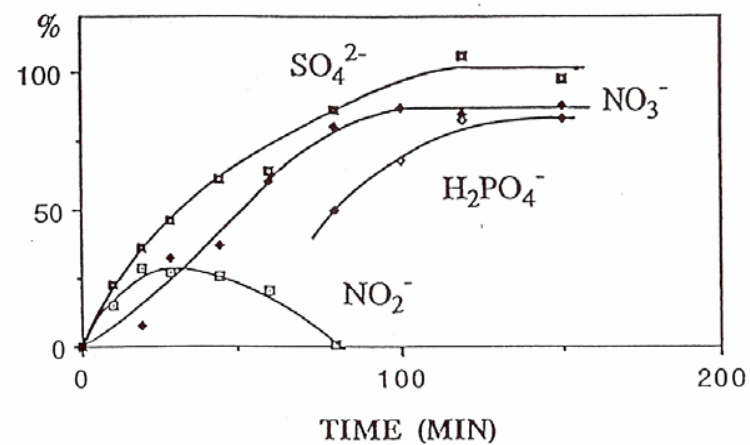


Phosphorothioic acid O,O-dimethyl-O-(3-methyl-4-nitrophenyl) ester

(insecticide, cholinesterase inhibitor)

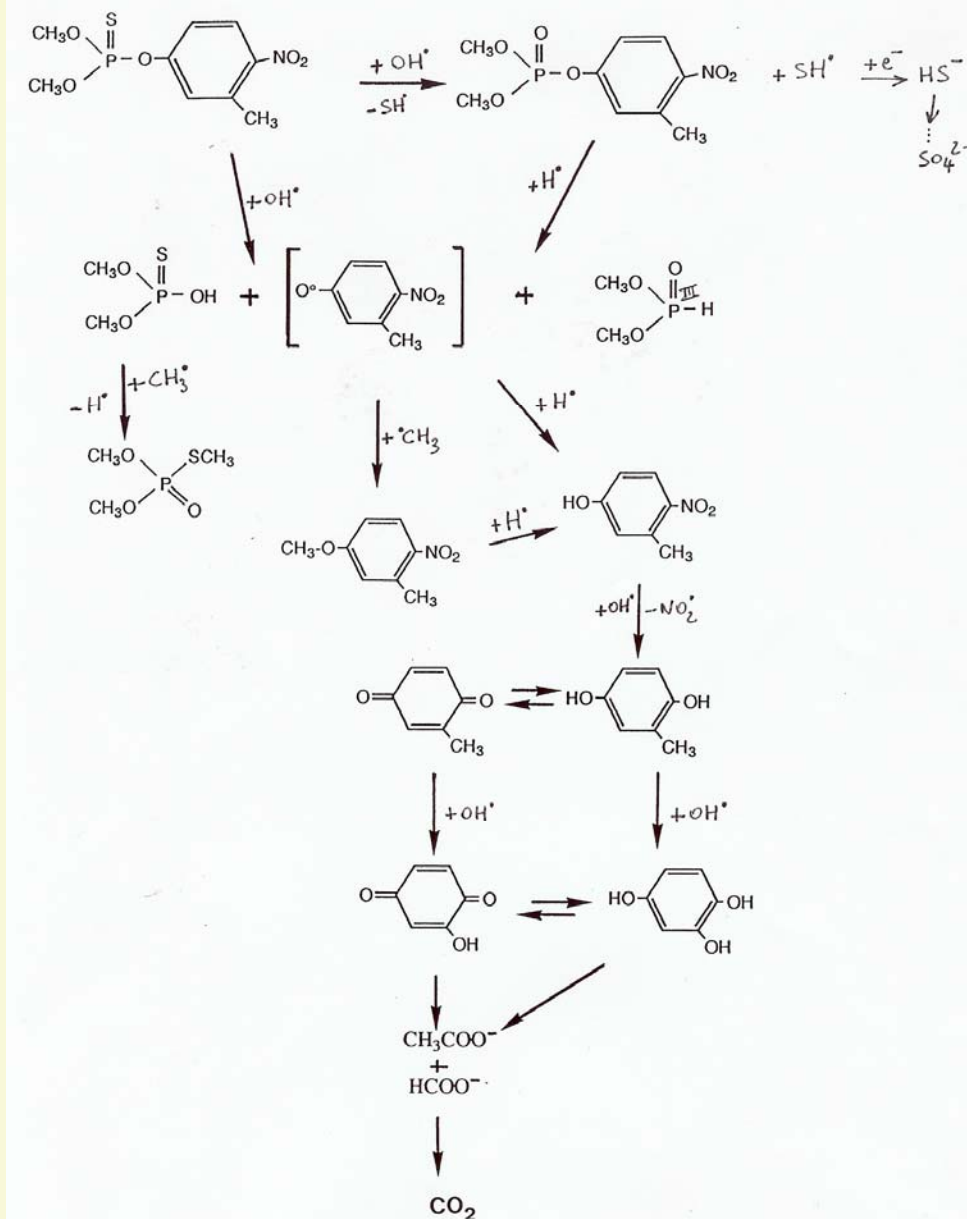


Kinetics of disappearance of Fenitrothion
A = TiO₂ + UV + air ; B = TiO₂ dark ; C= UV alone

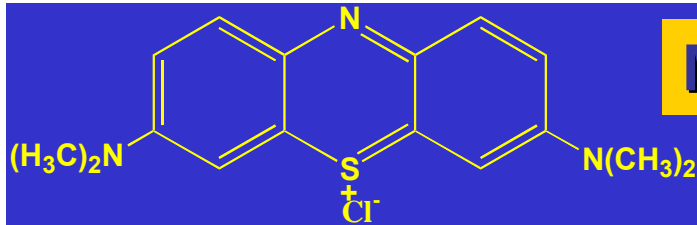


Kinetics of the formation of inorganic ions
during Fenitrothion catalytic photodegradation

Schematic photocatalytic degradation pathway of Fenitrothion



Dye Model Molecules

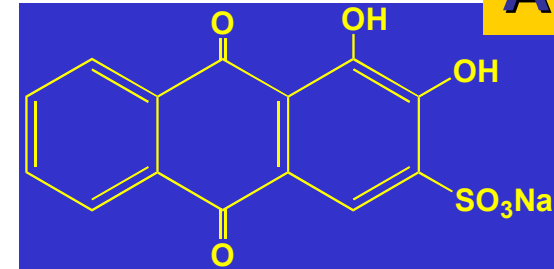


METHYLENE BLUE

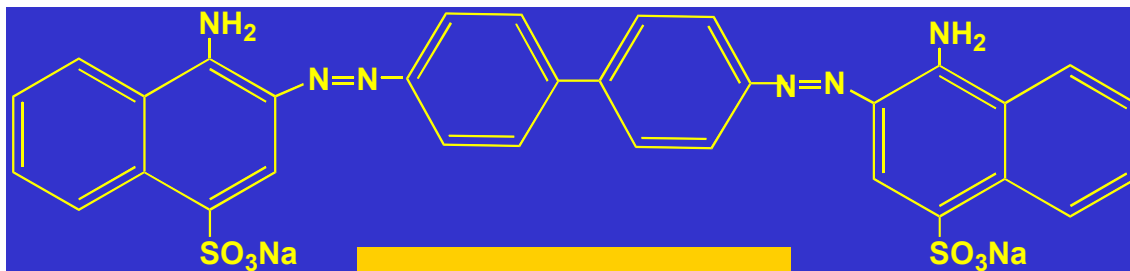
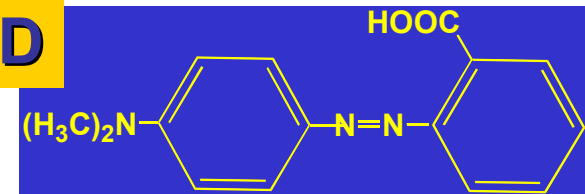
ORANGE G



ALISARIN



METHYL RED



CONGO RED

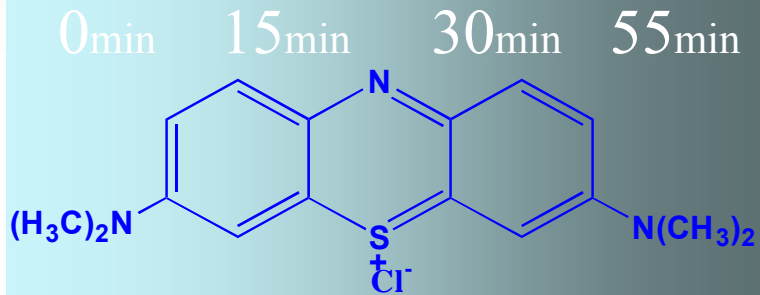
DECOLORIZATION



Methylene blue

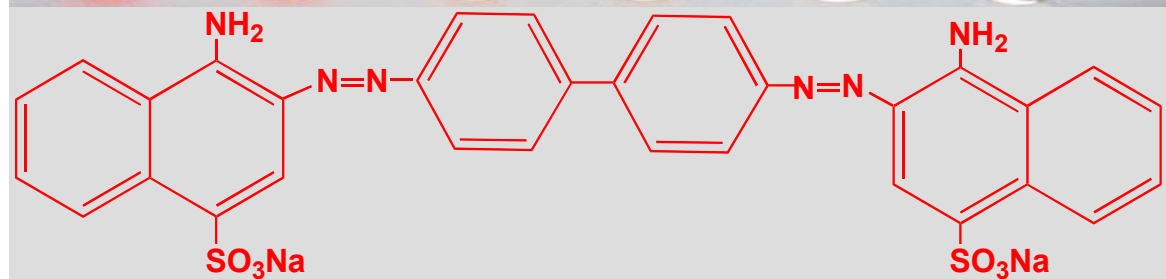
0min 15min 33min 56min

(In presence of TiO₂)



CONGO RED

0min 15min 30min 60min 120min 180min



NITROGEN MASS BALANCE IN AZO-DYES DEGRADATION

AZOIC or AZO-dyes :



They contain a stable internal –N=N- functional group



They are the most abundantly used

EVOLUTION of NITROGEN-CONTAINING FINAL PRODUCTS

➡ Case of ammonium ions

NH_4^+ ions originate from amino-groups *without any change* of the oxidation degree of nitrogen equal to -3.

This can occur via successive attacks by H° atoms:



H° atoms can be generated either

(i) by reduction of protons by photogenerated electrons (moderate driving force)



or (ii) by transient alcohol intermediate photodehydrogenation (Herrmann et al. (1980))



or (iii) by other redox reactions such as the photo-Kolbe reaction of formate penultimate metabolite:



By comparing the initial rates, NH_4^+ appears as a primary product by contrast to NO_3^-

No nitrogen balance in solution for both azo-dyes. \Rightarrow deeper analyses in the gas phase



Case of dinitrogen

Experimental evidence for dinitrogen formation:

 MS analysis in a static vacuum-tight cell

 GC analysis in an air-tight batch slurry photoreactor

For Congo Red, the mass balance in nitrogen was equal to 100 %.

The mol fraction x_N of N atoms in the final dinitrogen produced by CR degradation is equal to:

$$x_N = 2 n_{N_2} / [(n_{NH_4^+} + n_{NO_3^-}) + 2 n_{N_2}] = 0.65 \approx 2/3$$

The ratio 2/3 is just the mol fraction of N atoms contained in the double -N = N- azo-groups of Congo-Red.

