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Coupling heterogeneous photocatalysis with other technologies: a tool for abatement of pollutants in water

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SOLARSAFEWATER SYMPOSIUM
El Challanges of safe drinking water provision:
Technologies for the Latin-American region
Puerto Iguazú, Misiones, Argentina, October 2005

Summary

Photocatalysis: fundamentals and overview

Coupling photocatalysis with other technologies:

Biological treatment and Photofenton

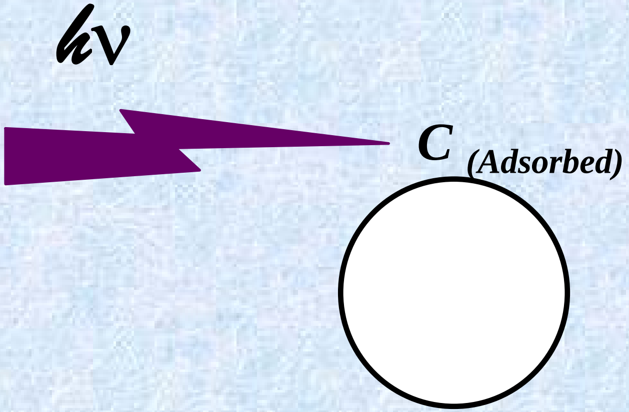
Ozonation

Electrochemical treatment

Membrane reactors

Microwaves

PHOTOLYTIC MECHANISM



$C^{*}_{(Adsorbed)} \rightarrow$ ***Products***

V. Augugliaro, L. Palmisano, M. Schiavello and A. Sclafani
J. Catal. **99** (1986) pp. 62-71

A. Sclafani, L. Palmisano, M. Schiavello, V. Augugliaro, S. Coluccia and L. Marchese
New J. Chem. **12** (1988) pp. 129-135

L. Palmisano, A. Sclafani, M. Schiavello, V. Augugliaro, S. Coluccia and L. Marchese
New J. Chem. **12** (1988) pp. 137-141

M. Anpo Ed. *Surface Photochemistry Vol. 1, J. Wiley & Sons Ltd,* 1996, Chichester, UK

REDOX MECHANISM

When a semiconductor is illuminated by light of suitable energy, i.e. greater than the band gap of the semiconductor:

⇨ electrons (e^-) are promoted from the valence band (vb) to the conduction band (cb) and they have the reducing power of the cb energy;

⇨ positive holes (h^+) are created in the vb and they have the oxidation power of the vb energy.

Evolution of the photoproduced pairs:

(i) recombination (emission of thermal energy and/or luminescence);

(ii) reaction with electron acceptor or donor species (redox reaction, trapping mechanism).

Note: The prevalence of (ii) enhances the photoactivity of the semiconductor, but if the trapping mechanism involves the components of the semiconductor, photocorrosion can occur (ZnO, CdS).

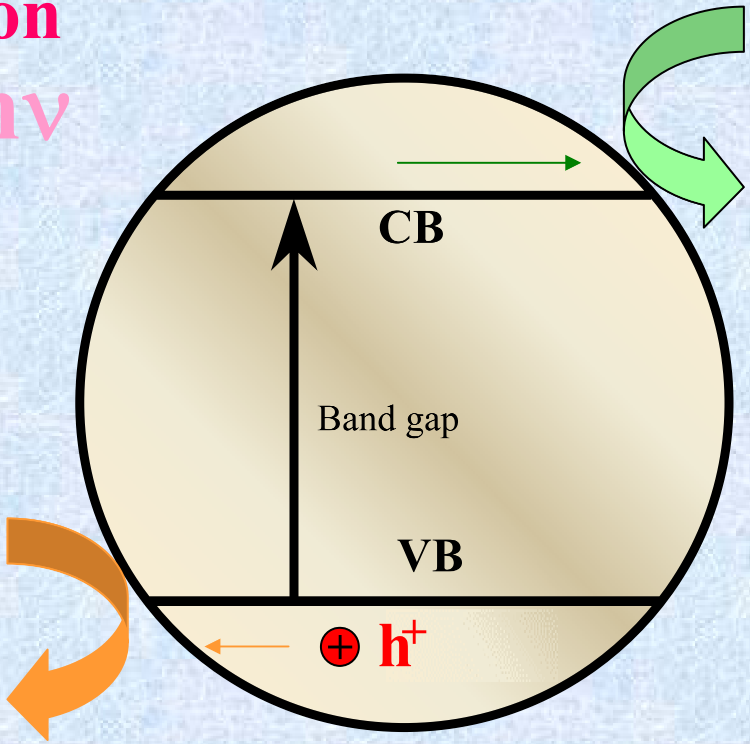
Redox Mechanism

1) Light Absorption

$h\nu$

2) Production of

e^- *e* h^+



3b) Reduction reaction

(with adsorbed O_2)

$A + e^- \longrightarrow A^-$

$O_2 + e^- \longrightarrow O_2^-$

3a) Oxidation reaction

$\text{Substrate} + h^+ \longrightarrow (\text{Substrate})^+$

4) Desorption of products

MAIN REACTION STEPS

$$TiO_2 + h\nu \longrightarrow TiO_2\ (e^-_{CB} + h^+_{VB})$$

$$OH^- + h^+_{VB} \longrightarrow {}^{\bullet}OH$$

$$O_2 + e^-_{CB} \longrightarrow O_2^{\bullet -}$$

$$O_2^{\bullet -} + H^+ \longrightarrow HO_2^{\bullet}$$

$$2\ HO_2^{\bullet} \longrightarrow O_2 + H_2O_2$$

$$HO_2^{\bullet} + H_2O \longrightarrow H_2O_2 + {}^{\bullet}OH$$

$$H_2O_2^{\bullet -} + O_2^{\bullet} \longrightarrow OH^- + {}^{\bullet}OH + O_2$$

$$H_2O_2 + e^-_{CB} \longrightarrow OH^- + {}^{\bullet}OH$$

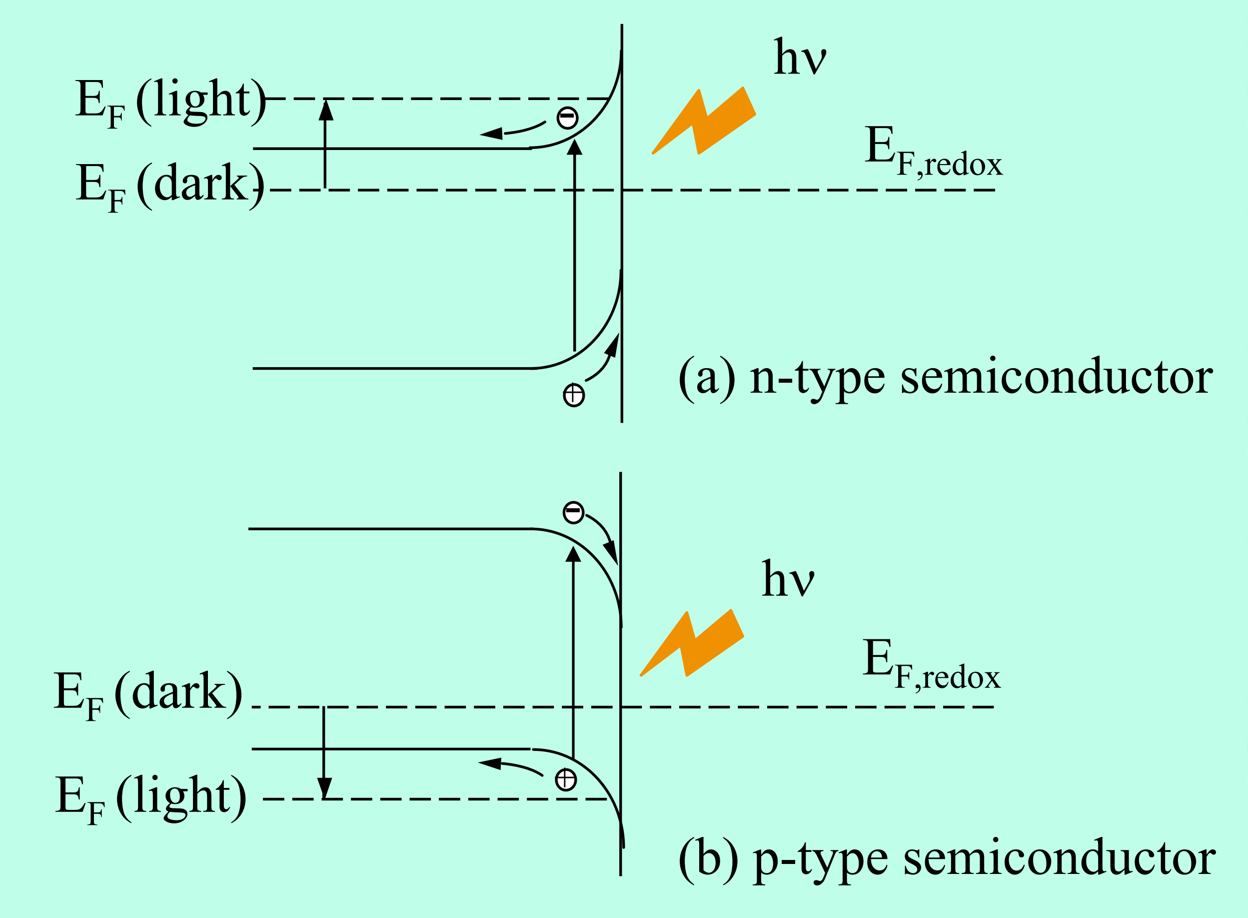
The photocatalytic oxidation is a radicalic reaction that is carried out mainly by means of ${}^{\bullet}OH$ and $HO_2^{\bullet}$ species

ILLUMINATED SEMICONDUCTOR

- Under illumination electrons are promoted from vb to cb and holes are created in the vb.
- The electric field of the space-charge region allows the separation of the photoproduced pairs.
- The equilibrium can be restored by means of a charge transfer to redox species present in the solution.

The system works similarly to an electrochemical cell continuously fed by the impinging photon flux.

ILLUMINATED SEMICONDUCTOR

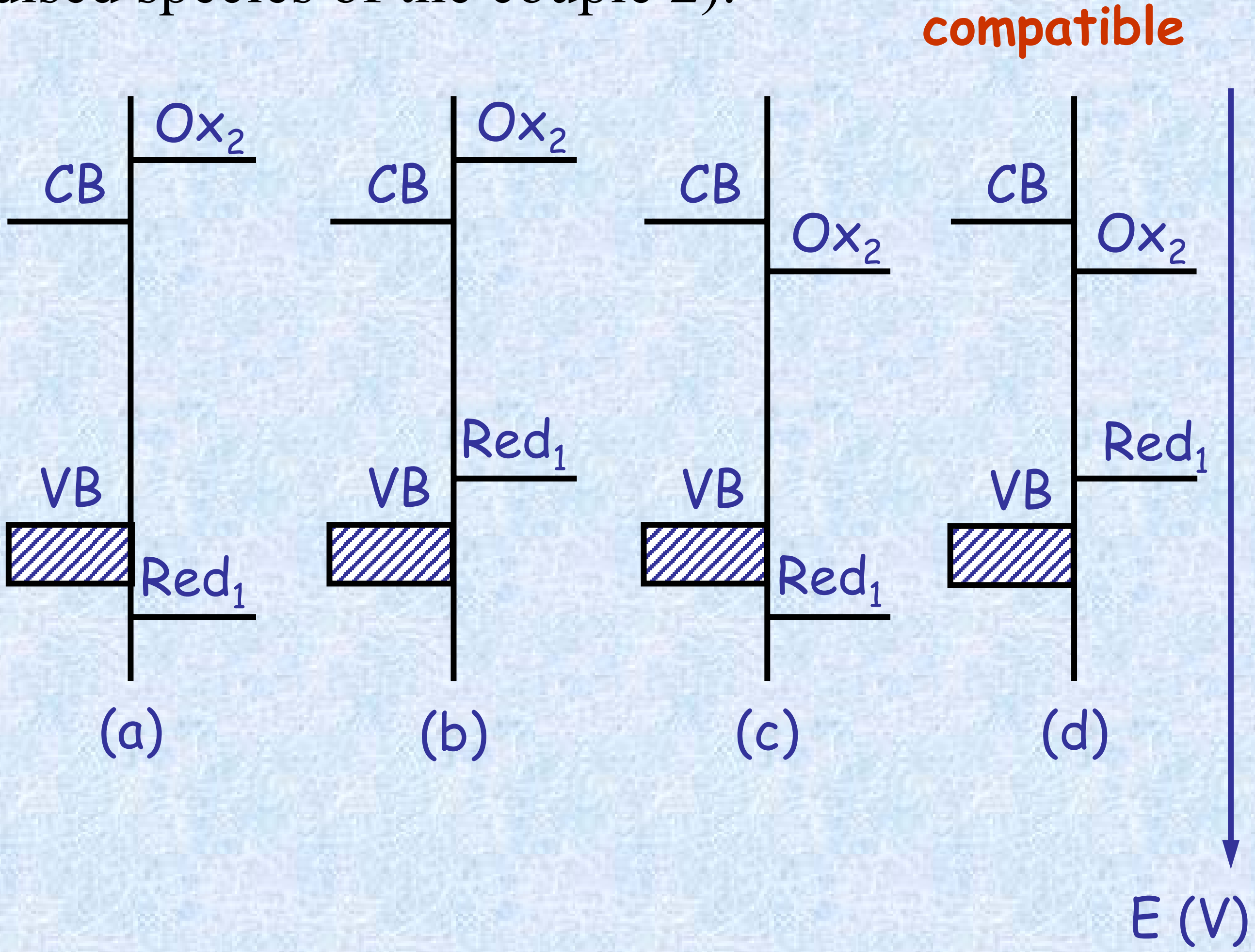


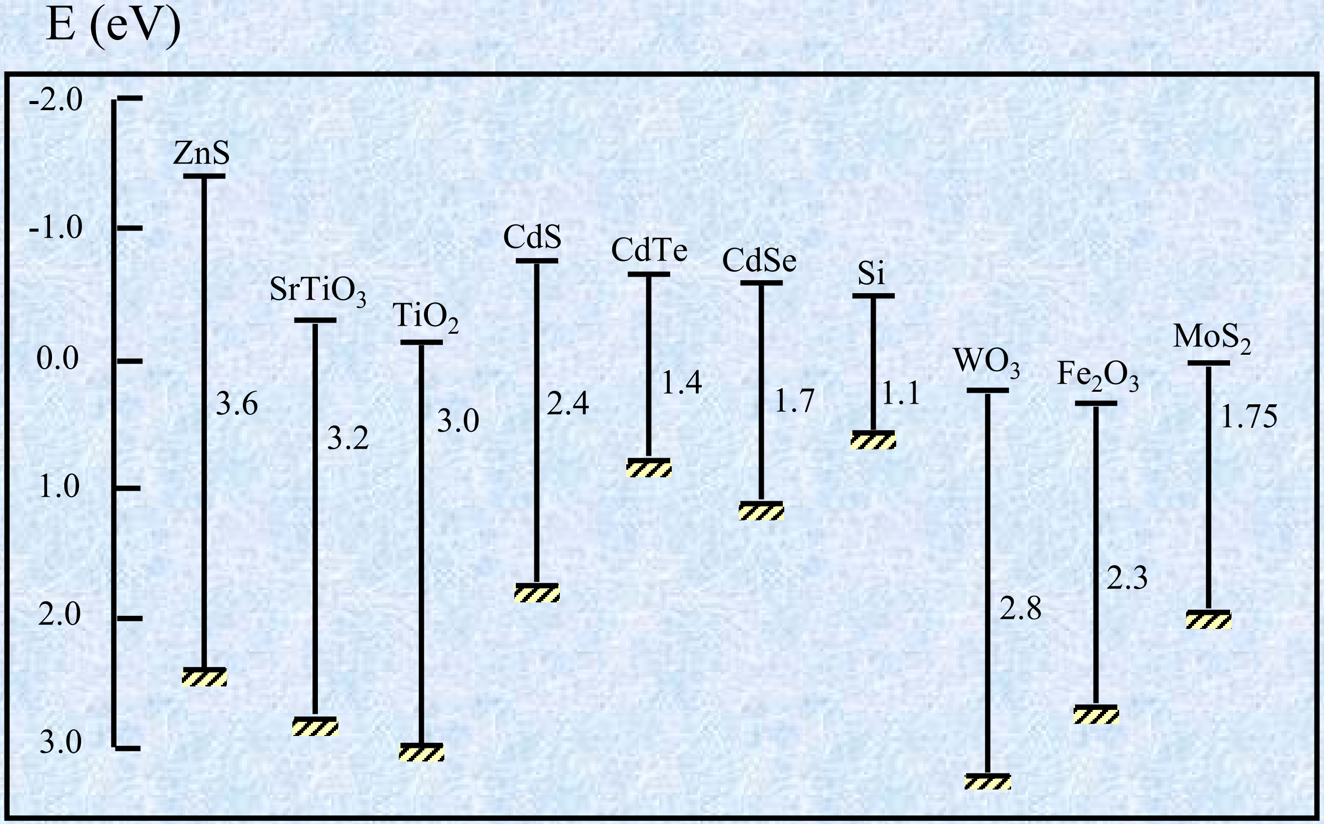
From a thermodynamic point of view, for the occurrence of photoreactions involving species adsorbed on the surface of the photocatalyst particle, the redox potential of the couple to which the species belongs, $E_{0,redox}$, must be compatible with the E_{vb} and E_{cb} edges.