Similar results were found with the single azo- group dye in Amaranth.

The photocatalytic degradation of “azo” groups generates gaseous nitrogen.

FORMATION OF N₂ FROM DIAZOIC DYES

It can be accounted for by a simple reaction with a radical, referring indifferently to an oxidation or to a reduction process such as:

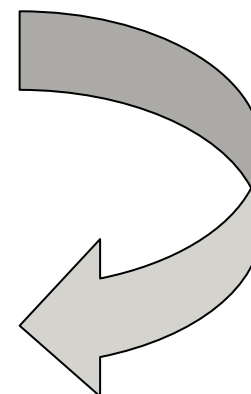
or :



or :



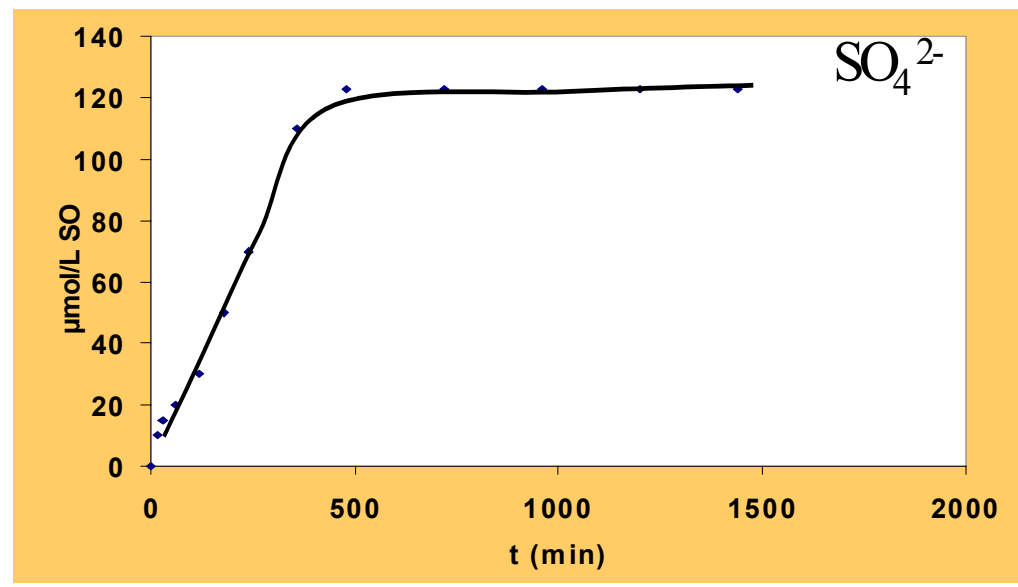
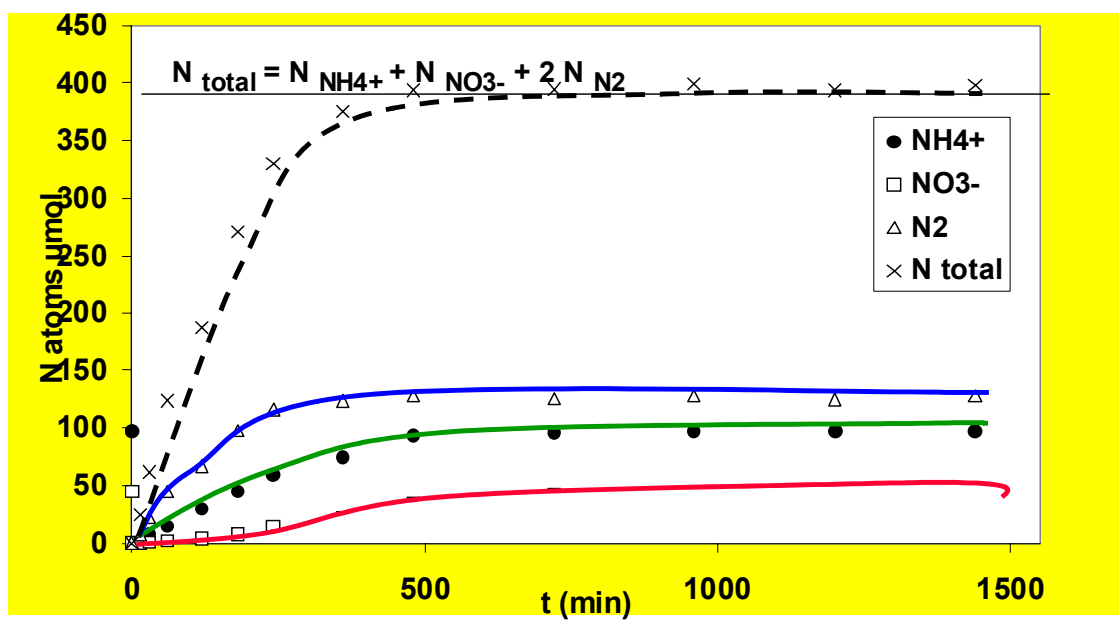
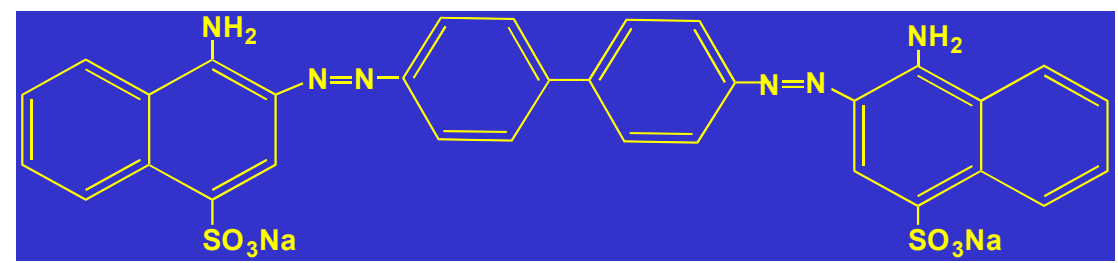
Then :



Radicals R[°] subsequently follow the same degradation process by additional OH[°] radicals.

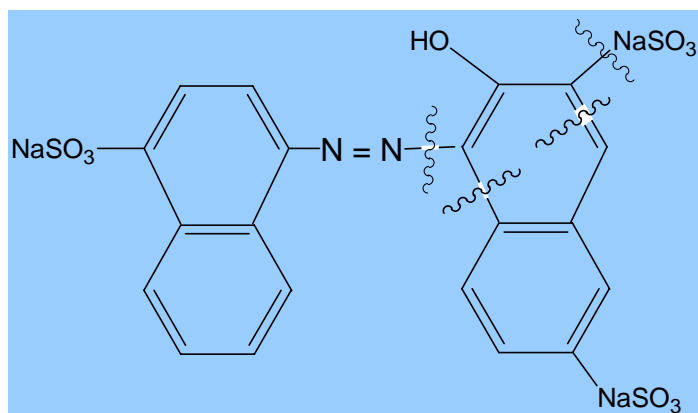
N₂ evolution constitutes the ideal case for a decontamination reaction involving totally innocuous nitrogen-containing final product.

Mineralization of CONGO RED heteroatoms

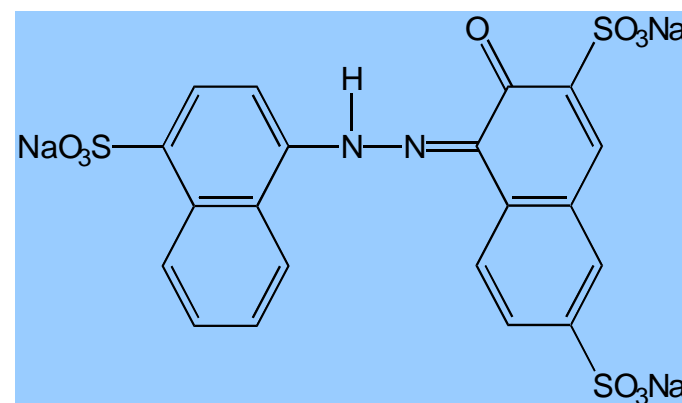
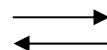


Case study of the photocatalytic degradation of the prohibited alimentary dye Amaranth

(PhD thesis of Mrs Maithaa Karkmaz-Le Du)



Azo form



Hydrazone form

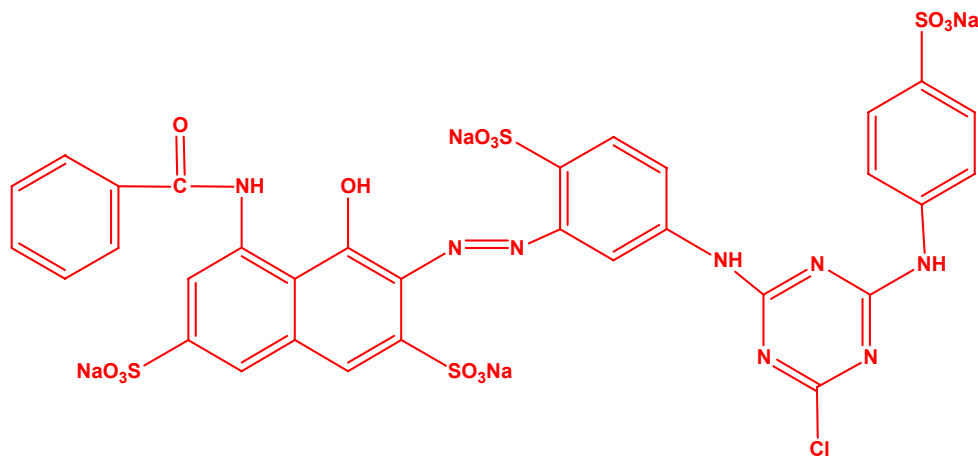
Establishment of the stoichiometric coefficients in Amaranth ($C_{20}H_{11}N_2O_{10}S_3Na_3$) photocatalytic degradation

Element in $C_{20}H_{11}N_2O_{10}S_3^{3-}$	Analytical Method	Final product containing the element	Stoichiometric coefficients found
Carbon $C_{20}H_{11}N_2O_{10}S_3^{3-}$	TOC	CO_2	20
Hydrogen $C_{20}H_{11}N_2O_{10}S_3^{3-}$	pH	H^+	3
Nitrogen $C_{20}H_{11}N_2O_{10}S_3^{3-}$	GC	N_2	1
Sulfur $C_{20}H_{11}N_2O_{10}S_3^{3-}$	ionic HPLC	SO_4^{2-}	3
Oxygen $C_{20}H_{11}N_2O_{10}S_3^{3-} + xO_2(g)$	DCO	H_2O	$\Sigma n_O = 56$ $xO_2 = 23$

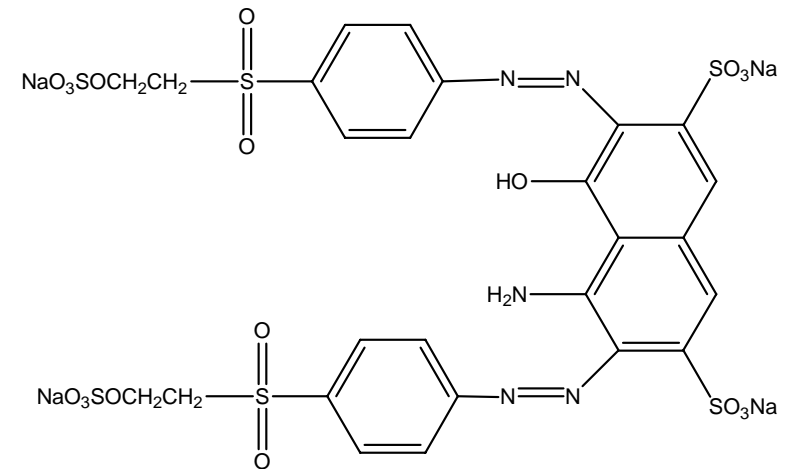
$$C_{20}H_{11}N_2O_{10}S_3^{3-} + 23 O_2 \rightarrow 20 CO_2 + N_2 + 3 SO_4^{2-} + 3H^+ + 4H_2O$$