WHAT DOES IT MEAN COMPATIBLE?

- less positive than E_{vb} of the semiconductor (holes can oxidise the reduced species of the couple 1);
- more positive than E_{cb} of the semiconductor (electrons can reduce the oxidised species of the couple 2).

Relative positions of the energy levels of semiconductor and of different redox couples ($E_{0,redox}$).





Positions of the band edges for some semiconductors in contact with aqueous electrolyte at pH = 0

HETEROGENEOUS PHOTOCATALYSIS FIELD BELONGS TO THE GENERAL AREA OF CATALYSIS

Heterogeneous photocatalytic reactions should be studied by following the same methodology used for heterogeneous catalytic reactions and similar problems must be faced.

Thermodynamic and kinetic constraints must be fulfilled.

Intrinsic Electronic Characteristics

vb and cb Energies

Band Gap Value

Lifetime of the Photogenerated Electron-Hole Pairs

Structural Features

Allotropic Phase

Defects

etc.

Physico-Chemical Properties

Specific Surface Area

Porosity

Point of Zero Charge

Surface Hydroxylation

Surf. Basicity and Acidity

Presence of Dopants

Photocatalysts

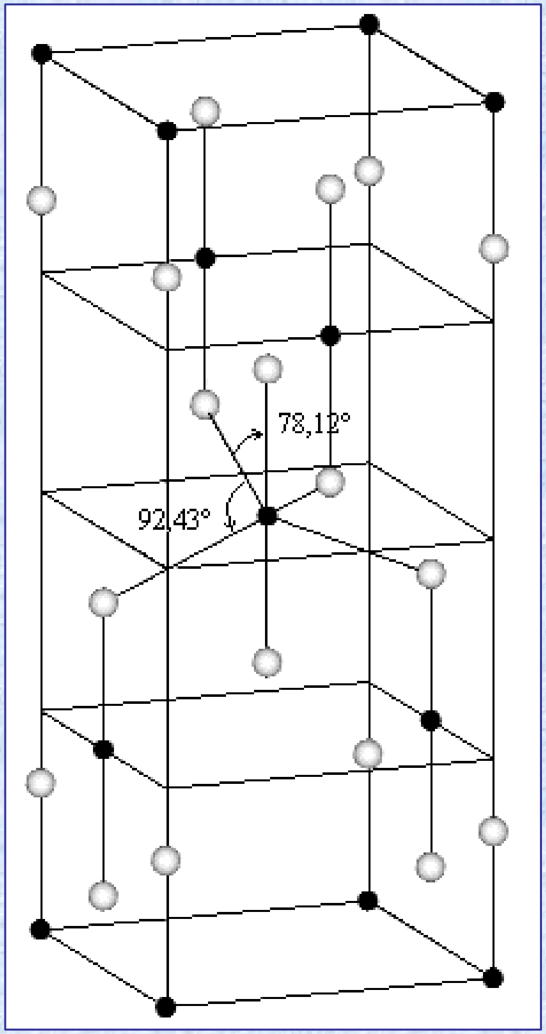
- Polycrystalline TiO_2 is the most used photocatalyst due to his (photo)stability, non toxicity, and cheapness. The anatase phase is generally the most photoactive allotropic phase.

- Other semiconductors (ZnO, WO_3, CdS, Fe_2O_3, ecc.) show lower photoactivity or problems linked to their non stability and anodic corrosion under irradiation.

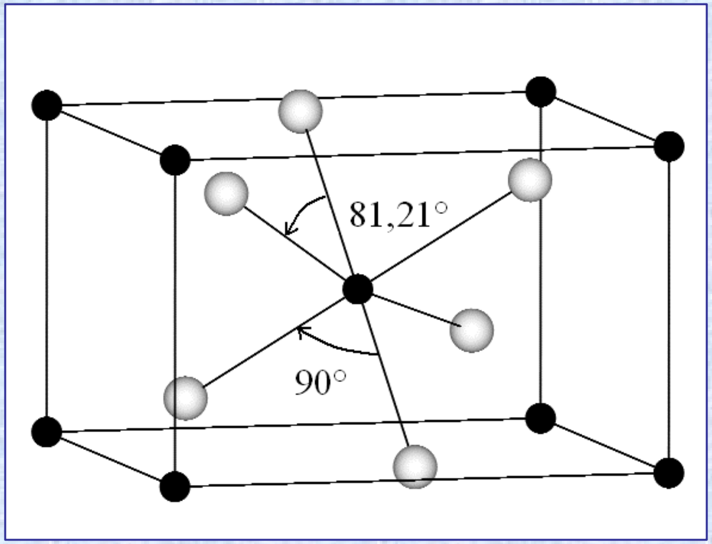
- Liquid-solid or gas-solid interfaces play an important role on the determination of reaction mechanism, quantum yield and deactivation of the photocatalyst. The presence of water can influence the photocatalytic process.

- Several applications of photocatalysis are present nowadays. Purification of water and air, films of TiO_2 and so on. Some examples commercially available are reported in the following.

TiO$_2$



anatase



rutile

○ oxygen

● titanium

SOME APPLICATIONS OF PHOTOCATALYSIS

In few cases it is possible to use heterogeneous photocatalysis without coupling it with other technologies.

TITANIA-COATED FILMS FOR MIRRORS

- A. Fujishima, K. Hashimoto, T. Watanabe, *TiO_2 Photocatalysis Fundamentals and Application*, Bkc inc. Tokyo, Japan, 1999.
- Tayca Corporation, www.tayca.co.jp.

Photocatalysis makes titania surface hydrophilic to avoid clouding

Gas-solid systems

TITANIA-COATED WINDOW GLASS

Due to the photocatalytically induced super hydrophilicity of titania-coated glass, no fogging occurs.

Titania-coated glass

Bare glass

Gas-solid systems

TITANIA-COATED TENT FABRICS

Exposed for 5 months

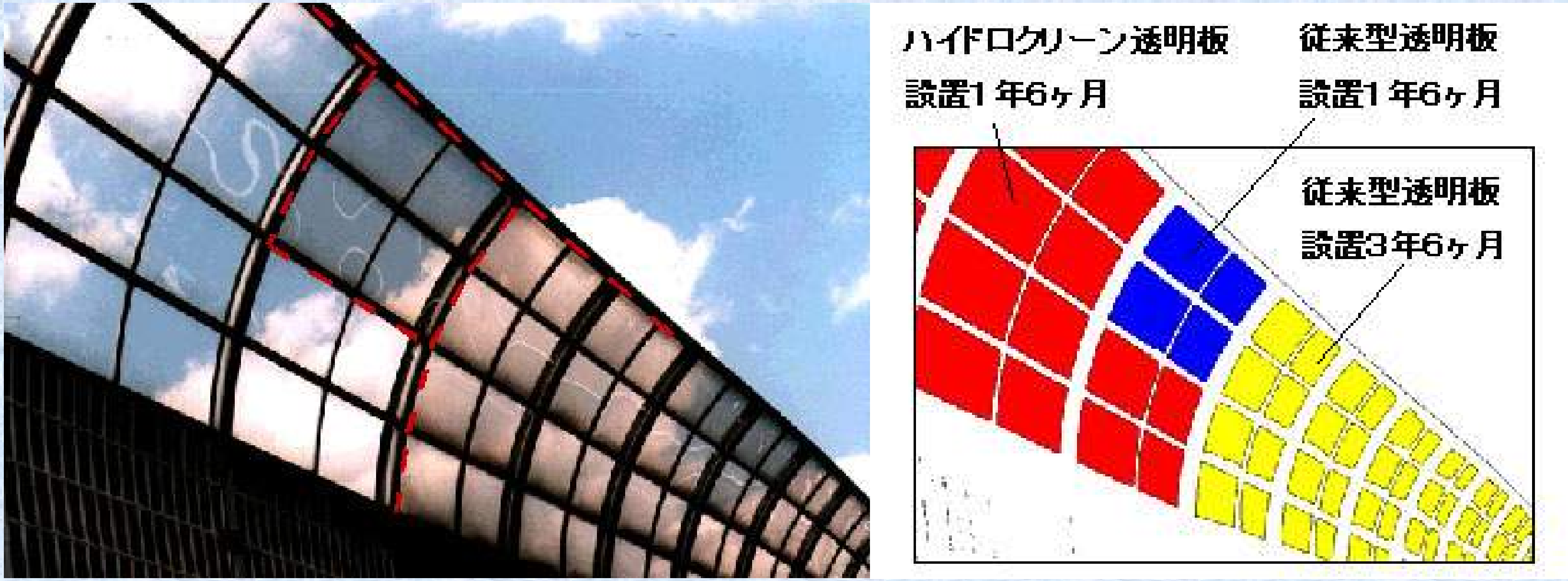
Regular material

PTFE-coated material

Titania-coated material

Gas-solid systems

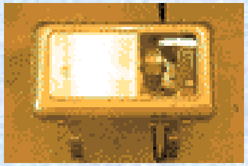
TITANIA-COATED SOUNDPROOF WALL FOR HIGHWAYS



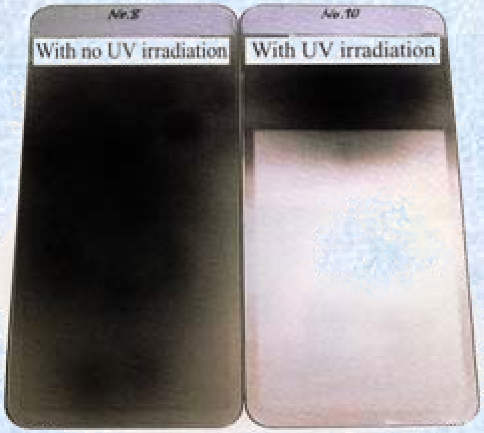
Polycarbonate plates coated with titania on both sides (Red part/1.5 year). Non-coated plates (blue: 1.5 year/yellow 3.5 year).

Gas-solid systems

TITANIA-COATING LIGHT HOUSING FOR TUNNELS



Mori Tunnel
In Nagano Prefecture, Japan



For parks and roads

Fluorescent light

Gas-solid systems

PHOTOCATALYTIC TITANIA PAINTING

Photocatalytic decomposition and super hydrophilicity keep the surface of materials clean.

Left: photocatalytic painting
Right: normal painting

Painting walls in highways

Gas-solid systems

TITANIA-COATED PARTITION WALL PANELS

PERSPECTIVES FOR APPLICATION OF HETEROGENEOUS PHOTOCATALYSIS IN LIQUID-SOLID SYSTEMS[1]

- The difficulty to make a clear ***assessment of the costs*** or the ***expensiveness*** of the photocatalytic processes have prevented a wider development of them by an application point of view.
- The chemical industry is characterised by the almost exclusive use of continuous processes. This type of operation calls for ***continuous (flow) reactors***.
- The need to fulfil the requirement of continuous operation determines that the photocatalyst powder for potential application purposes should present ***suitable size and mechanical and fluidodynamic characteristics in addition to good catalytic properties.***

1. L. Palmisano Ed. *Processi e Metodologie per il Trattamento delle Acque*, Spiegel, Milan, 2000.

- Nanostructured photocatalysts have been reported recently to be **more efficient** (*size quantization effect*) than the bulk polycrystalline ones. The use of these materials implies difficulties in their separation from the liquid phase, consequently their application seems more promising for the preparation of thin films on various rigid supports.

Liquid-solid system

- An example of a possible application of heterogeneous photocatalysis is the photodegradation (polycrystalline TiO_2 as the photocatalyst) of divinylsulfone (DVS) used as a crosslinker for the preparation of a biodegradable cellulose based superabsorbent hydrogel.[2,3]
- This material was obtained by chemical crosslinking of cellulose polyelectrolyte derivatives, Carboxymethylcellulose (CMC) and Hydroxyethylcellulose (HEC) using DVS as the crosslinker which covalently bounds different polymer molecules in a 3D hydrophilic network.
- **Superabsorbent hydrogels** are used mainly for personal care products, biosensing, etc.

2. M.A. Del Nobile, F. Esposito, G. Mensitieri, A. Sannino, Patent WO 98/58686.
3. G. Marcì, G. Mele, L. Palmisano, P. Pulito, A. Sannino, submitted.

Gel after absorption of water

Gel before absorption of water

- A drawback for an industrial application is **the large amount of water** needed to wash the hydrogel before its desiccation.

- DVS is a well known toxic agent and it is present in low concentrations **(ca. 30-200 mg·L^{-1})** in washing waters deriving from the preparation together with the unreacted polymers and oligomers.

$$C_4H_6SO_2 \xrightarrow[h\nu]{TiO_2} \text{intermediates} \xrightarrow[h\nu]{TiO_2} CO_2 + H_2O + SO_4^{2-}$$

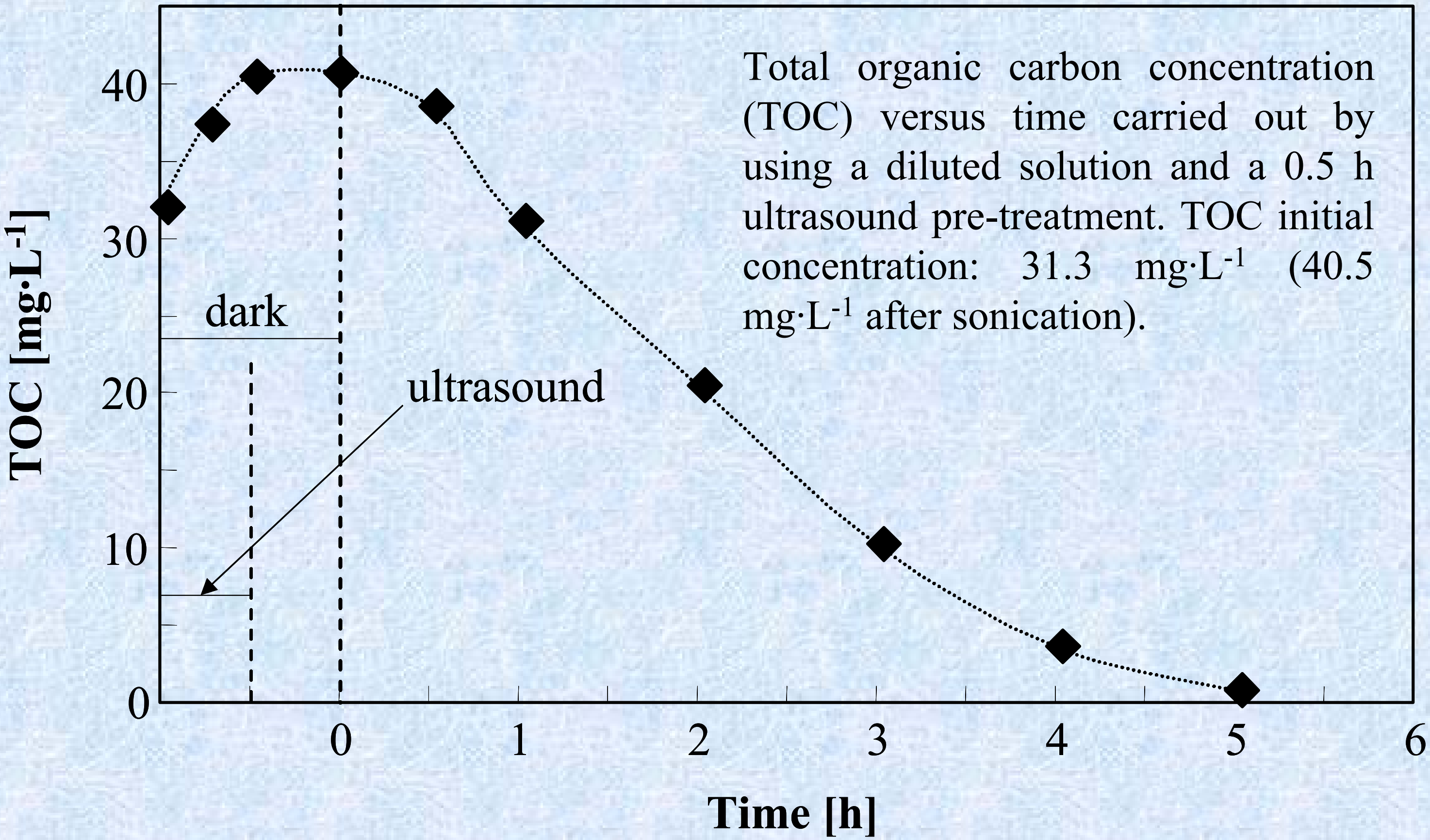
- This is **a fortunate case** because the concentration of pollutants to be photodegraded is quite low, consequently to use other kinds of technologies could be not convenient.

- Moreover it is worth noting that the initial concentration of DVS can be modulated not only as a function of the degree of crosslinking to be induced in the network, but also in order to obtain **more diluted solutions to be treated more efficiently by heterogeneous photocatalysis.**

- The purification of the washing water could allow its re-utilization making interesting the process both by an environmental and economical point of view.

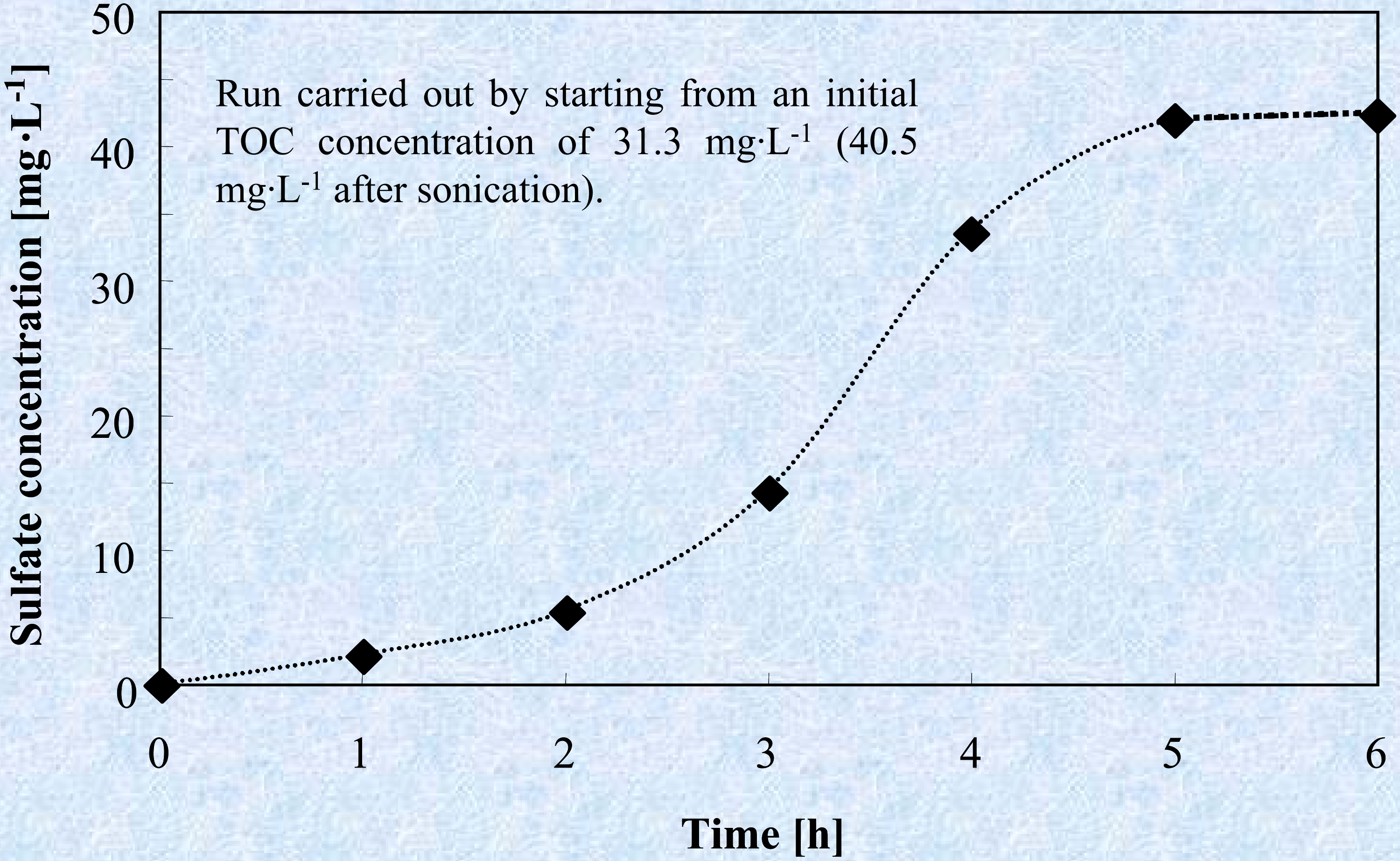
- The idea is to couple a photocatalytic reactor with the pilot plant (that is coming to be built) for the production of the hydrogel.

Photocatalyst: TiO_2 Degussa P25, 0.8 g·L^{-1}.
Photoreactor: 0.5 L, batch photoreactor of cylindrical shape.
Lamp: 125 W medium pressure Hg lamp.



Total organic carbon concentration (TOC) versus time carried out by using a diluted solution and a 0.5 h ultrasound pre-treatment. TOC initial concentration: 31.3 mg·L^{-1} (40.5 mg·L^{-1} after sonication).

TOC concentration increases during the ultrasound treatment from 31.3 mg·L^{-1} to **40.5 mg·L^{-1}**, due to breaking of small pieces of hydrogel present in the solution.
5 hours are needed for the complete disappearance of TOC.



A plateau is achieved after 5 hours irradiation time corresponding to the complete disappearance of TOC.

The plateau corresponds to an initial TOC concentration due to DVS equal to ca. **21 mg·L^{-1}**. Consequently ca. **19 mg·L^{-1}** of TOC can be attributed to other organic species (unreacted polymers and/or oligomers used during the preparation).

Summary

✓Photocatalysis: an overview

Coupling photocatalysis with other technologies:

Biological treatment and Photofenton

Ozonation

Electrochemical treatment

Membrane reactor

Microwaves

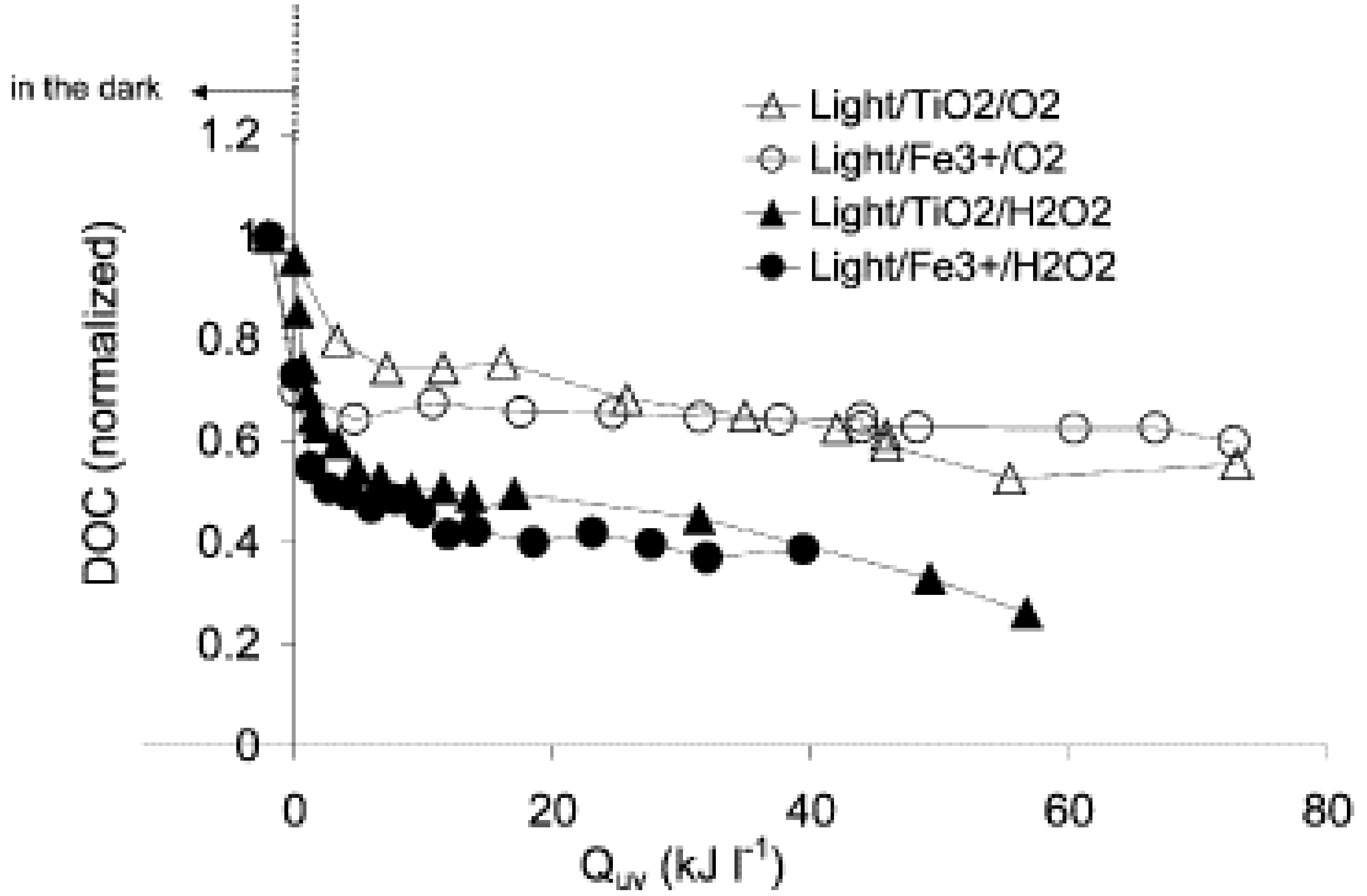
- ***Biological methodologies.*** Some substances are ***bio-resistant***, while photocatalysis is not specific for particular substrates.

- It has been investigated the possibility **to couple biological methods with some photochemical methods**.

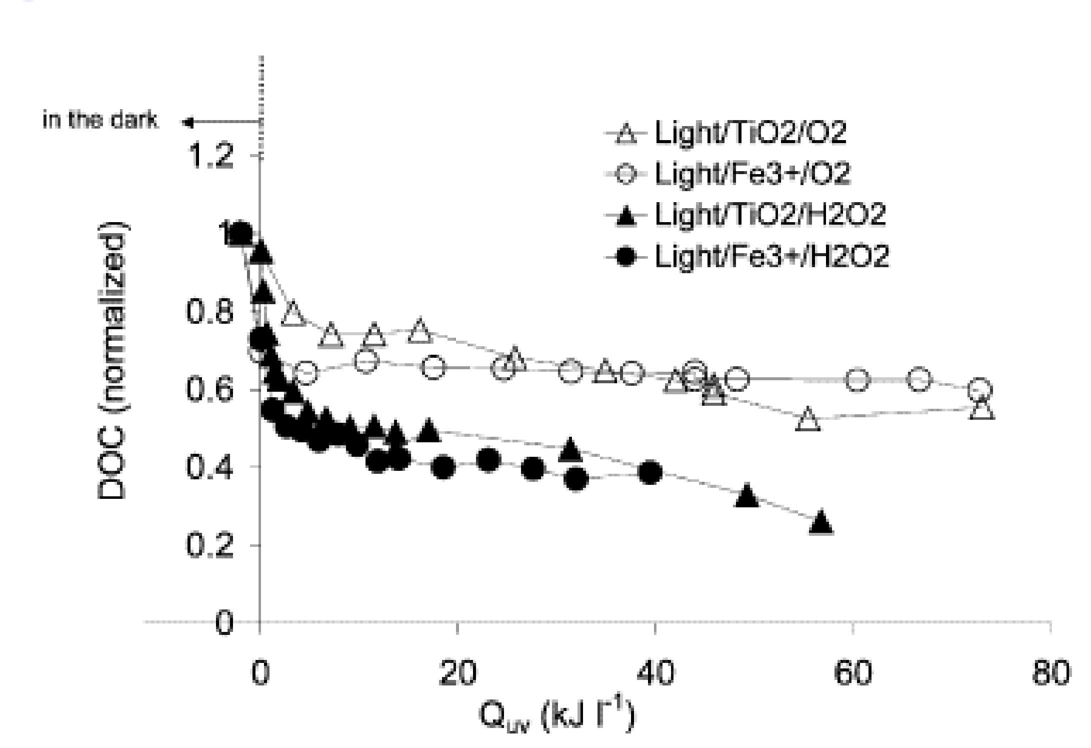
- Some pollutants, as for instance metobromuron and isoproturon (herbicides) and AMBI (5-amino-6-methyl-2-benzimidazolone, used in the manufacture of dyes), are biorecalcitrant molecules.[1-3]

1. S. Parra, V. Sarria, S. Malato, P. Peringer, C. Pulgarin, *Appl. Catal. B: Environ.* **27** (2000) 153.
2. C. Pulgarin, M. Invernizzi, S. Parra, V. Sarria, R. Polania, P. Peringer, *Catal. Today* **54** (1999) 341.
3. V. Sarria, P. Peringer, J. Caceres, J. Blanco, S. Malato, C. Pulgarin, *Energy* **29** (2004) 853.