Case study of the photocatalytic degradation of two textile dyes polluting waters in Vietnam

(PhD thesis of Miss Thu Hoai BUI)

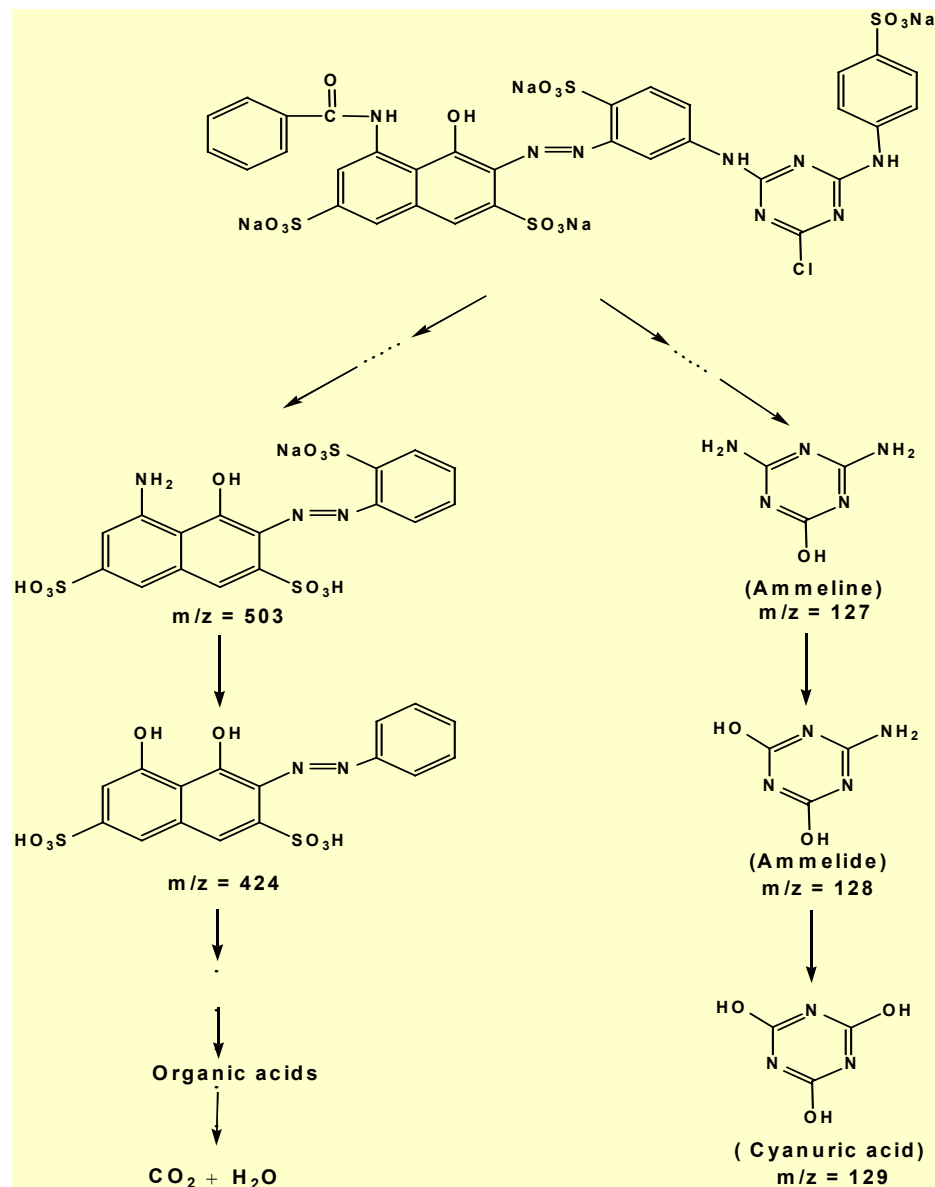


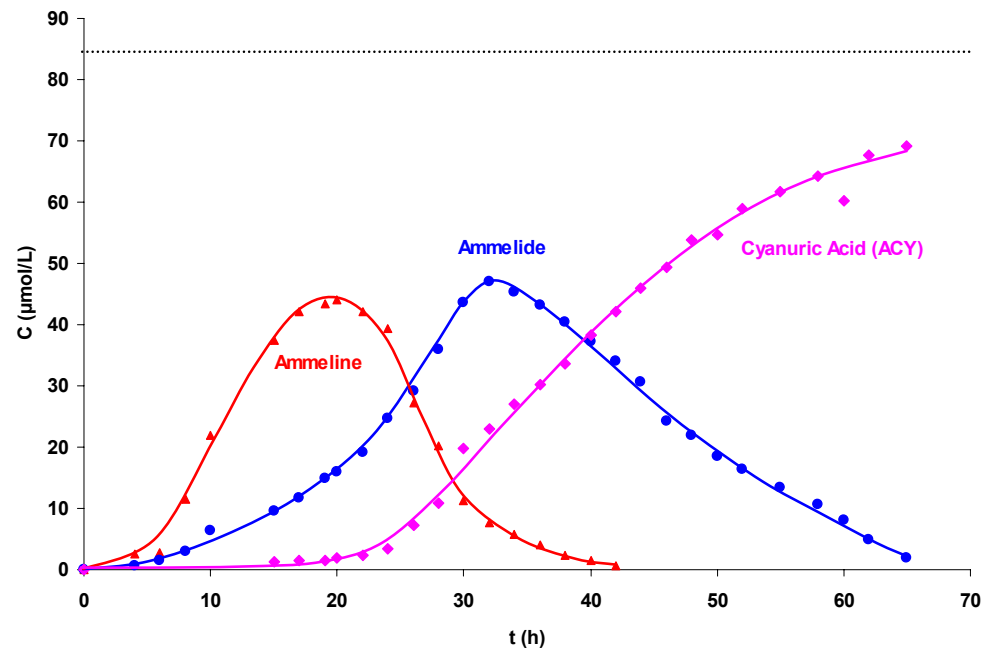
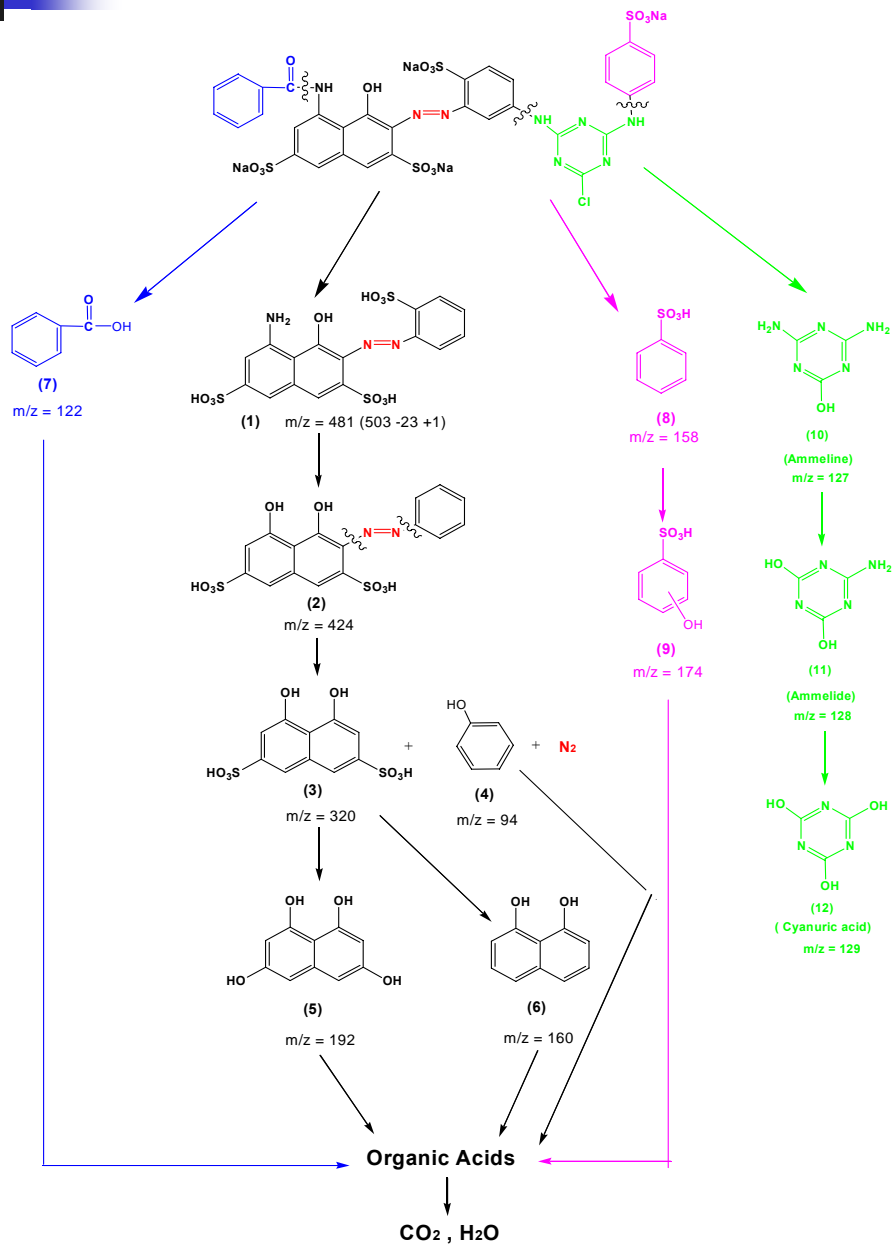
Reactive Red - 4 (Cibacron Brilliant Red 3B-A); $\lambda_{\max} = 517 \text{ nm}$