- An exhaustive study was carried out for AMBI with different photocatalytic systems[3].
- In order to enhance its biodegradability, solar photocatalytic degradation methods were explored by using a pilot plant (Compound Parabolic Collector, CPC's) at the Plataforma Solar de Almeria consisting of three modules (each module consists of eight tubes, collector surface, 3.08 m^2, photoreactor volume 22 l and total reactor volume 39 l):
    - **Light/TiO_2/O_2**
    - **Light/Fe^{3+}/O_2**
    - **Light/TiO_2/H_2O_2**
    - **Light/Fe^{3+}/H_2O_2**



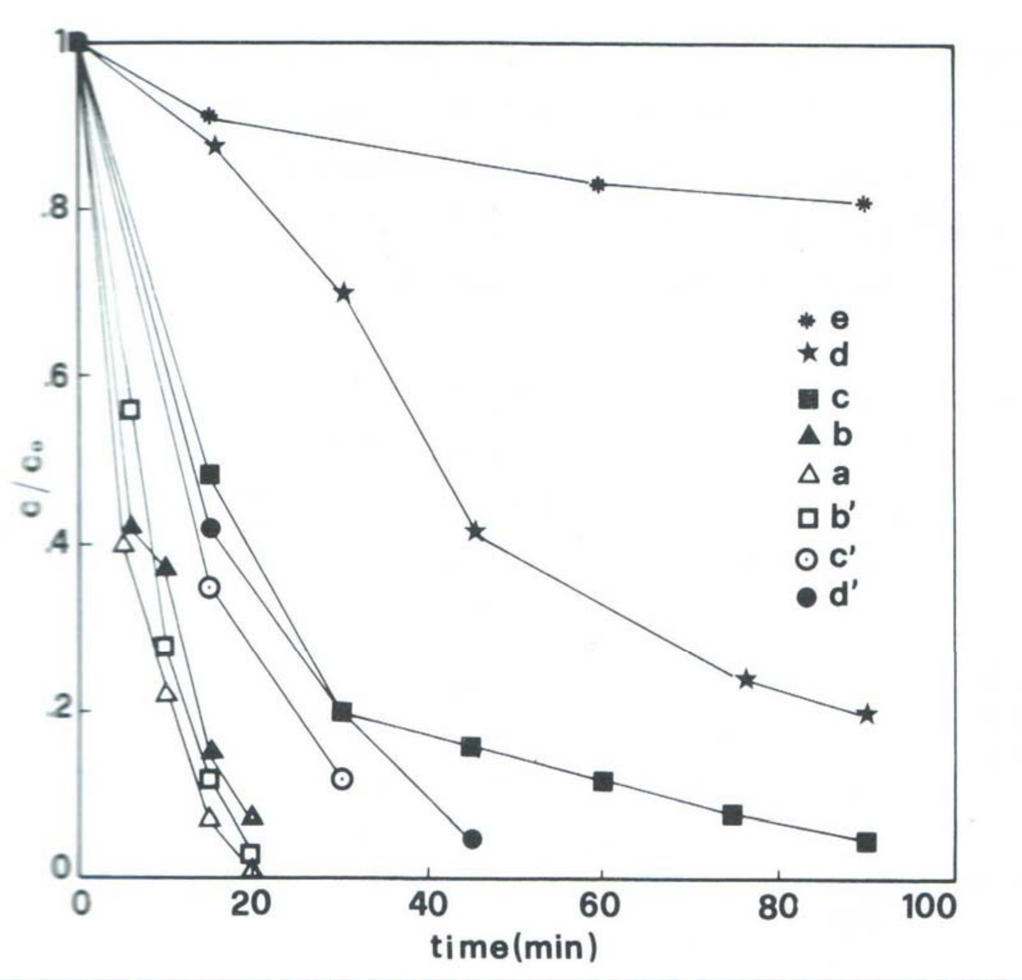
Evolution of DOC during AMBI degradation as a function of the accumulated solar energy. AMBI (1.0 mmol·l^{-1}), H_2O_2 (11 mmol·l^{-1}), TiO_2 (1 g·l^{-1}) and Fe^{3+} (1.0 mmol·l^{-1}). Q_{UV} is the accumulated energy (per unit of volume, kJ·l^{-1}) incident on the reactor for each sample taken during the experiment.



AA, despite the Light/TiO_2/H_2O_2 system shows **the most significant decrease of DOC**, suggest that the Light/Fe^{3+}/O_2 and Light/Fe^{3+}/H_2O_2 systems could be chosen to be coupled with a biological process.

Homogeneous systems, indeed, according to the point of view of AA, show probably **the best engineering conditions**.
The concentrations of Fe^{3+} and H_2O_2 and the amount of TiO_2 should be considered in these systems.

In old papers an optimum of concentration of Fe^{3+} and/or H_2O_2 has been found for phenol photodegradation.[4,5]



C/C_0 vs. reaction time.
TiO_2 anatase (0.5 g l^{-1}) in the presence of oxygen and various Fe^{3+} concentrations:
$5\cdot10^{-4}$ M (a);
$1\cdot10^{-3}$ M (b);
$2.5\cdot10^{-3}$ M (c);
$5\cdot10^{-3}$ M (d);
$5\cdot10^{-2}$ M (e);
$1\cdot10^{-4}$ M (b');
$5\cdot10^{-5}$ M (c');
$1\cdot10^{-5}$ M (d').
Initial phenol concentration $C_0 = 10^{-3}$ M.

4. A. Sclafani, L. Palmisano, E. Davì, *J. Photochem. Photobiol. A: Chem.* **56** (1991) 113

5. V. Augugliaro, E. Davì, L. Palmisano, M. Schiavello, A. Sclafani, *Appl. Catal.* **65** (1990) 101

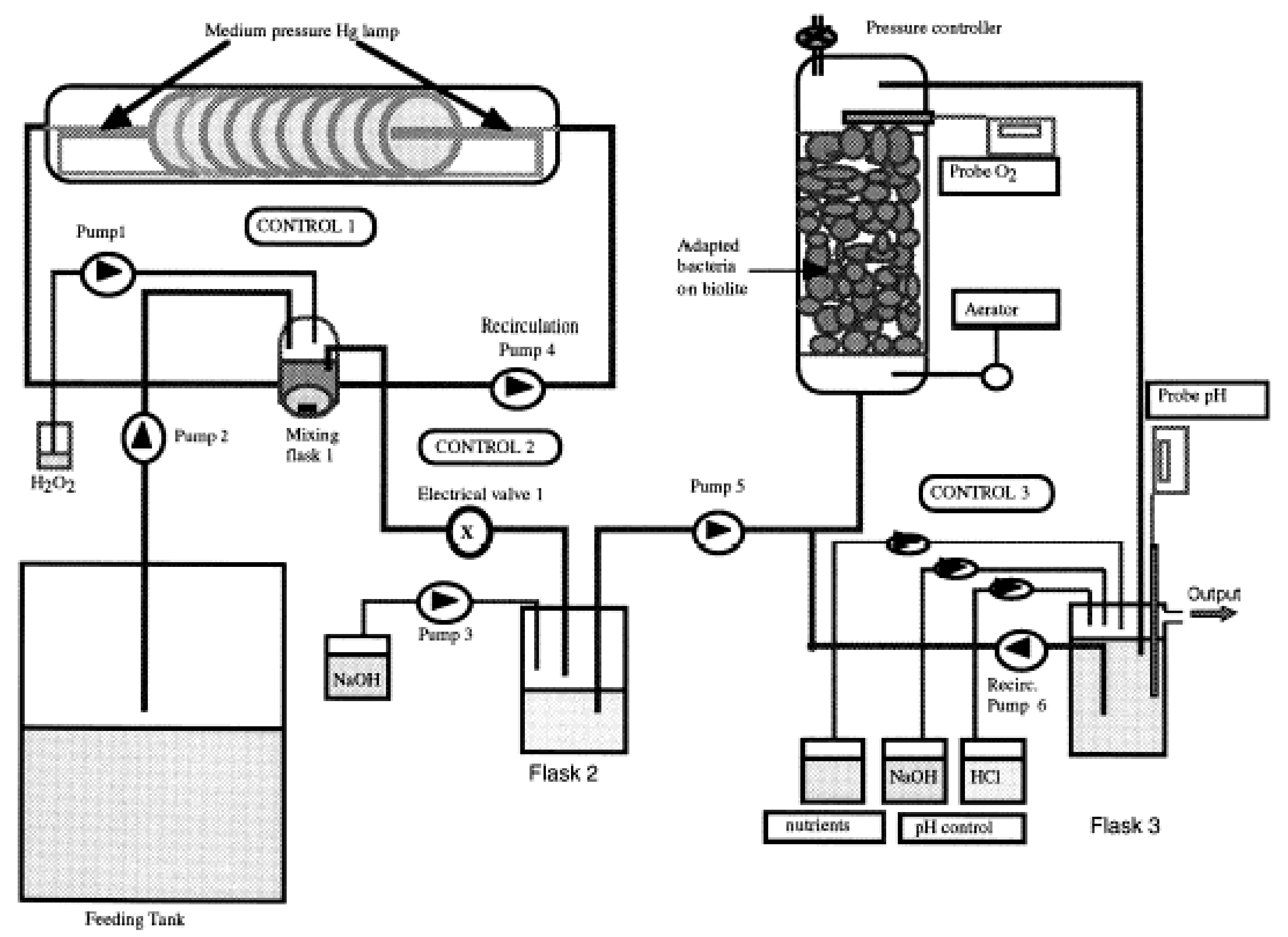
A study on **coupling photochemical and biological flow reactors** for the degradation of *p*-nitrotoluene-ortho-sulfonic acid (*p*-NTS) has been carried out.[6]

a) *p*-NTS (presence of nitro and sulphate electron withdrawing groups) is present in effluents from the Swiss chemical industry.

b) The mineralization of *p*-NTS via photo-Fenton treatment in batch or continuous mode is not a cost-effective strategy.

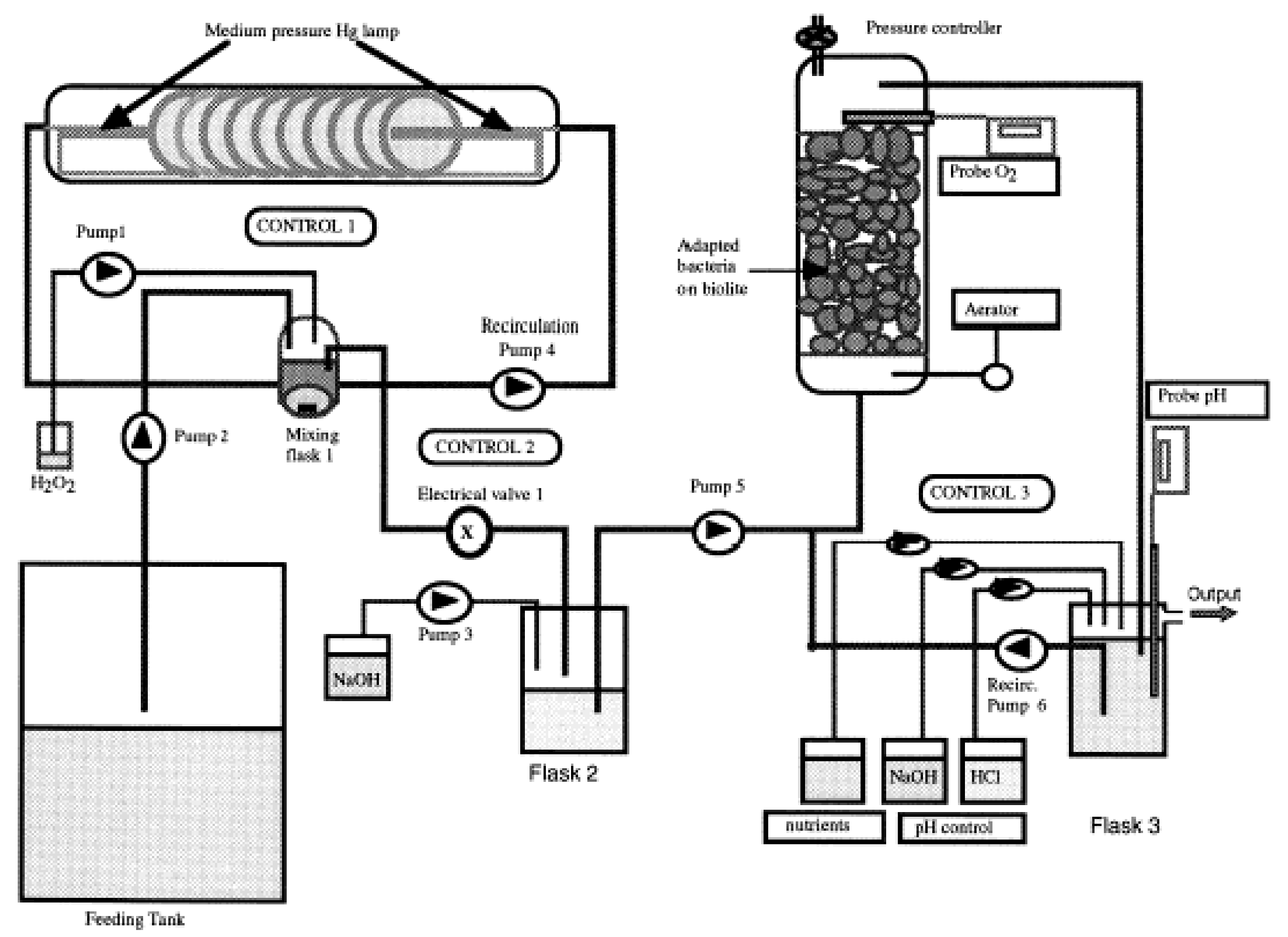
c) *p*-NTS is not satisfactorily mineralized by heterogeneous photocatalysis (TiO_2/H_2O_2).[7]

6. V. Sarria, P. Peringer, J. Cáceres, J. Blanco, S. Malato, C. Pulgarin, *Energy* **29** (2004) 853.
7. L. Minsker, C. Pulgarin, P. Peringer, J. Kiwi, *New J. Chem.* **18** (1994) 793.



Schematic drawing of coupled photo-Fenton-biological flow reactor.

Photochemical reactor. Lamp: 400 W medium pressure Hg lamp. Mixing flask 1: 1 L. p-NTS solution fed into the coil reactor from a 20 L feeding tank, DOC concentrations up to ca. 350 mg/L. H_2O_2 automatically added by means of the peristaltic pump 1. Solution recirculated at 22 L/h through the illuminated part of the reactor by pump 4. pH neutralised by NaOH at the outlet of the reactor via pump 3.



Schematic drawing of coupled photo-Fenton-biological flow reactor.

Fixed bed bioreactor: column containing biolite colonised by activated sludge and having 1 L of water capacity. The effluent deriving from the photochemical stage was circulated from flask 2 by the pump 5 through the bottom of the column. pH was adjusted at 7.0 in flask 3 where the nutrients (N, P, K and oligoelements) for the bacterial activity were also added. O_2 concentration was controlled by an O_2 probe at the top of the column.

- The photo-assisted Fenton system used as a pre-treatment generates in a very short period of time intermediates with very oxidised functional groups, not toxic and as biodegradable as urban wastewater.
- The main parameter affecting the performance of the photo-assisted reactor in continuous mode is related **to the high residual H_2O_2 concentration** after the photochemical pre-treatment. To overcome this inconvenience the semi-continuous mode was applied.
- A good efficiency was reached operating **in semi-continuous** mode: before leading the treated water into the biological reactor the optimal time is 70 min.

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Homogeneous system

- O_3 oxidation has been carried out in the past by using often oxalic acid/oxalate ion as probe species.

- Ozone can react in aqueous solution with organic/inorganic compounds by following two pathways:

  - direct selective reaction with specific functional groups (double bonds, nucleophilic positions);

  - reaction through free radicals generated from ozone decomposition.

Hoignè and Bader[1] investigated the ozonation of oxalic acid/oxalate ion at various pH's and concluded that the direct reaction can be considered negligible.

The oxidation of oxalate ion at alkaline pH's, for example, is due to attack by free radicals generated by O_3 decomposition:[2]

$$O_3 + OH^- \rightarrow O_2^{\cdot -} + HO_2^{\cdot} \qquad (1)$$

$$O_3 + HO_2^{\cdot} \rightarrow 2O_2 + {}^{\cdot}OH \qquad (2)$$

or alternatively:

$$2HO_2^{\cdot} \rightarrow O_2 + H_2O_2 \qquad (3)$$

$$H_2O_2 + O_2^{\cdot -} \rightarrow OH^- + {}^{\cdot}OH + O_2 \qquad (4)$$

The produced oxidant species can induce the mineralization of the oxalate anion:

$$C_2O_4^{2-} + 2\,{}^{\cdot}OH \rightarrow 2CO_2 + 2OH^- \qquad (5)$$

1. J. Hoignè, H. Bader, *Water Res.* **17** (1983) 18

2. B. Kasprzyk-Hordern, M. Ziółek, J. Nawrocki, *Appl. Catal. B: Environ.* **46** (2003) 639

Heterogeneous system

- When O_3 is present in the photocatalytic suspension, in addition to the homogeneous pathway described by reactions 1-4, the role of O_3 as an electron trap must be considered.

- FTIR studies[3,4] report different modes of ozone interaction with TiO_2 surface such as:
  - physical adsorption;
  - formation of weak hydrogen bonds with surface hydroxyl groups of the catalyst;
  - molecular or dissociative adsorption on Lewis acid sites.

[3] Y. Maeda, A. Fujishima, K. Honda, *J. Electrochem. Soc.* **128** (1981) 1731

[4] K.M. Bulanin, J.C. Lavalley, A.A. Tsyganenko, *Colloid Surf. A* **101** (1995) 153

Strong surface Lewis acid sites lead to distortion of the ozone molecule affording its decomposition with formation of a free oxygen molecule and a surface oxygen atom that remains attached to the site.[4]

O_3 adsorbed onto TiO_2 surface acts as a very strong electrophylic agent:

$O_{3(ads)} + e^-_{cb} \rightarrow O_3^{\bullet -}$ (6)

$O_3^{\bullet -} + H_2O \rightarrow {}^{\cdot}OH + OH^- + O_2$ (7)

The above reported mechanism gives rise to the formation of a hydroxyl radical per each trapped electron (reactions 6 and 7), whereas **three electrons** are needed for the generation of a hydroxyl radical when oxygen acts as electron trap (see reactions 8-11).

$$O_{2(ads)} + e^{-}_{(cb)} \rightarrow O_2^{\cdot -} \qquad (8)$$

$$O_2^{\cdot -} + H_2O \rightarrow HO_2^{\cdot} + OH^{-} \qquad (9)$$

$$2HO_2^{\cdot} \rightarrow O_2 + H_2O_2 \qquad (10)$$

$$H_2O_2 + O_2^{\cdot -} \rightarrow OH^{-} + {}^{\cdot}OH + O_2 \qquad (11)$$

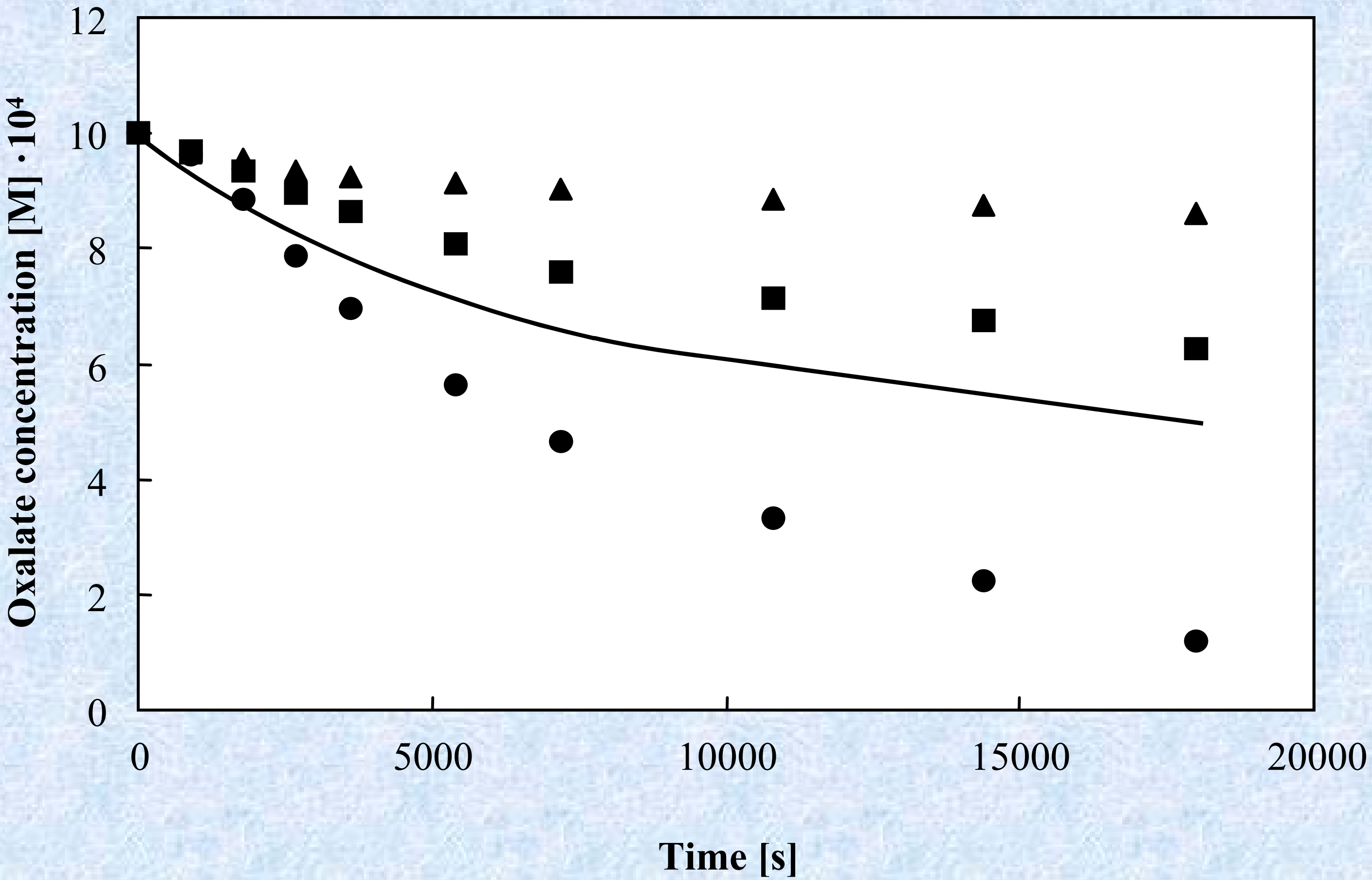
Consequently, when the photocatalyst is irradiated in the presence of O_3 a greater number of $^{\cdot}OH$ radicals is produced.

EPR studies[5], moreover, confirmed that O_2 is less electrophylic than O_3 on respect to photogenerated electrons onto TiO_2 surface.

The above considerations can justify the observed positive effect of photocatalysis coupled with ozonation on the oxidation rate of oxalate anion.[6]

5. M.D. Hernandez-Alonso, J.J. Coronado, A.J. Maira, J. Soria, V. Loddo, V. Augugliaro, *Appl. Catal. B: Environ.* **39** (2002) 257

6. M. Addamo, V. Augugliaro, E. García-López, V. Loddo, G. Marcì, L. Palmisano, *Catalysis Today*, in press (paper presented during the XIX Iberoamerican Symposium of Catalysis).



Comparison between oxalate ion degradation runs both in homogeneous and heterogeneous regimes.[6]

(■) O_3/air/near-UV; (▲) TiO_2/air/near-UV; (●) TiO_2/O_3/air/near-UV;

(─) sum of the contribution of the substrate degradation of O_3/air/near-UV and TiO_2/air/near-UV.

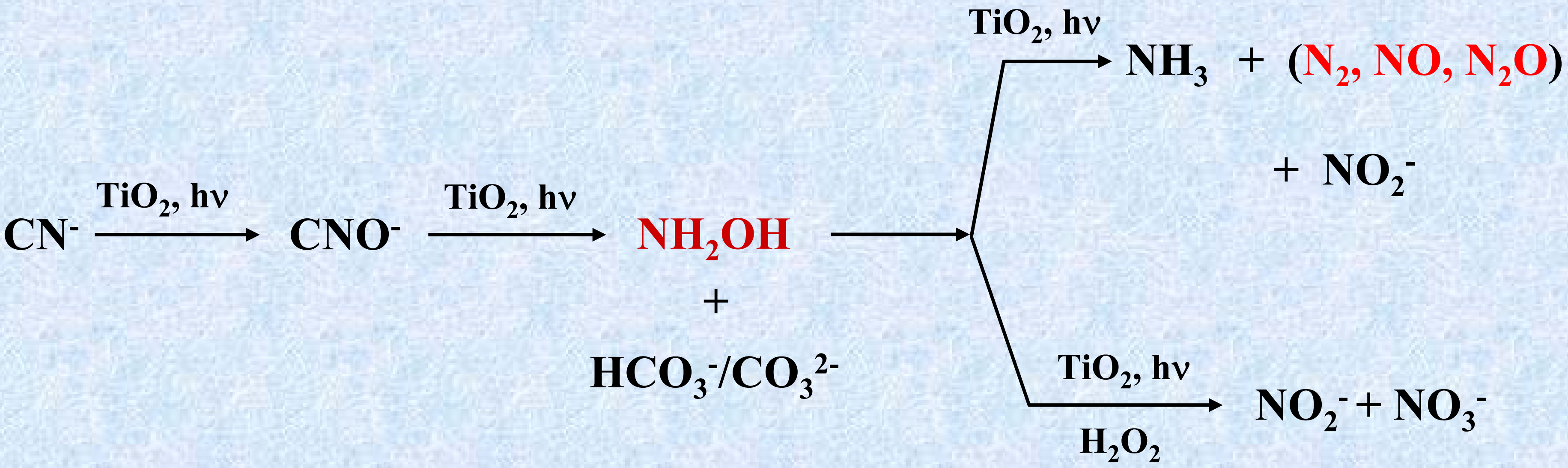
Lamp: 700W, medium pressure Hg lamp. Photocatalyst: 0.24 g L^{-1} TiO_2 Degussa P25. $[O_3] = 8.1\ 10^{-4}$ M; $[O_2] = 2.6\ 10^{-4}$ M.

CIANIDE ION

Artificial light

$$\mathrm{CN^-} \xrightarrow{\mathrm{TiO_2,\ h\nu}} \mathrm{CNO^-} \xrightarrow{\mathrm{TiO_2,\ h\nu}} \mathrm{NO_2^- + NO_3^- \ + \ HCO_3^-/CO_3^{2-}}$$

Solar light

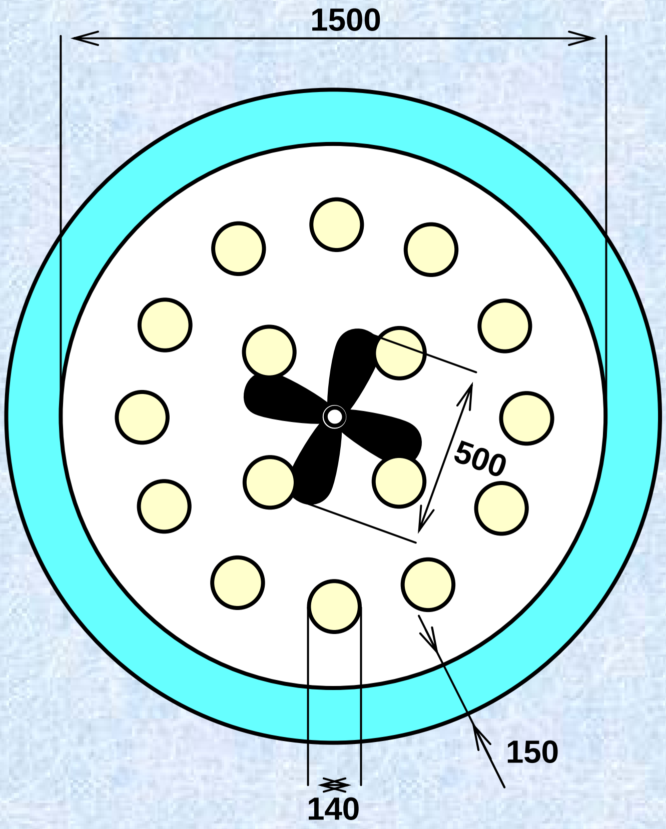


$$\mathrm{CN^-} \xrightarrow{\mathrm{TiO_2,\ h\nu}} \mathrm{CNO^-} \xrightarrow{\mathrm{TiO_2,\ h\nu}} \mathrm{NH_2OH} + \mathrm{HCO_3^-/CO_3^{2-}} \longrightarrow$$

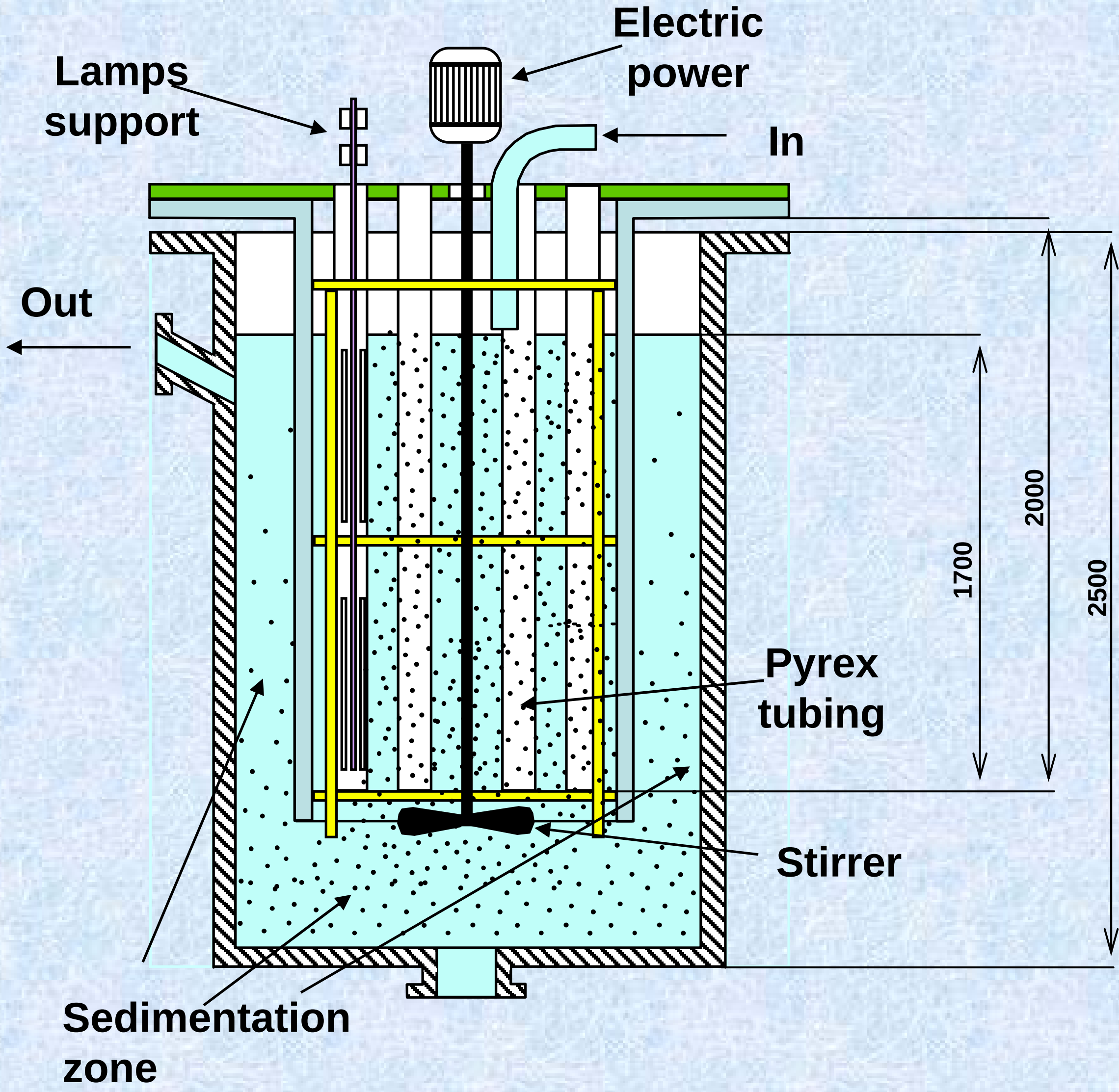
$$\xrightarrow{\mathrm{TiO_2,\ h\nu}} \mathrm{NH_3 \ + \ (N_2, NO, N_2O) \ + \ NO_2^-}$$

$$\xrightarrow[\mathrm{H_2O_2}]{\mathrm{TiO_2,\ h\nu}} \mathrm{NO_2^- + NO_3^-}$$