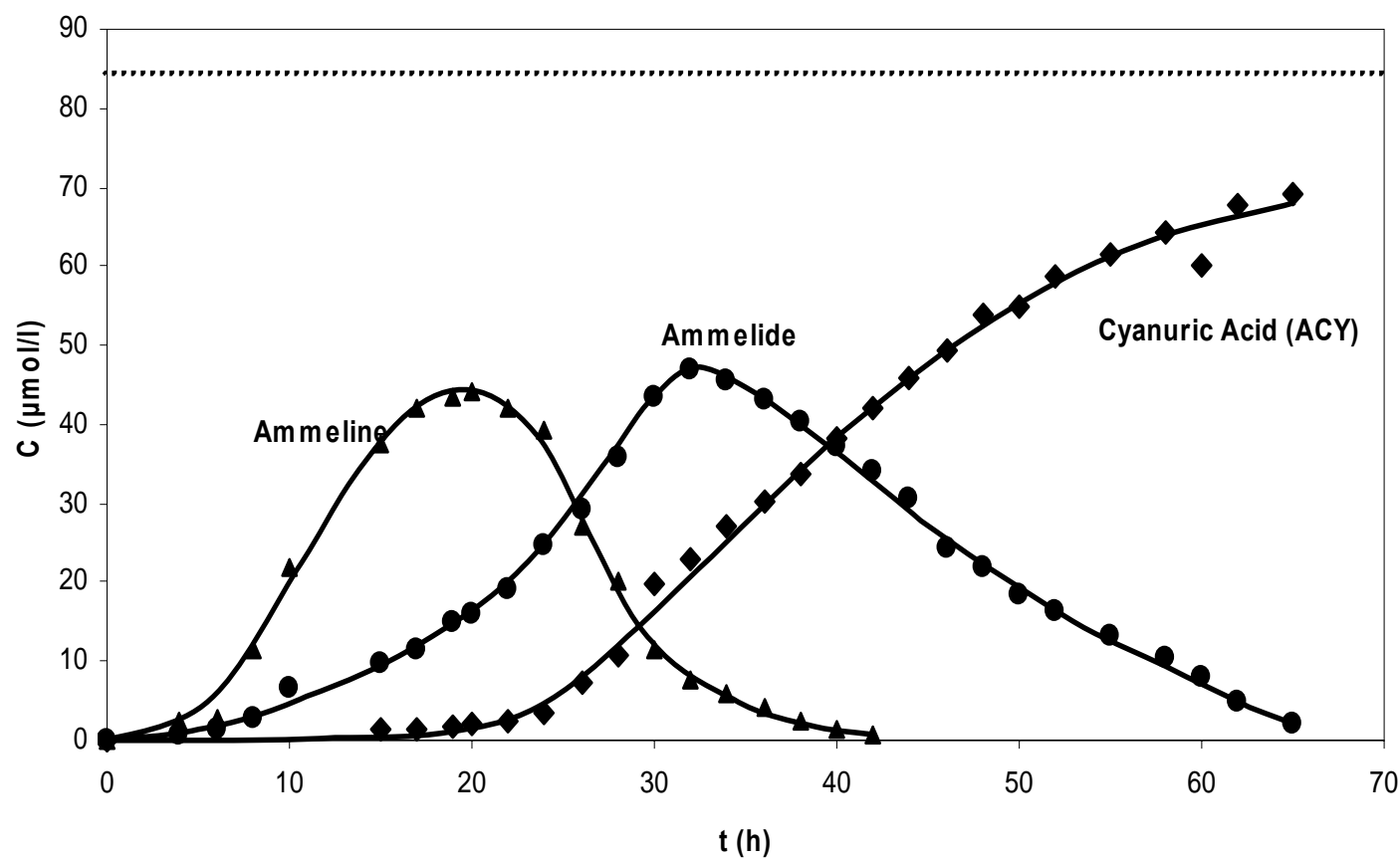
Reactive Black - 5 (Remazol Black B); $\lambda_{\max} = 597 \text{ nm}$

Degradation scheme of Reactive Red 4 into aromatic products

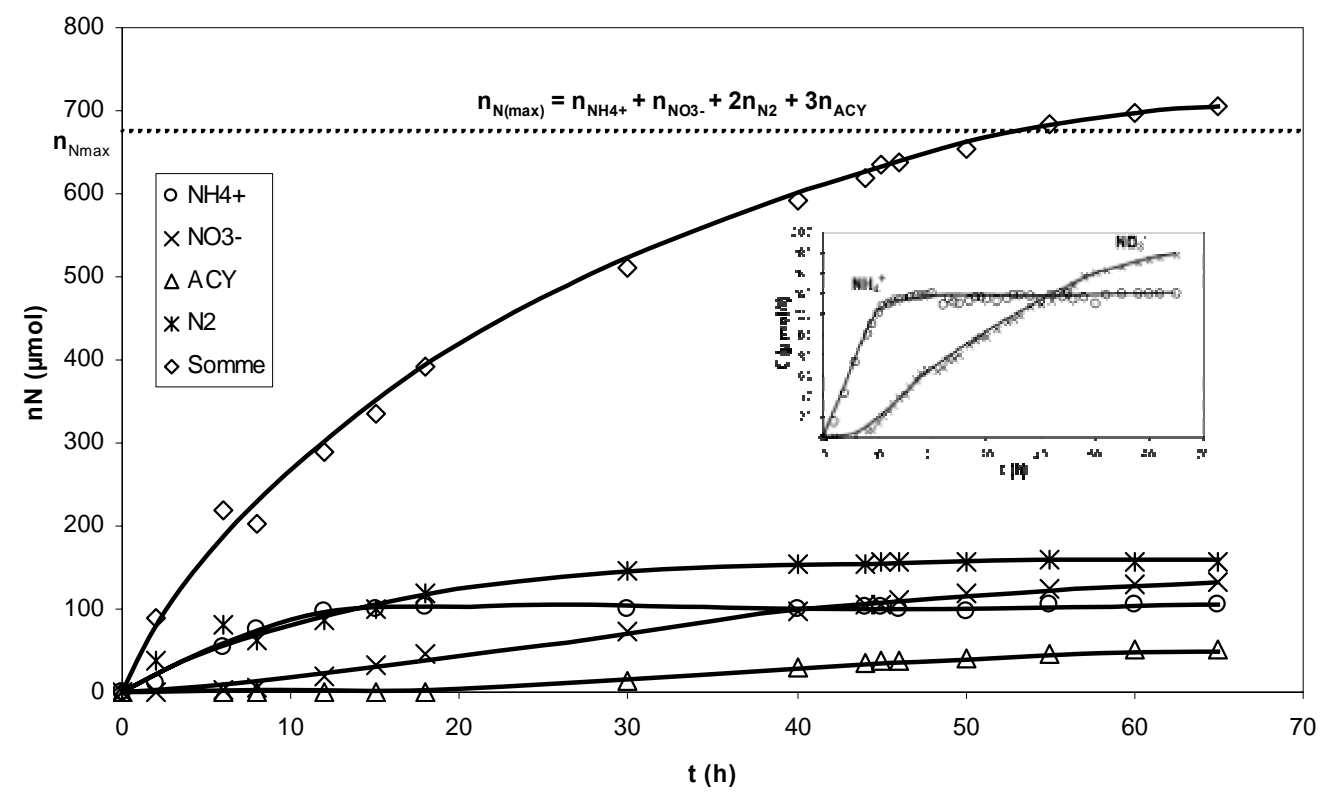




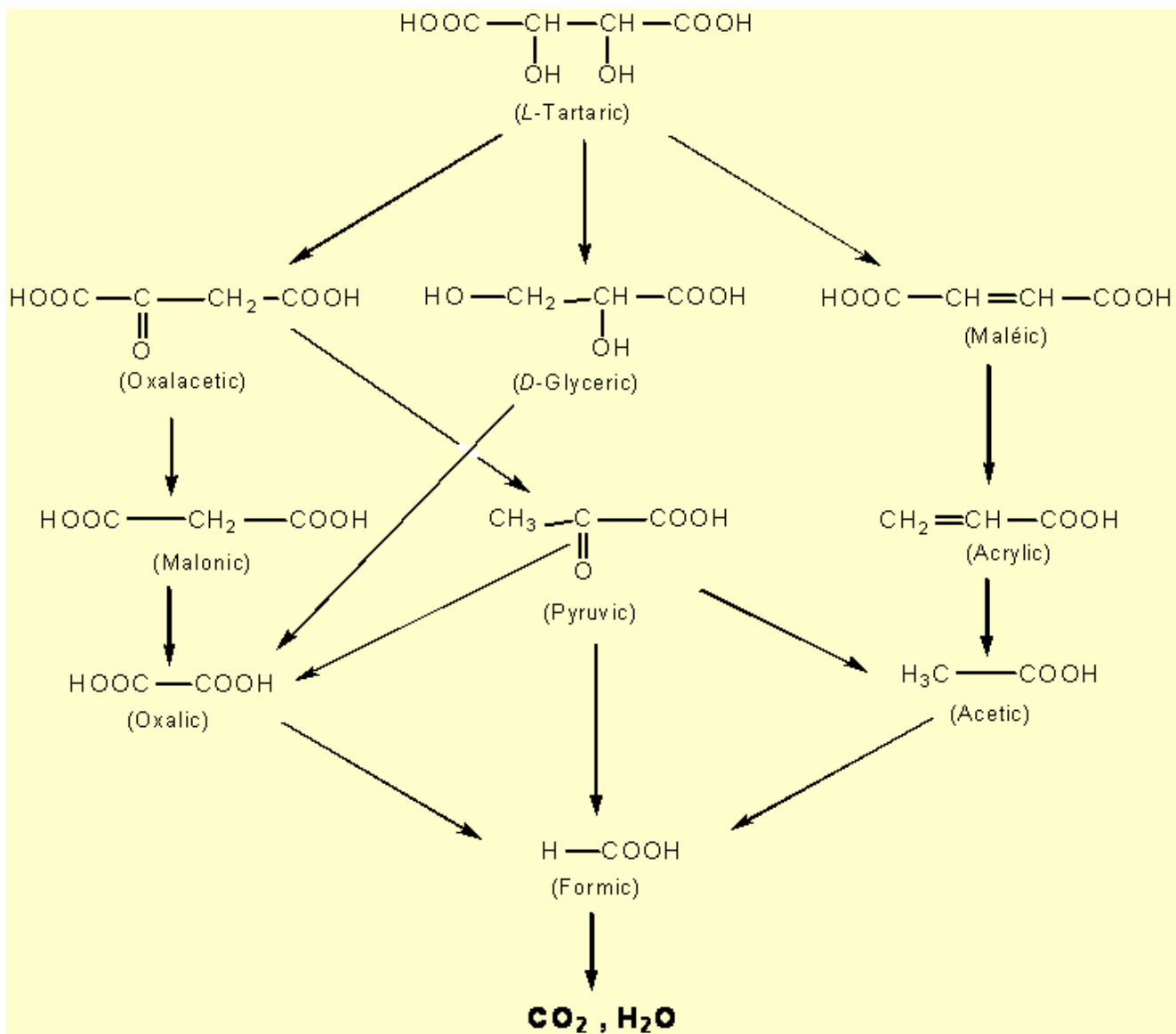
Temporal variations of intermediate products containing a triazinic aromatic ring and identified by UV-HPLC during the photocatalytic degradation of Reactive Red 4