PILOT PLANT ASSEMBLED AND TESTED IN THE GASIFICATION COAL POWER PLANT OF PUERTOLLANO, SPAIN

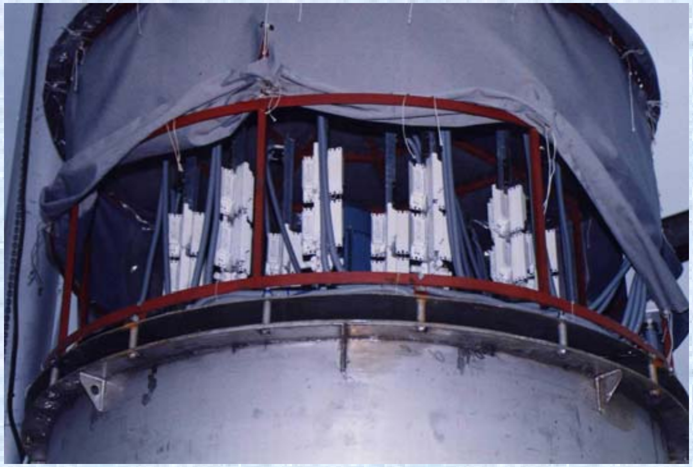


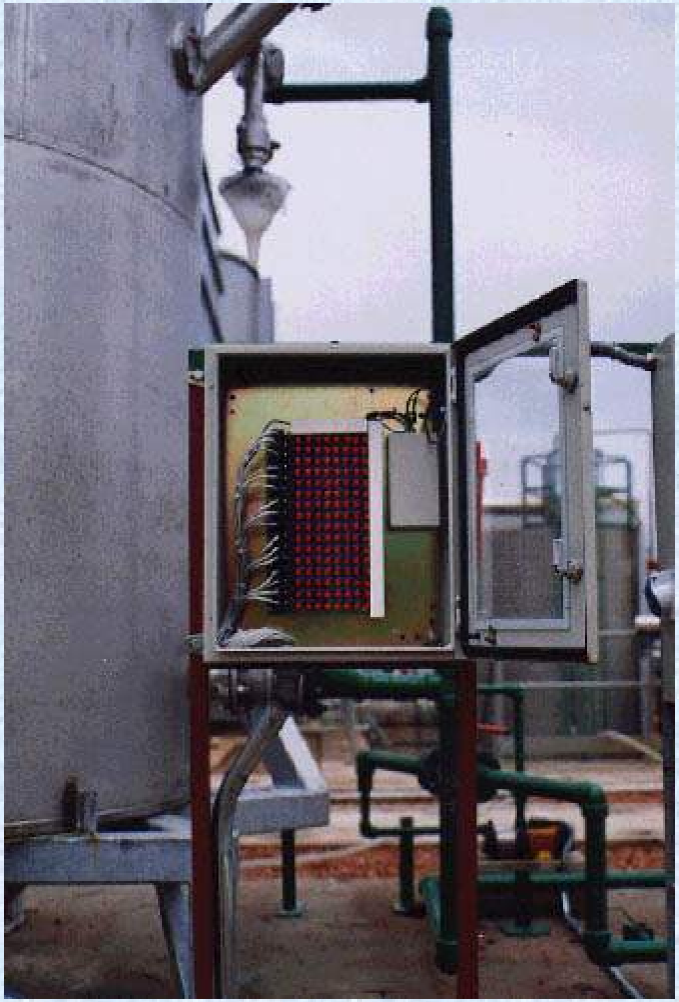
Reactor scheme



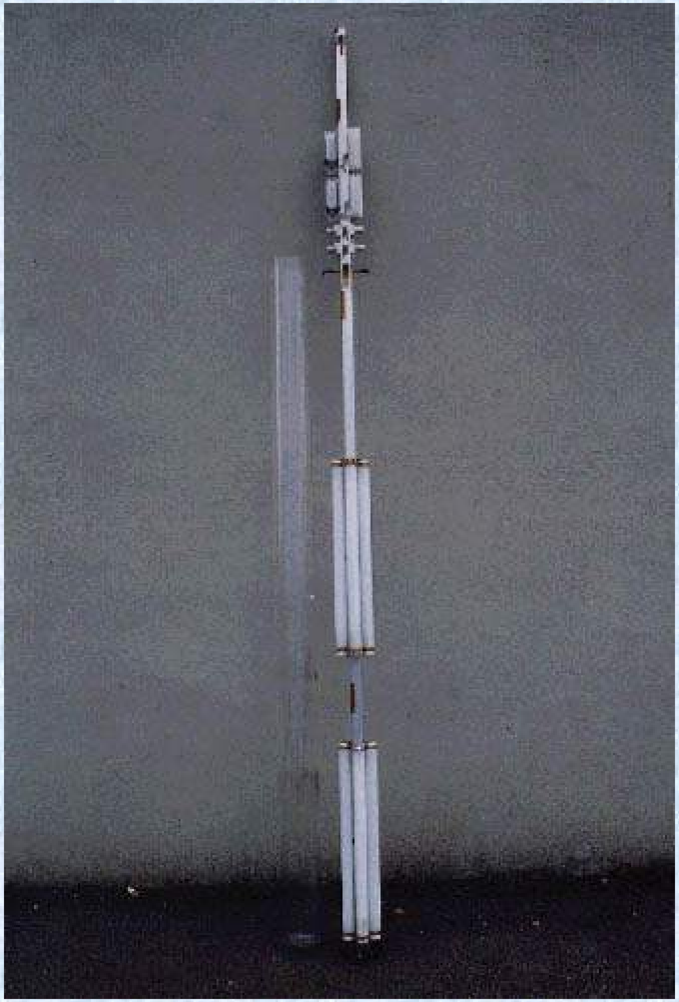
PILOT PLANT

PILOT PLANT





PILOT PLANT



Experimental conditions of pilot plant

Liquid phase: 24 $m^3 \cdot d^{-1}$
Initial concentration of cianide: C_i = 10 ppm
Final concentration of cianide: C_f = 0.2 ppm
Reaction volume: 2.4 m^3
Total volume: *ca.* 6 m^3

Used catalyst: TiO_2 (anatase) supported on Al_2O_3
(particle size: 90 – 110 μm).

Irradiating system consisted of 16 cilinder Pyrex tubes (lenght *ca.* 2 m).
Every tube contain 8 fluorescent lamps of
40 W (height 60 cm).

Electric power needed to mantein a turbulent regime into the reactor was 12 KW.

Summary

✓Photocatalysis: an overview

Coupling photocatalysis with other technologies:

✓Biological treatment and Photofenton

✓Ozonation

Electrochemical treatment

Membrane reactor

Microwaves

DIC
P M

- This method presents versatility and simplicity of the reactors in terms of construction and management (particularly suitable for automation).[1]

- Large application limited by the difficulty to find materials with specific characteristics to make the process competitive.

---

[1] K. Rajeshwar and J. Ibanez, *“Fundamentals and Applications in Pollution Abatement”* Academic Press, New York, 1997

- **Ti/PbO$_2$, Ti/SnO$_2$, Ti/IrO$_2$, glassy carbon** are generally used as the materials, but some suffers for loss of activity due to surface fouling (glassy carbon) or limited service life (Ti/IrO$_2$).

- **Silicon** coated by a **layer of synthetic diamond**, heavily **doped with boron**[2,3] (to obtain acceptable electric conductivity), was proposed as anode for the oxidation of organic compounds[4].

- On this boron-doped diamond **(BDD)** anode, discharge of water does not occur in a wide potential range.

2. F. Beck, H. Krohn, W. Kaiser, M. Fryda, C.P. Klages, L. Schafer, *Electrochim. Acta* **44** (1998) 525
3. V. Fisher, D. Gandini, S. Laufer, E. Blank, Ch. Comninellis, *Electrochim. Acta* **44** (1998) 521
4. M. Panizza, P.A. Michaud, G. Cerisola, Ch. Comninellis, *Electrochem. Commun.* **3** (2001) 336

- Some **biorefractory organic compounds** present in water (phenol,[5] 4-chlorophenol,[6] surfactants,[7] diuron and dichloroaniline,[8] triazines and cyanuric acid[9]) were treated successfully by using BDD anode.

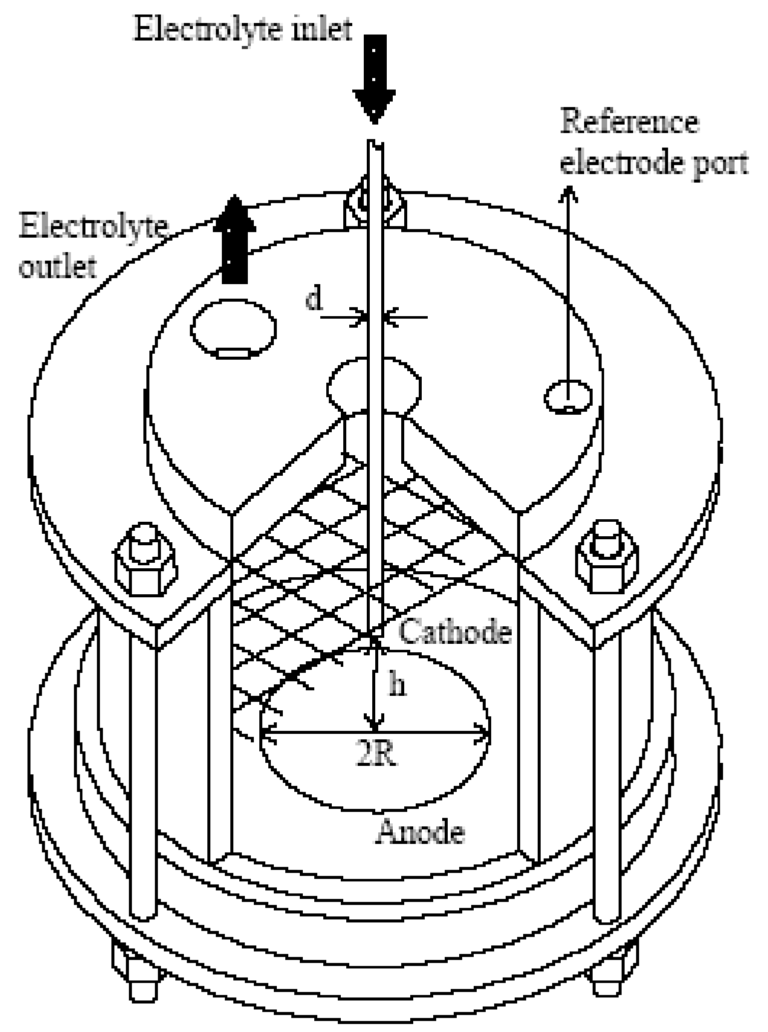
5. J. Iniesta, P.A. Michaud, M. Panizza, G. Cerisola, A. Aldaz, C. Comninellis, *Electrochim. Acta* **46** (2001) 3573
6. M.A. Rodrigo, P.A. Michaud, I. Duo, M. Panizza, G. Cerisola, C. Comninellis, *J. Electrochem. Soc.* **148** (2001) D60
7. G. Lissens, J. Pieters, M. Verhaege, L. Pinoy, W. Verstraete, *Electrochim. Acta* **48** (2003) 1655
8. A.M. Polcaro, M. Mascia, S. Palmas, A. Vacca, *Electrochim. Acta* **49** (2004) 649
9. A.M. Polcaro, A. Vacca, M. Mascia, S. Palmas, *Electrochim. Acta* **50** (2005) 1841

- Oxidation in the potential region of water stability can lead to **electrode fouling** due to the formation of polymeric materials.

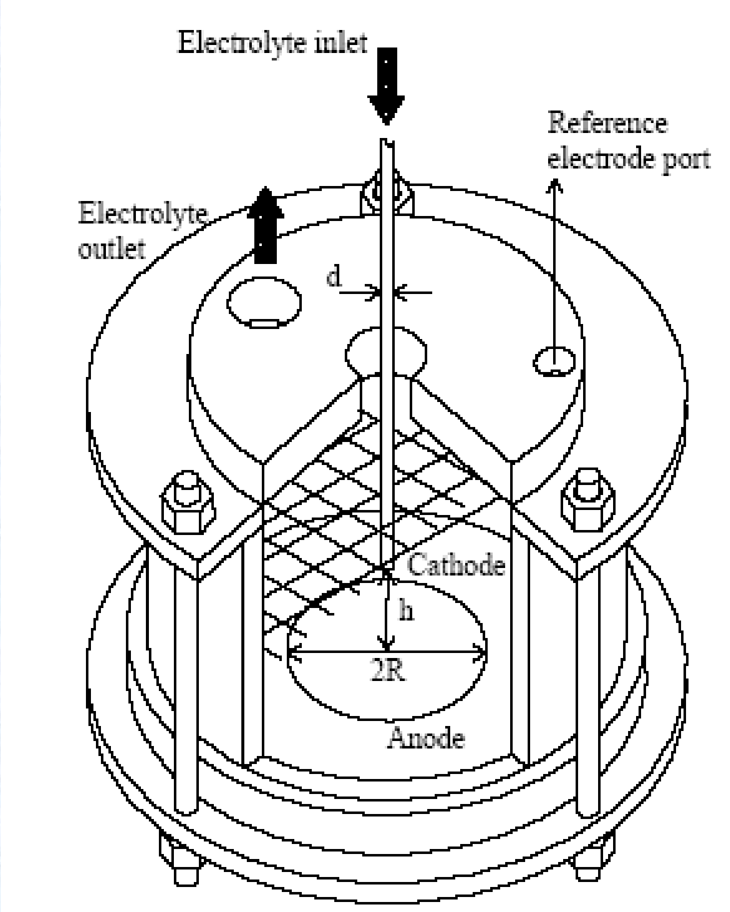
- The electrochemical process is **competitive** with other advanced oxidation processes (AOPs) when the oxidation is carried out in the **potential region of water discharge (**O_2 evolution**)**.