Kinetics of Nitrogen-containing final products

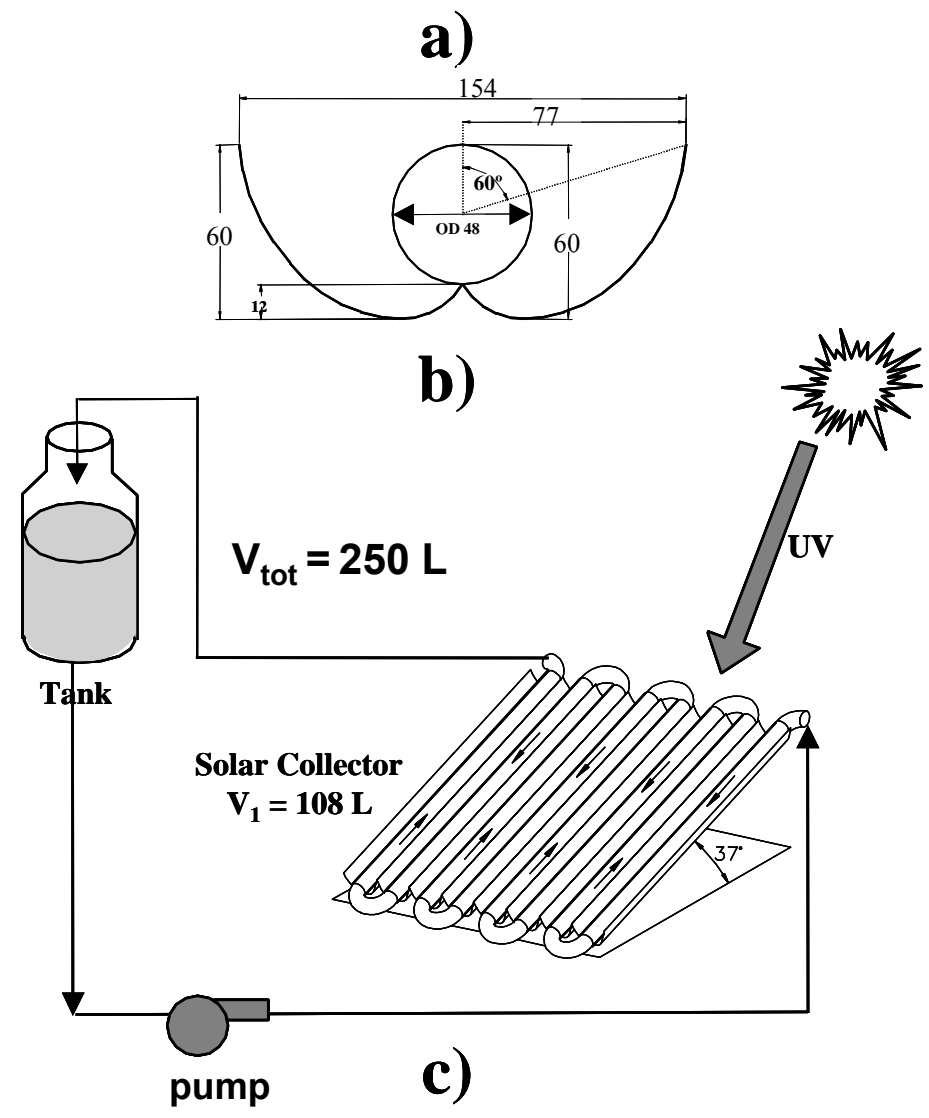


Reaction pathway of the formation of organic acids during RN5 photodegradation

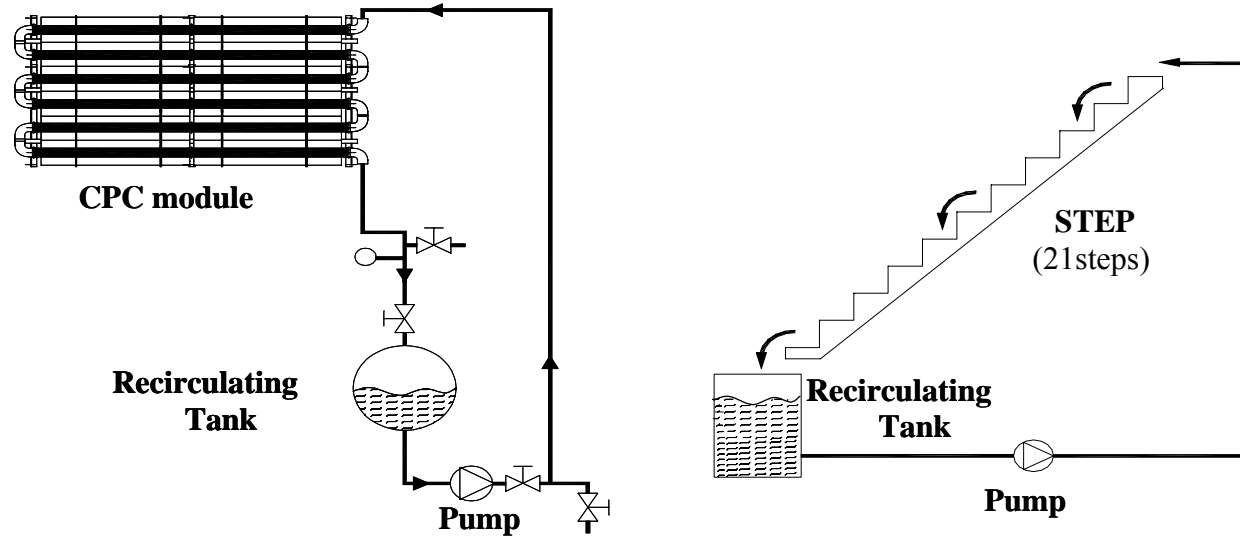




Slurry solar photoreactor at PSA (3 modules in series)



Pilot experimentations at Plataforma Solar de Almeria



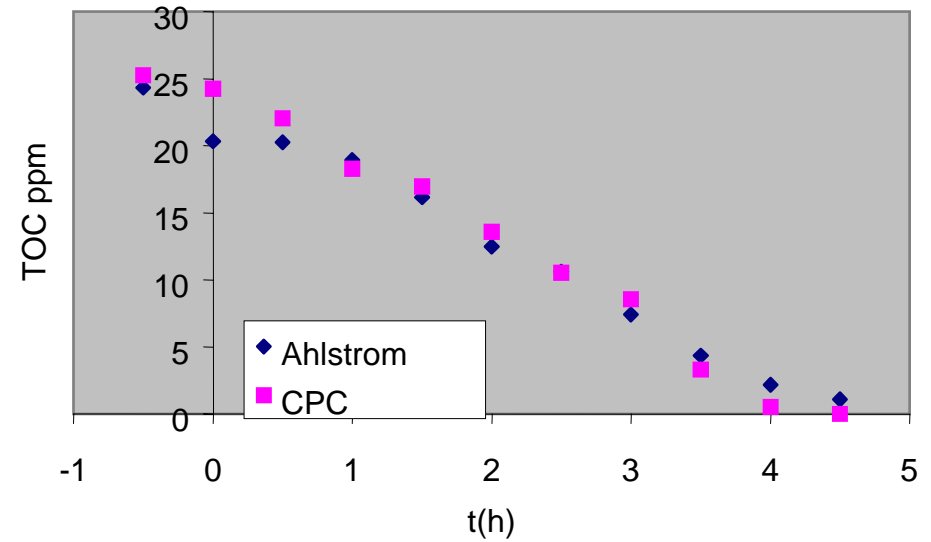
The two pilot photoreactors used in the experiment performed in the presence of (A) TiO_2 powder (CPC photoreactor) and (B) coated titania (STEP photoreactor)

CPC: Compound Parabolic Collector

Degradation of 4-Chlorophenol



Comparison of Ahlstrom and CPC photoreactors with 0.2g/L P-25



Domaine Latour (Burgundy, France)

Pulverisation of pesticides

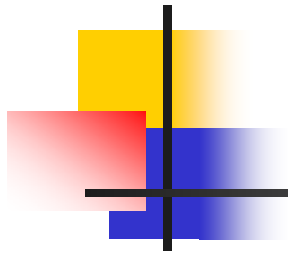




**Washing of the tractor
(+ tank + nebulizers)**



Collection and transport of the effluent



Photocatalysis treatment of the effluents



with UV-A lamps tested in 2001-2002

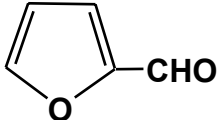
FiberSolutions



with natural UV-A in 2000

Ahlstrom 

Examples of some typical bad-smelling molecules totally degraded by photocatalysis

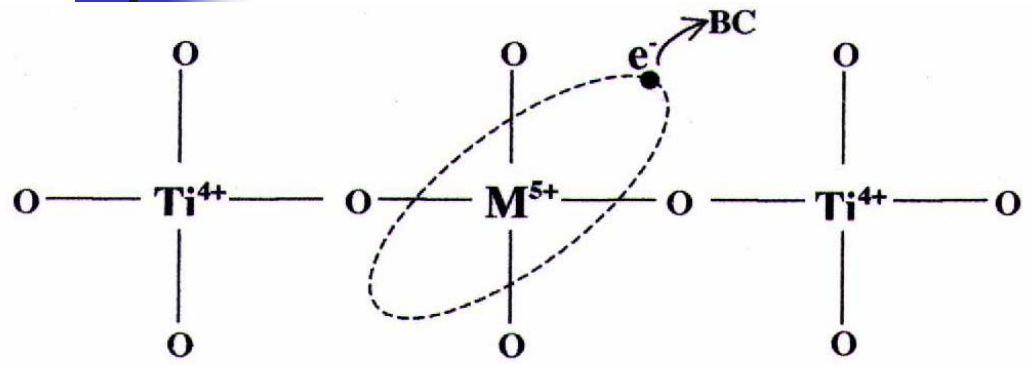
Name	Formula	Origin
Butadione	$\text{CH}_3\text{-CO-CO-CH}_3$	Odor of rancid butter
Dimethyl-disulfide	$\text{CH}_3\text{-S-S-CH}_3$	Odor de cabbage
Furfural		Odor of burnt milk
Valeric Acid	$\text{CH}_3\text{-(CH}_2\text{)}_3\text{-COOH}$	Odor of corporal perspiration
2-heptanone	$\text{CH}_3\text{-CO-(CH}_2\text{)}_4\text{-CH}_3$	Odor of strong cheese (Roquefort,...)

French patent on Photocatalytic elimination of odors in refrigerators (2004)

Photocatalytic device for air and odor treatment in domestic refrigerators

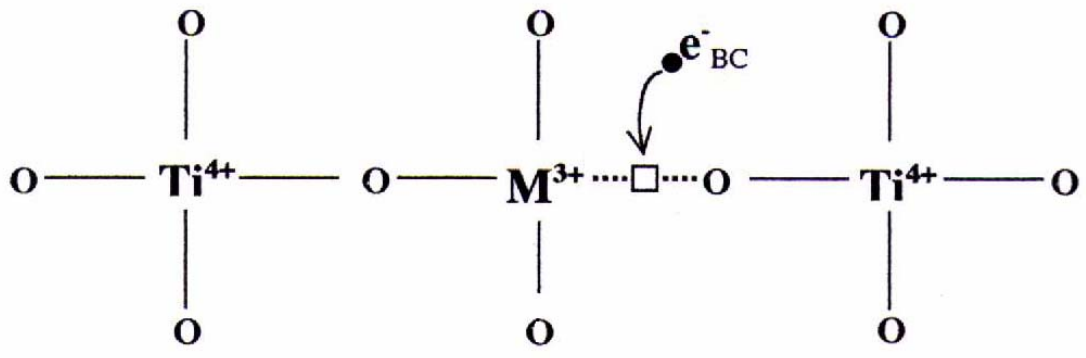
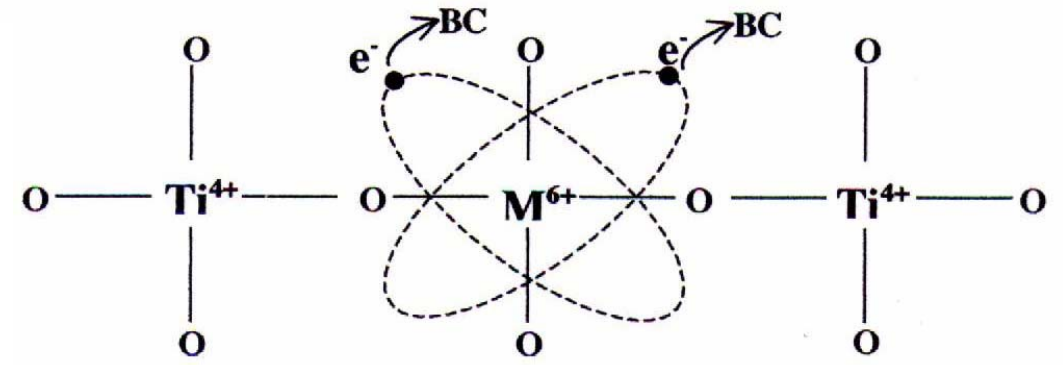


French Patent (n° 0403448 (01/04/04)) **Odor treatment device, especially in refrigerators**
C.GUILLARD, JM HERRMANN, JP CHEVRIER, C BERTRAND, E. PHILIBERT
Patent immediately followed by 40,000 units production



n-doping by M^{5+} (Nb, Ta, Sb)

n-doping by M^{6+} (Mo)

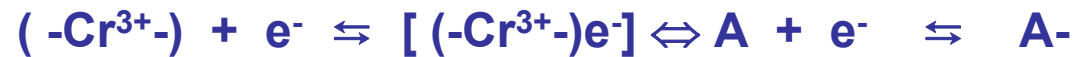


p-doping by M^{3+} (Cr, Ga, Fe, Al)

EFFECT OF Cr³⁺-DOPING OF TiO₂ FOR VARIOUS REACTIONS AND MEDIA

Medium	Reaction	Inhibition factor
liquid organic	$\text{Cyclo-C}_6\text{H}_{12} + \text{O}_2 \longrightarrow \text{cyclo-C}_6\text{H}_{10}\text{O} + \text{H}_2\text{O}$	25
liquid organic	$\text{CH}_3 - \text{CHOH} - \text{CH}_3 (\text{liq}) + \frac{1}{2} \text{O}_2 \longrightarrow \text{H}_2\text{O} + \text{CH}_3 - \text{CO} - \text{CH}_3$	25
gaseous organic	$\text{CH}_2 = \text{CH} - \text{CH}_3 (\text{g}) + \frac{1}{2} \text{O}_2 \longrightarrow \text{CH}_2 - \underset{\text{O}}{\text{CH}} - \text{CH}_3$	55
aqueous phase	$\text{HC}_2\text{O}_4^- (\text{aq}) + \frac{1}{2} \text{O}_2 + \text{H}^+ \longrightarrow 2\text{CO}_2 + \text{H}_2\text{O}$	~ 85
surface	$^{18}\text{O} = ^{18}\text{O} (\text{g}) + ^{16}\text{O}_\text{S} \longrightarrow ^{18}\text{O} = ^{16}\text{O} (\text{g}) + ^{18}\text{O}_\text{S}$	~ 10 ³

Substitutional doping of titania by M^{3+} dissolved trivalent cations ($M = Fe ; Cr ; Ga$)



A = acceptor center

N = neutral center



Balance



$$[Cr^{3+}] = 0.86 \text{ at.}\% \Rightarrow [Cr^{3+}] = 2.50 \times 10^{20} \text{ ions/cm}^3$$

Recombination rate R:

- undoped sample : $R = k_R [e^-] [h^+]$

- doped sample : $R' = k_R ([e^-] + [A^-]) [h^+] = k_R ([e^-] + [2.50 \times 10^{20}]) [h^+] \approx k'_R [h^+]$

$$\Rightarrow R' \gg R$$

The recombination rate R is of second order \Rightarrow It strongly increases with concentrations and becomes of apparent first order

SOLAR PHOTOCATALYSIS: « HELIO-PHOTOCATALYSIS »

Two European Programs on « Water Potabilization by Photocatalysis in Semi-Arid Countries »

Aim : Potabilization of 1m³ water per day by photocatalysis using deposited titania in a robust solar photoreactor.



AQUACAT Project

Coordinator Jean-Marie HERRMANN (LACE, France)

Europe (France, Spain, Portugal, Switzerland) – North Africa (Egypt, Morocco, Tunisia)



SOLWATER Project

Coordinator Julian BLANCO (PSA, Spain)

Europe (Spain, Portugal, France, Switzerland, Greece) – Latin America (México, Peru, Argentina)



Life Applications



- ↪ Purification of air in confined atmospheres :
Offices, workshops, cellars, planes, submarines, automobiles, « molecular » air purity required in Electronics clean rooms – **Joseph DUSSAUD**
- ↪ Elimination of odors :
Toilets, refrigerators (Thomson-Brandt, French Patent (2004) + 40.000 units produced ; pig farms - **Pr Alain LAPLANCHE**
- ↪ Self cleaning glasses (St Gobain, Pilkington, LACE) – **Mrs Dr. Chantal GUILLARD, CNRS**
- ↪ Photocatalytic antibacteriologic Gas masks – **Michael HOFFMANN**
Research for US Army (future extension to civilians??)
- ↪ Purification of used farming waters : elimination of usual pesticides - **Joseph DUSSAUD**
- ↪ Drink water production ($1\text{m}^3/\text{d}$) for isolated populations in semi-arid countries by autonomous solar pilot plants
European Programmes AQUACAT (coordinated by LACE) (North Africa) and SOLWATER coordinated by J. Blanco (Latin America)



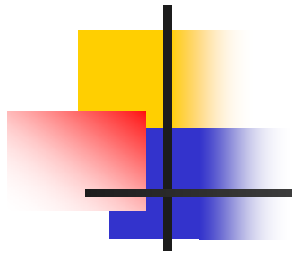
Present **Challenges in Photocatalysis**



- 1) Are we « condemned » to exclusively work with titania?
- 2) Can TiO_2 be photosensitized in the visible by doping ?
 - 1) cationic doping = no ; 2) anionic doping = to be proved
- 3) Can we find a new photocatalyst different from TiO_2 and directly active in the visible ?
- 4) Is photocatalysis suitable for preparative Fine Chemistry ?
- 5) Is photocatalysis enough bactericide in water and in air ?
- 6) Is Photocatalysis really « cancericide » ?
- 7) Are we able to define a few standardized tests for any photocatalytic system ?

Advantages of the Photocatalytic Purification of Water

- ↪ Total mineralization of aqueous pollutants (into CO_2 , H_2O , Cl^- , NO_3^- , SO_4^{2-} , HPO_4^{2-} ) in most cases (exception of atrazine → cyanuric acid)
- ↪ Wide applicability (many pollutants treated)
- ↪ Safety of the process (harmless TiO_2 catalysts, no chemical additives to water)
- ↪ Unexpensive reactants : air, cheap catalyst ($\approx 15 \text{ € / kg}$)
- ↪ High stability of the catalyst under UV at various pH and possibility of recycling it
- ↪ Process active at room temperature ($-40 \leq t^\circ\text{C} \leq 80^\circ\text{C}$) : no need of thermal energy for heating water (known as having a very high heat capacity)
- ↪ Efficient process for purifying air (suppression of odors)
- ↪ Use of solar energy



UP
LACE
CS



The Twelve Principles of Green Chemistry*

1. Prevention
2. Atom Economy
3. Less Hazardous Chemical Syntheses
4. Designing Safer Chemicals
5. Safer Solvents and Auxiliaries
6. Design for Energy Efficiency
7. Use of Renewable Feedstocks
8. Reduce Derivatives
9. Catalysis
10. Design for Degradation
11. Real-time analysis for Pollution Prevention
12. Inherently Safer Chemistry for Accident Prevention

* Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*, Oxford University Press: New York, 1998, p.30. By permission of Oxford University Press.

1. Prevention

It is better to prevent waste than to treat or clean up waste after it has been created.

2. Atom Economy

Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

3. Less Hazardous Chemical Syntheses

Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4. Designing Safer Chemicals

Chemical products should be designed to effect their desired function while minimizing their toxicity.

5. Safer Solvents and Auxiliaries

The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.

6. Design for Energy Efficiency

Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

*Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*, Oxford University Press: New York, 1998, p.30. By permission of Oxford University Press.

7. Use of Renewable Feedstocks

A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

8. Reduce Derivatives

Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

9. Catalysis

Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10. Design for Degradation

Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

11. Real-time analysis for Pollution Prevention

Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

12. Inherently Safer Chemistry for Accident Prevention

Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

* Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*, Oxford University Press: New York, 1998, p.30. By permission of Oxford University Press.

Agricultural Perspectives

AGRICULTURAL AREA OF EL EJIDO (SPAIN)

100 000 HA OF GREEN HOUSES

5X10⁶ CONTAINERS

10⁶ M³ OF CONTAMINATED WATERS TO BE RECYCLED

A PILOT PLANT HAS BEEN BUILT FOR COLLECTING, RINSING AND RECYCLING PLASTIC OF USED BOTTLES OF PESTICIDES : WATER IS PURIFIED BY SOLAR PHOTOCATALYSIS FOR ITS RECYCLING.

BURGUNDY (FRANCE)

PHOTOCATALYTIC PURIFICATION OF USED WATERS RESULTING FROM THE RINSING OF AGRICULTURAL MACHINERY (TRACTORS, NEBULIZERS, EMPTY PEST BOTTLES...) BEFORE THEIR RELEASE TO THE RIVER.

Possibilities

- ↪ Small photocatalytic units for recovering silver from photographic baths.
- ↪ Use of UV-lamps working at night (cheap electricity out of rush hours)
- ↪ High final ratios $m_{\text{Ag}}/m_{\text{TiO}_2}$
- ↪ Easy separation of Ag from TiO_2
(chemical treatment in HNO_3 , sonolysis, decantation, filtration).
- ↪ Need of more stringent environmental regulations