- In the last case oxidation of organic compounds at BDD anodes involves production of **OH radicals** scarcely adsorbed at BDD surface (they are consequently desorbed and can attack the organic pollutant).

- BDD anode behaves like an OH radicals **generator**.



Schematic view of the three-electrode flow electrochemical cell used to oxidize 2-Cl-4-ethylamino-6-isopropylamino-1,3,5-triazine (**ATR**) and 2-Cl-4,4-diammino-1,3,5-triazine (**DAA**) and 2,4,6-tri-hydroxy-1,3,5-triazine (**CA**, cyanuric acid).[9]



Electrolyte was fed to the cell perpendicularly to the centre of the anode (pollutants concentration 70-500 ppm, depending on the molecule).

A grid of stainless steel as the catode.

A disk of boron doped diamond (BDD) as the anode.

A saturated calomel electrode (SCE) as the reference electrode.

- BDD electrode **is effective** to oxidise not only the ATR and DAA but also CA, that is known to be refractory to most of advanced oxidation processes, including heterogeneous photocatalysis.[10]

- The **best operating conditions** to photo-oxidise CA in the electrochemical reactor are not the best ones to photo-oxidise **the starting molecule** (atrazine or some other triazine).

[10] C. Minero, G. Mariella, V. Maurino, E. Pelizzetti, *Langmuir*, **16** (2000) 2632

- Heterogeneous photocatalysis is effective to photodegrade atrazine and other triazine herbicides, but CA represents the final oxidation product.[10]
- An **intriguing** future possibility could be **to couple heterogeneous photocatalysis** with the **electrochemical technology** to perform in a **hybrid system** the photocatalytic degradation of atrazine or some other triazine followed by the electrochemical oxidation of CA.

Summary

✓Photocatalysis: an overview

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Microwaves

Membrane Technology coupled with Photocatalysis

1) Photocatalyst deposited on the membrane;

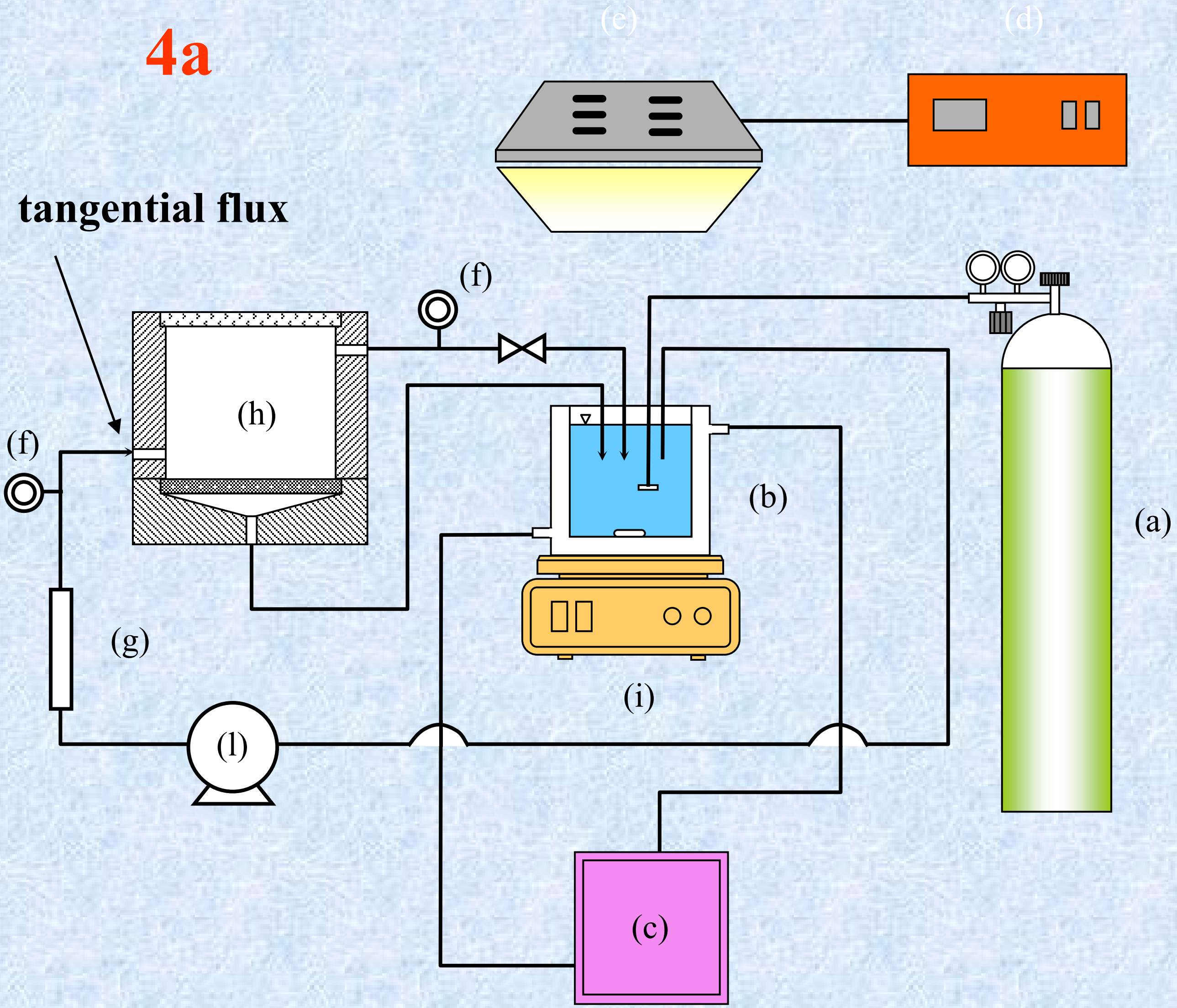
2) Photocatalyst in suspension confined by means of the membrane;

3) Entrapment of the photocatalyst in a PSF membrane;

4a) Irradiation of a photocatalytic reactor and catalyst in suspension confined by means of the membrane;

4b) as 4a), but the system works in continuous regime.

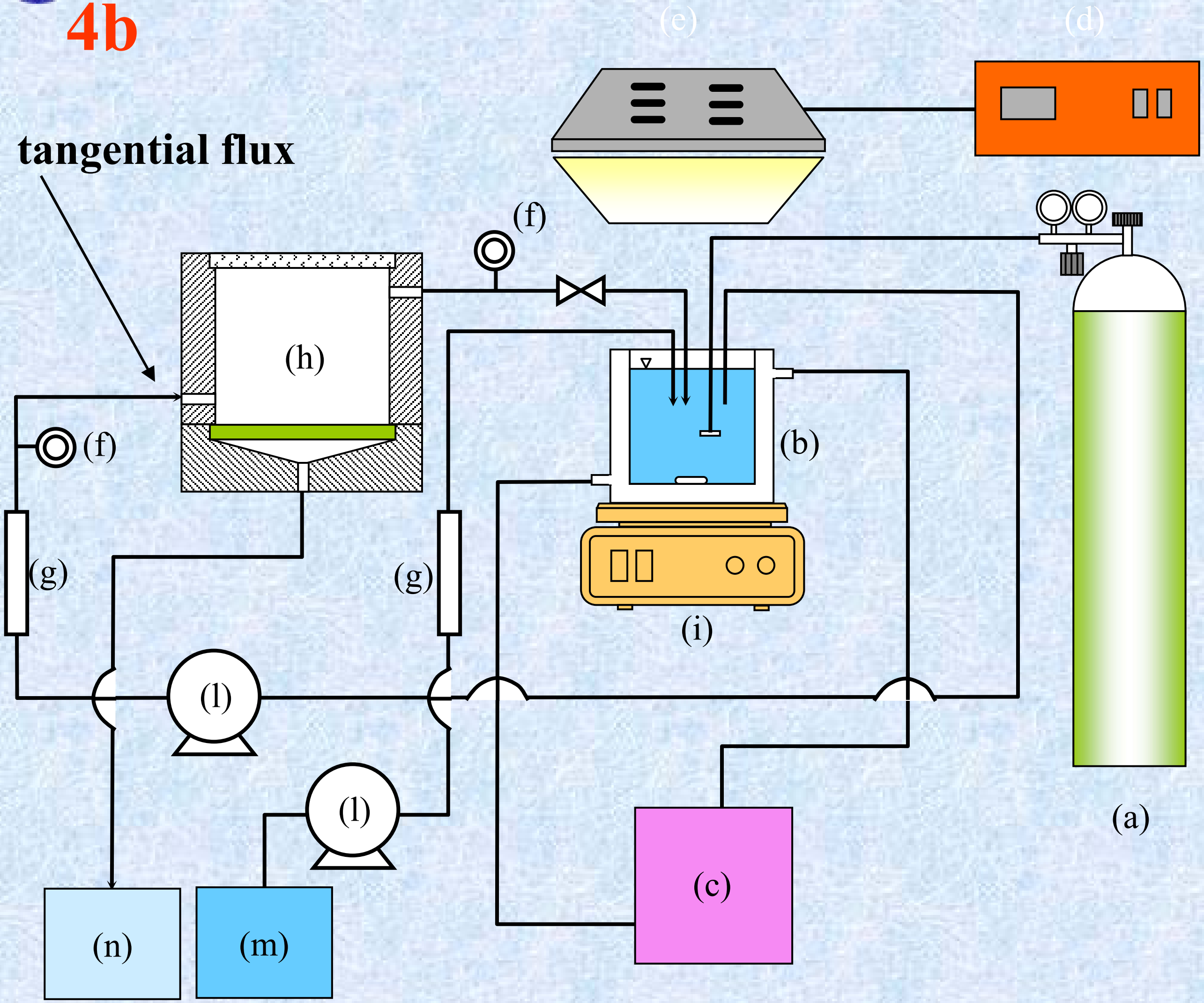
4a



(a) oxygen cylinder;
(b) cylindrical reactor with cooling jacket;
(c) thermostatted bath;
(d) power supply;
(e) medium pressure Hg lamp with conic reflector;
(f) manometer;
(g) rotameter;
(h) cell containing the membrane;
(i) magnetic stirrer;
(l) pump.

Scheme of the **Total Recycled Batch Photoreactor** system used with suspended catalyst.

4b



(a) oxygen cylinder;
(b) cylindrical reactor with cooling jacket;
(c) thermostatted bath;
(d) power supply;
(e) medium pressure Hg lamp with conic reflector;
(f) manometer;
(g) rotameter;
(h) cell containing the membrane;
(i) magnetic stirrer;
(l) pump;
(m) feed reservoir;
(n) permeate reservoir.

Scheme of the **Continuous Photoreactor** system used with suspended catalyst.

- Among the various configurations presented, **the configuration 4b** seems the most promising by an application point of view because it takes the advantages both of the classical photoreactors (catalyst in suspension) and of the membrane processes (separation at molecular level).

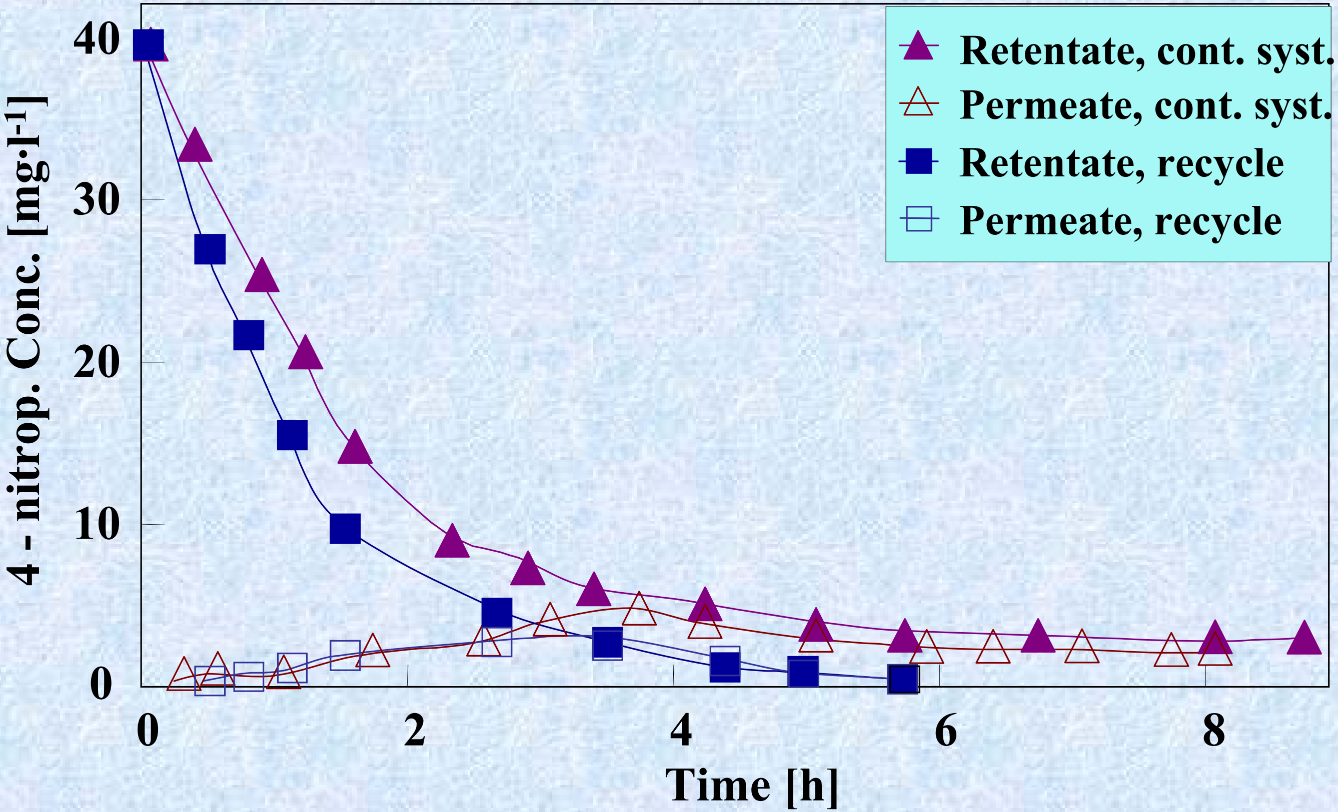
- The best **polymeric ultrafiltration membranes** used (good photostability checked by SEM and TOC, acceptable values of wpf, rejection unfortunately negligible etc.):

- PAN (polyacrylonitrile)
- FS50PP (fluoride + polypropylene)
- GR51PP (polysulfone + polypropylene).

- In order to improve the rejection effects, **polymeric nanofiltration membranes** were used in the systems 4a and 4b. The best ones were **NF-PES-010** (more permeable, polyethersulfone, Hoechst) and **N30F** (less permeable, modified polysulphone, Hoechst).

- The choice of the membrane depends on the size of the pollutants to be treated. pH can influence very strongly the rejection (Donnan Exclusion).

As an example: a representative run for 4-NP photodegradation is shown. For the recycle system the 4-NP maximum $C_{permeate}$ is 4 mg/l (10% with respect to the initial one); for the continuous system 7 mg/l (17% with respect to the initial one).