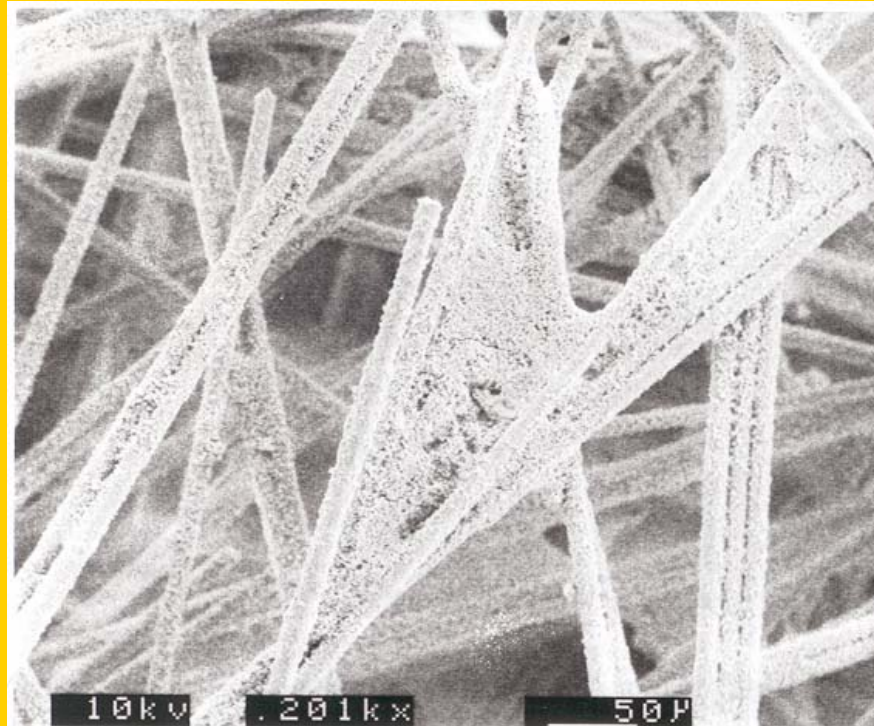
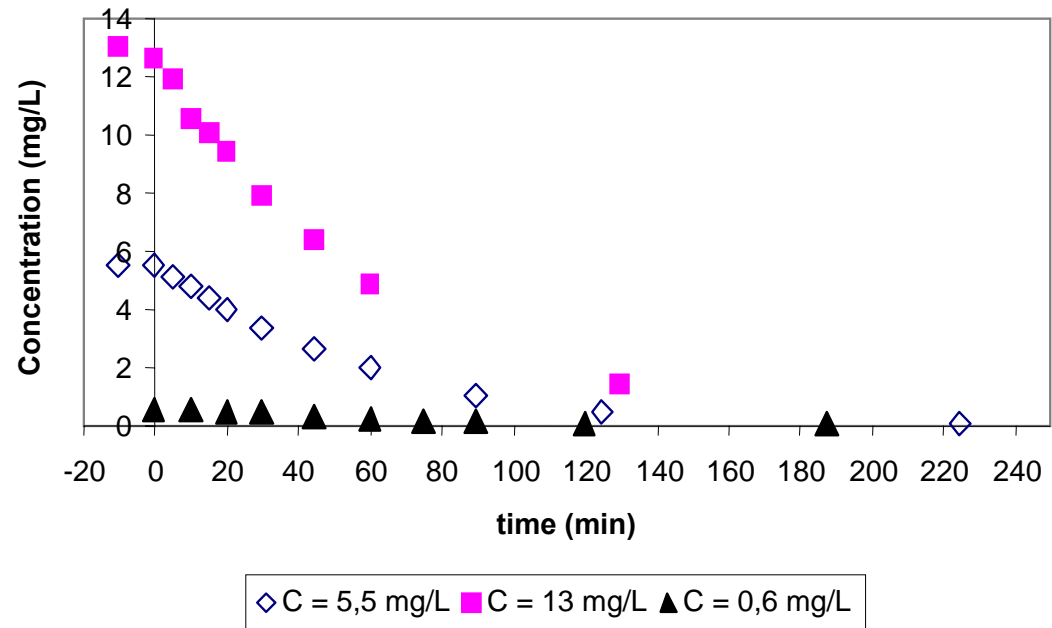
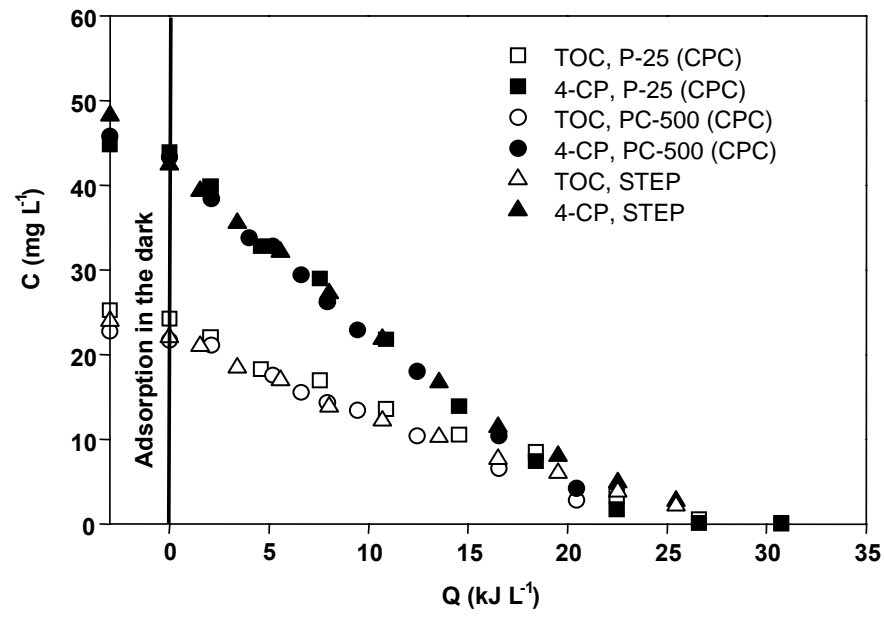


Figure 1

Photocatalytic filter (SEM observation)

Imidaclopride/ Step Reactor





Comparison of the disappearance of 4-chlorophenol and of its TOC when using suspended Millennium PC500 and Degussa P25 in CPC and Millennium PC500 coated on non-woven paper in the STEP photoreactor.

ORIGIN OF GASEOUS DINITROGEN EVOLUTION

Two favorable reasons :

- (i) the $-N=N-$ azo-group appears as an easy potential precursor of $N\equiv N$, with already one double bond existing ;
- (ii) nitrogen atoms in $-N=N-$, are already formally at an oxidation state close to zero, i.e. that of nitrogen in N_2 (by convention).

Actually, what is the oxidation degree of nitrogen in an azoic dye?



1st attempt of calculation:

$R-N=N-R'$ is a “di-imide-like” product

$$\Rightarrow \mathbf{2 + 2x = 0 \Rightarrow x = -1}$$

2nd attempt of calculation:

$R-N=N-R'$ results from $R^{\delta-}-H^{\delta+}$

$$\Rightarrow \mathbf{-2 + 2x = 0 \Rightarrow x = +1}$$

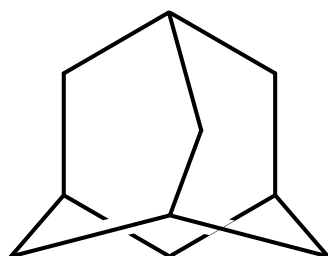
3rd attempt of calculation (based on $R-N=N-R'$ synthesis) :



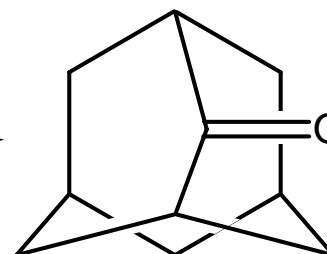
$$(+1)(-3) \quad (-2)(+3)(-1) \quad (+1)(x)(x)(-1)$$

$$\Rightarrow \mathbf{2x + 1 - 1 = 0 \Rightarrow x = 0}$$

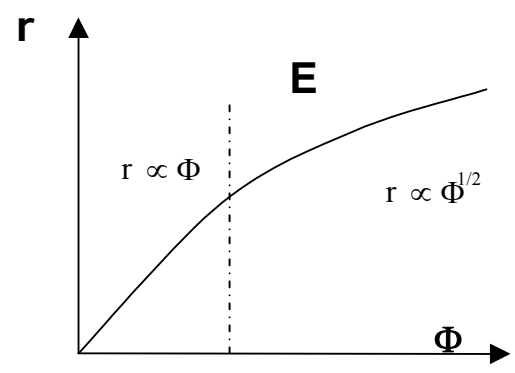
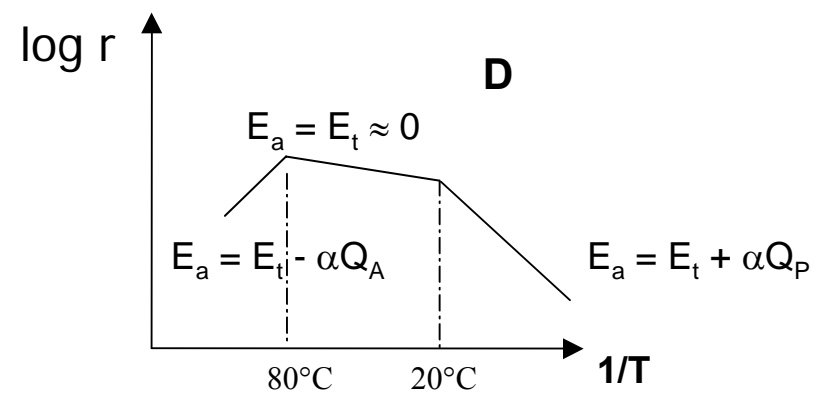
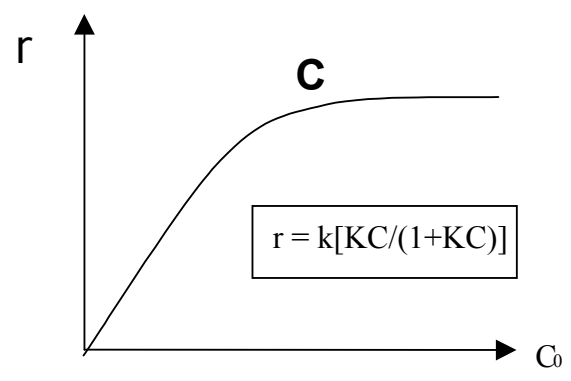
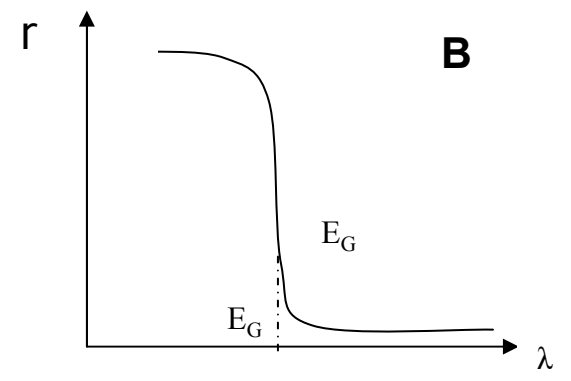
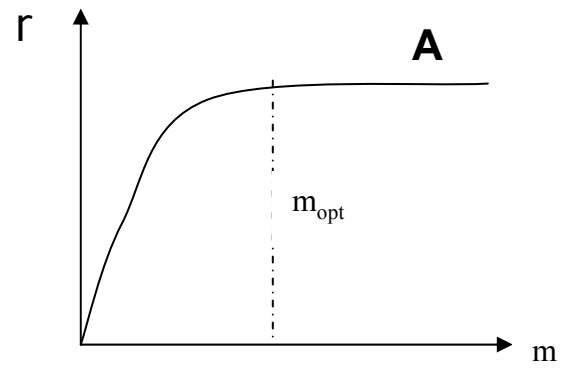
Other example (Ch. Giannotti)



adamantane



adamantone



Influence of the different physical parameters which govern the reaction rate. (A): mass of catalyst; (B): wavelength; (C): initial concentration of reactant; (D): temperature; (E): radiant flux.

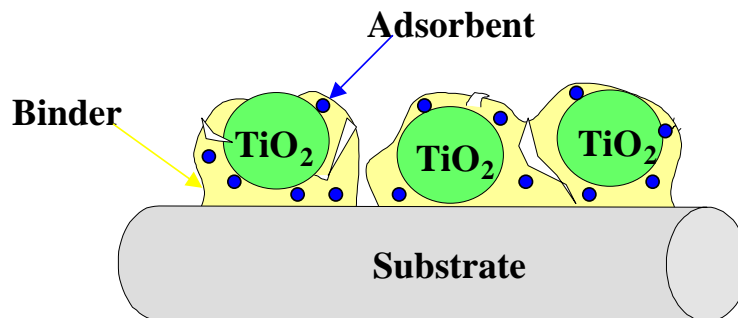


Falling film and slurry solar photoreactors

Ahlstrom photocatalytic coating

Development of a photocatalytic slurry/coating process to coat substrates

- to avoid the necessary postfiltration stage to separate TiO_2 particles from treated effluent



Ahlstrom patent
 EP1069950 granted
 AU 735798 granted
 US 09/467650 pending
 JP 2000-542104 pending

Inorganic binder

- not destroyed by photocatalysis
- transmits UV irradiation

Photocatalytic TiO_2

- selection of the most efficient TiO_2 according to
 - pollution to be treated
 - radiation system (visible, UV)

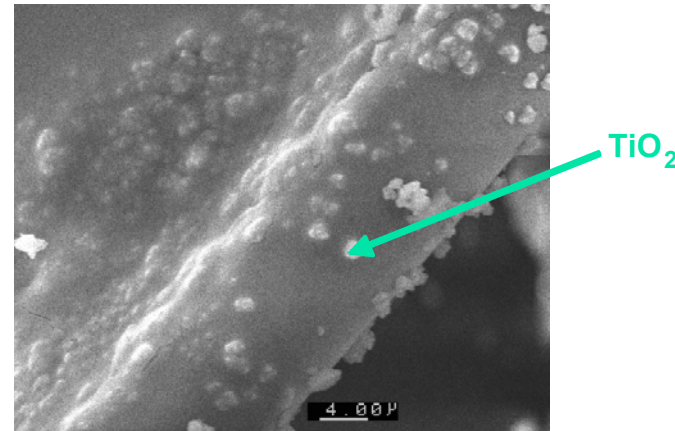
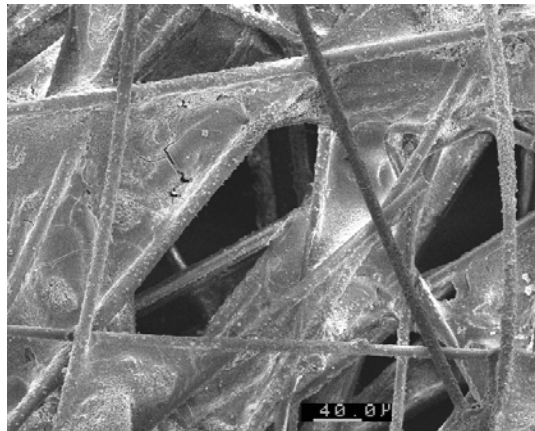
Adsorbent

- removes pollution peak
- regenerated by photocatalysis

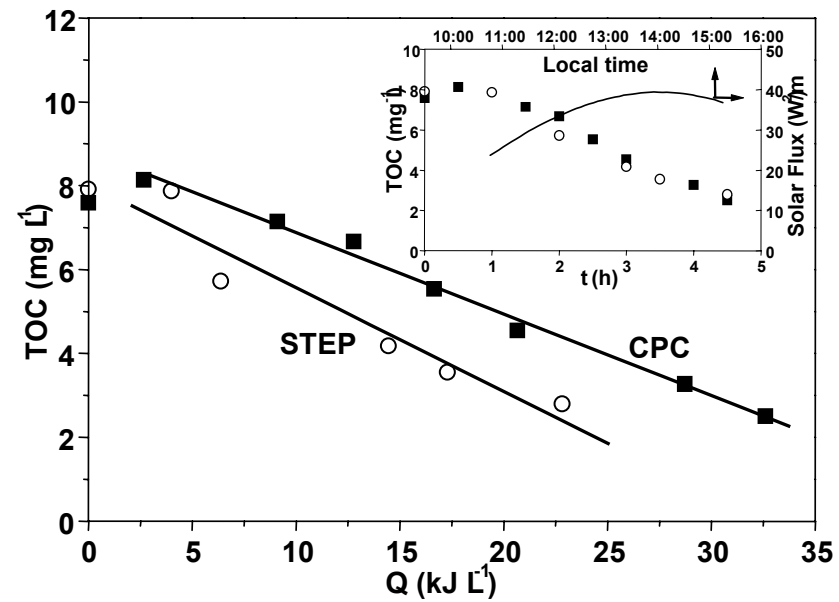
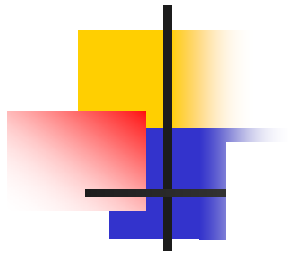
Example

Coating

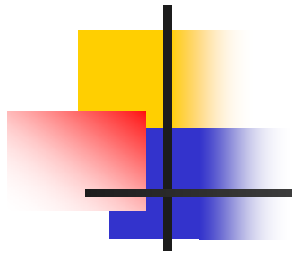
- slurry = as a **paint**
- many substrates such as fibrous ones (filters)



SEM image of a photocatalytic glassfiberpaper (without adsorbent)



Degradation of a pesticide mixture as a function of the total energy collected per litre of solution. In the inset, the variations in the overall solar UV -flux and of TOC concentration are shown as a function of local time.



Jean-Marie Herrmann (DR1)
HEAD

Ch. Delbecque
General Secretary

A. Boréave, IE2, Spectro Masse
C. Duchamp, TRCE, Microscopie
P. Conchon, TRF
Facilities

N. Lapierre (AGT), C. Chanu (AGT)
G. Chapuis (CDD Ezus)
Administrative and Financial Management

S. Chétrit (ADT) 20%, S. Fernandez (AST)
50%, B. Nuhaj (CDD) 50%
Maintenance

Redox Catalysis for the Environment
Group Leader : F. Gaillard

Photocatalysis – Photochemistry
Group Leader : C. Guillard

Functionalized Materials
Group Leader : R. Lamartine

Environmental
Photocatalysis

Photochemistry
of Pesticides

Atmospheric
Photochemistry

Catalytic
Combustion

DeNOx
Catalysis

Progressive
Reforming of
Methane

Oxidation of
Traces

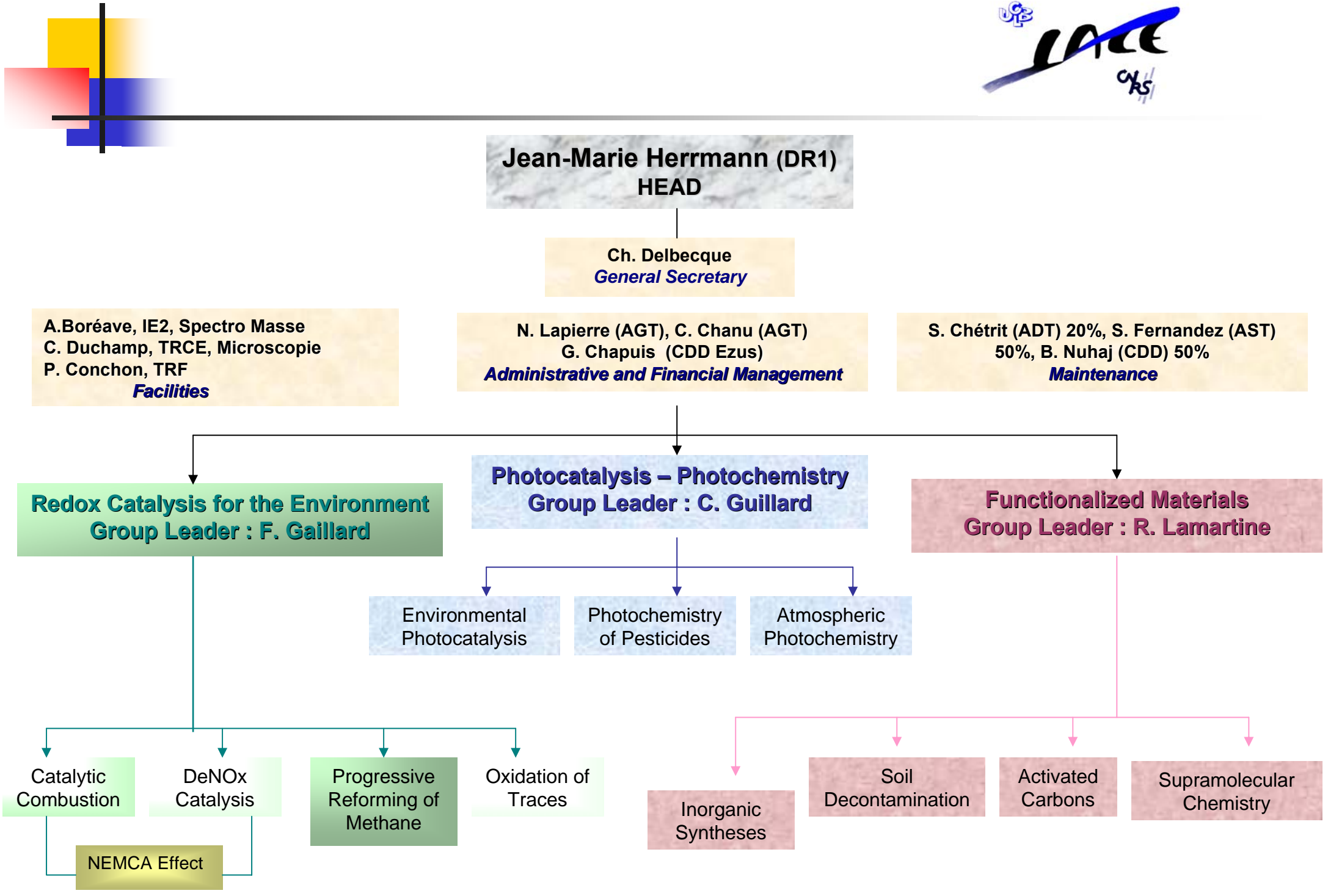
Inorganic
Syntheses

Soil
Decontamination

Activated
Carbons

Supramolecular
Chemistry

NEMCA Effect



DOMAINS OF COMPETENCES OF THE LACE



Themes Environmental Domains	Redox Catalysis	Photocatalysis Photochemistry	Functionalized Materials Adsorption
AIR	<ul style="list-style-type: none"> - Catalytic combustion - DeNOx catalysis - Elimination of traces by catalytic combustion at low temperature - Diesel exhaust catalyts 	<ul style="list-style-type: none"> - Degradation of VOC 's - Elimination of Odors - Reactivity and fate of atmospheric pollutants - Role of water in atmospheric chemistry - Air purification in confined atmospheres - Ultrapurification of air(cleans rooms) 	<ul style="list-style-type: none"> - Synthesis of adsorbants - Activation of carbons - Grafting of macrocycles on supports - On site adsorption of volatile pollutants
WATER		<ul style="list-style-type: none"> - Total degradation of organic pollutants (<i>pesticides,dyes...</i>) - Potabilisation of water by photocatalysis - Solar photocatalytic engineering 	<ul style="list-style-type: none"> - Elaboration of selective adsorbing materials - Grafting of macrocycles on supports - Heavy ions selective traps
SOILS		<ul style="list-style-type: none"> - Solar photochemical degradation of phytosanitary agents - Purification of surface waters - Natural photocatalytic processes 	<ul style="list-style-type: none"> - Adsorption-desorption of pesticides in soils - Soil treatment by thermodesorption and/or by extraction under reduced pressure - Analyses and treatments of gaseous emissions
CLEAN ENERGY	<ul style="list-style-type: none"> - Catalytic combustion of natural gas (without formation of NOx) - Reforming of methane - Production of hydrogen for fuel cells (SOFC) - Exhaust catalyts 	<ul style="list-style-type: none"> - Utilization of solar energy - Valorisation of biomass : Hydrogen production 	<ul style="list-style-type: none"> - Synthesis of thermostable catalyts - Synthesis of water-and sulfur-resistant catalyts