4-NP concentration in the retentate and permeate versus time for continuous and recycle system configurations (T = 30 °C, P = 3.5 bar, $[TiO_2]$ = 1 g/l, $[O_2]$ = 22 ppm, I = 3.6 mW/cm^2, tangential flowrate = 500 ml/min, permeate flux = 10 l/h·m^2). Membrane used: N30F[1,2]

[1] R. Molinari, L. Palmisano, E. Drioli and M. Schiavello, *J. Membrane Science* **206** (2002) 399

[2] R. Molinari, L. Giorno, E. Orioli, L. Palmisano, M. Schiavello in “*Nanofiltration Principles and Applications*”, A.I. Schäfer, A.G. Fane, T.D. Waite (Eds.), Elsevier, Oxford, U.K., 2005, Cap. 18, pp. 435-458, and references therein.

- ⇨ In addition to 4-NP, degradation tests were successfully carried out by using humic acids, phenol, benzoic acid, olive mill wastewater, organic dyes, drugs.

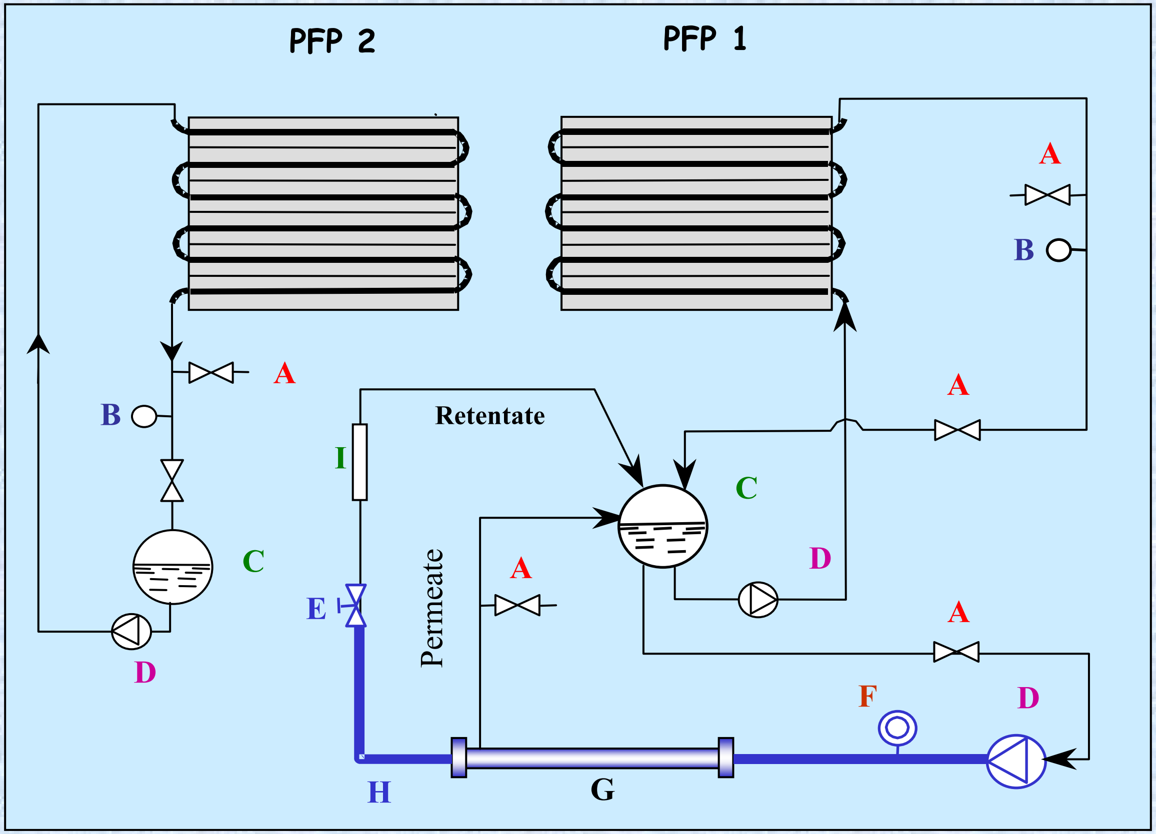
- ⇨ The membranes selected showed the capability to retain the photocatalyst and to reject partially organic species controlling the residence time in the reacting system.

- ⇨ Further work is required to look for other types of membranes, high rejection NF-type or low rejection reverse osmosis-type membranes. (To be efficient also when low molecular weight pollutants are studied).

- ⇨ Some tests by using sunlight (Plataforma solar de Almeria) to photodegrade lyncomicin[3] were carried out.

3. V. Augugliaro, E. García-López, V. Loddo, S. Malato, I. Maldonado, G. Marcì, R. Molinari, L. Palmisano, *Solar Energy* **79** (2005) 402.

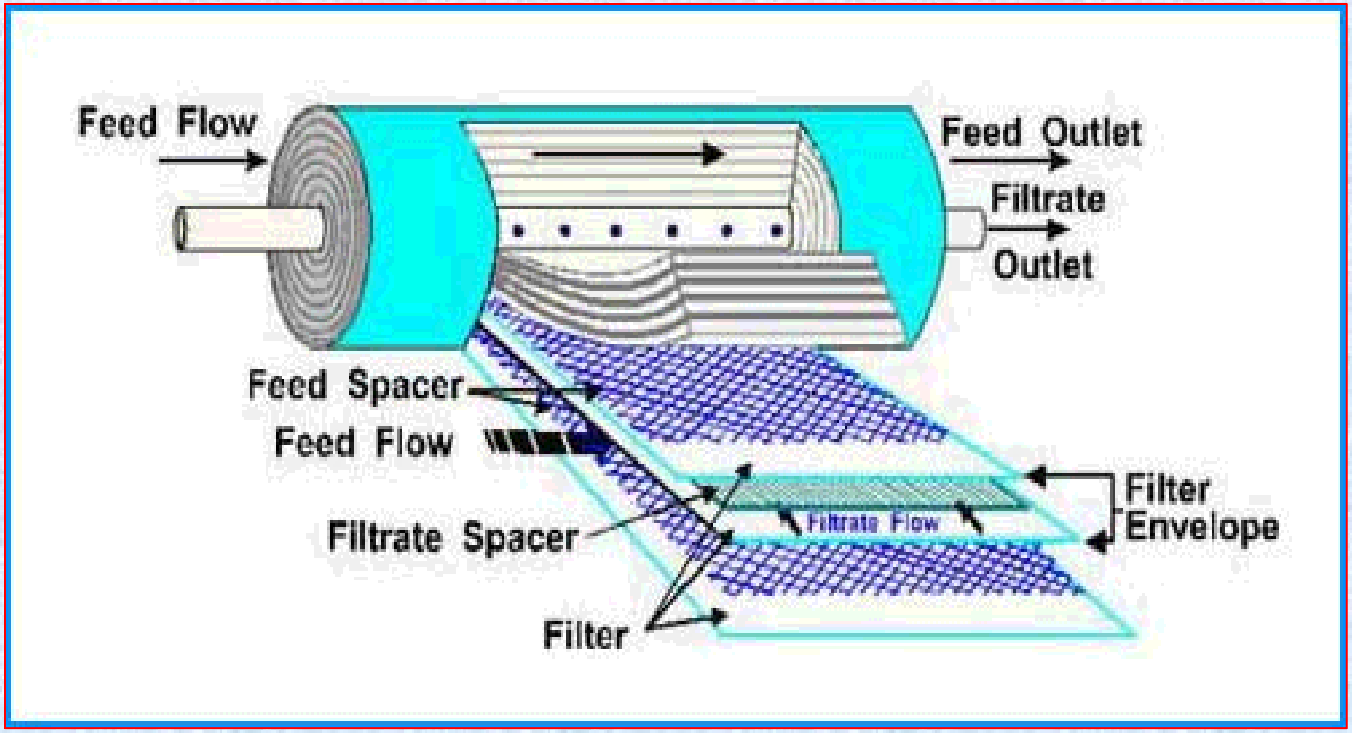
Scheme of the photoreacting batch systems



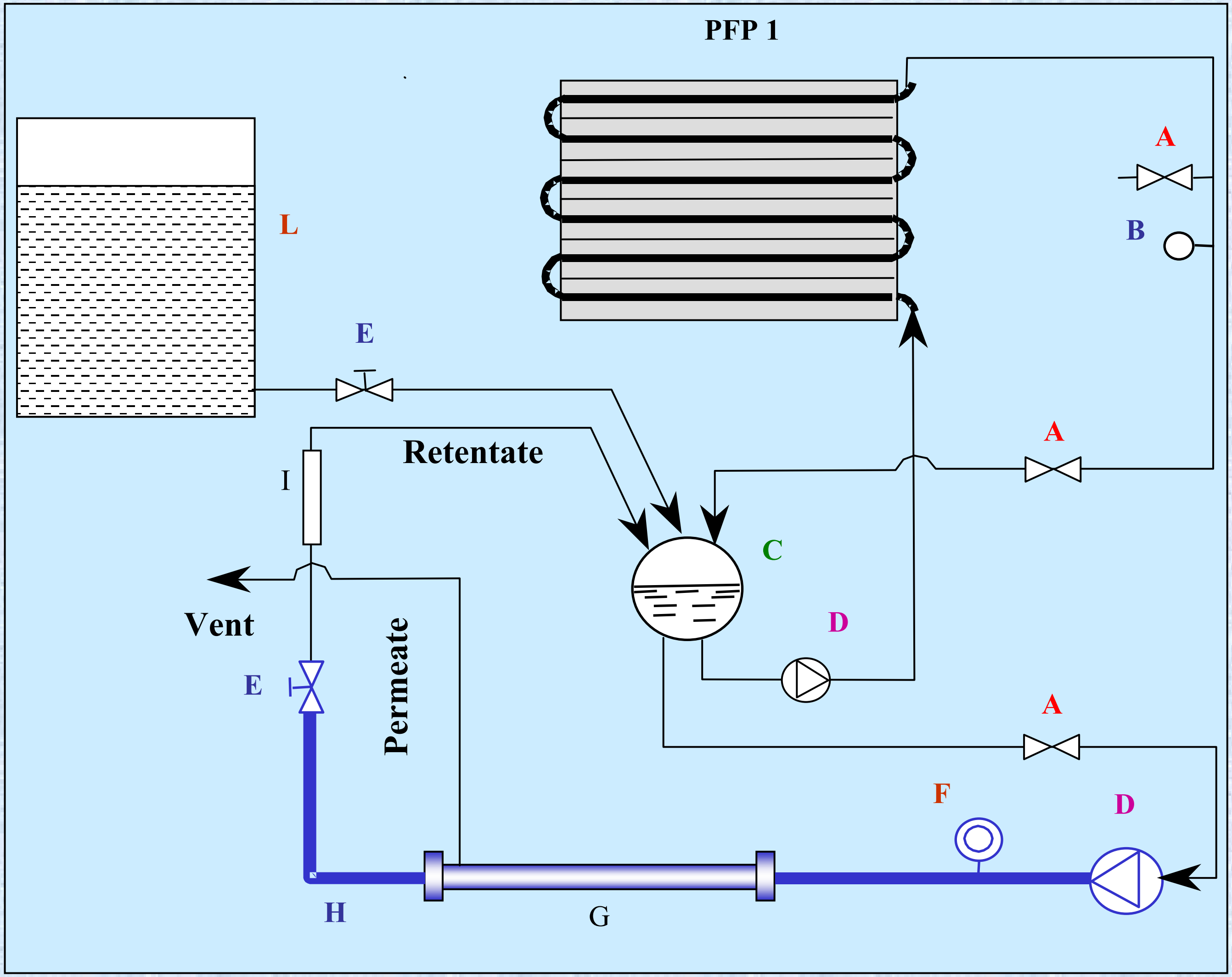
(A) switch valve; (B) thermocouple; (C) not-reacting tank;
(D) pump; (E) regulation valve; (F) manometer;
(G) membrane vessel; (H) line under pressure; (I) rotameter;
(PFP) plug flow photoreactor.

EXPERIMENTAL

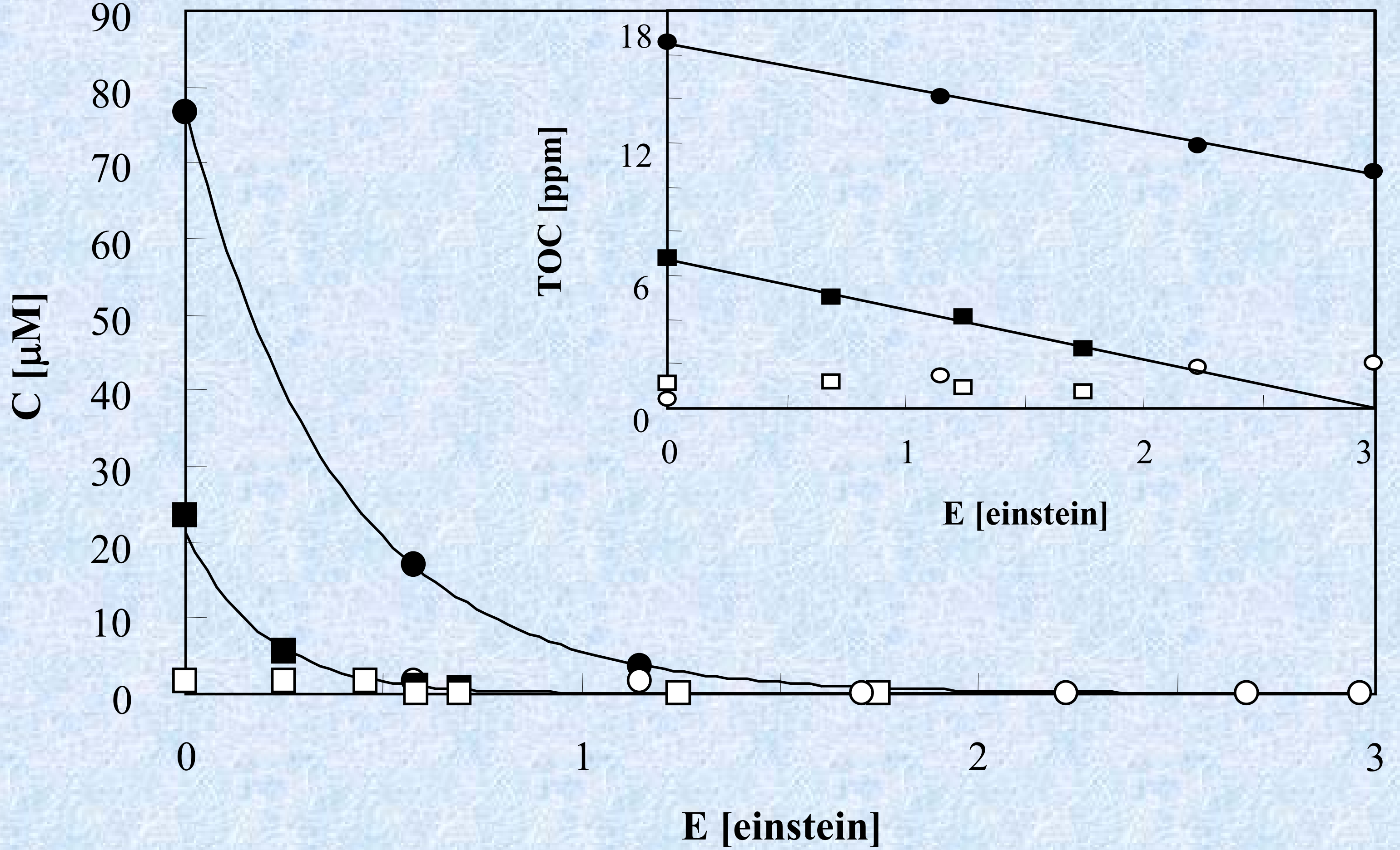
Commercial nanofiltration membrane modules (DL2540C and DK2540C, Ø=2.5 inch, L=40 inch; Permeare srl, Italy) were used at an operative pressure of 4 bar.



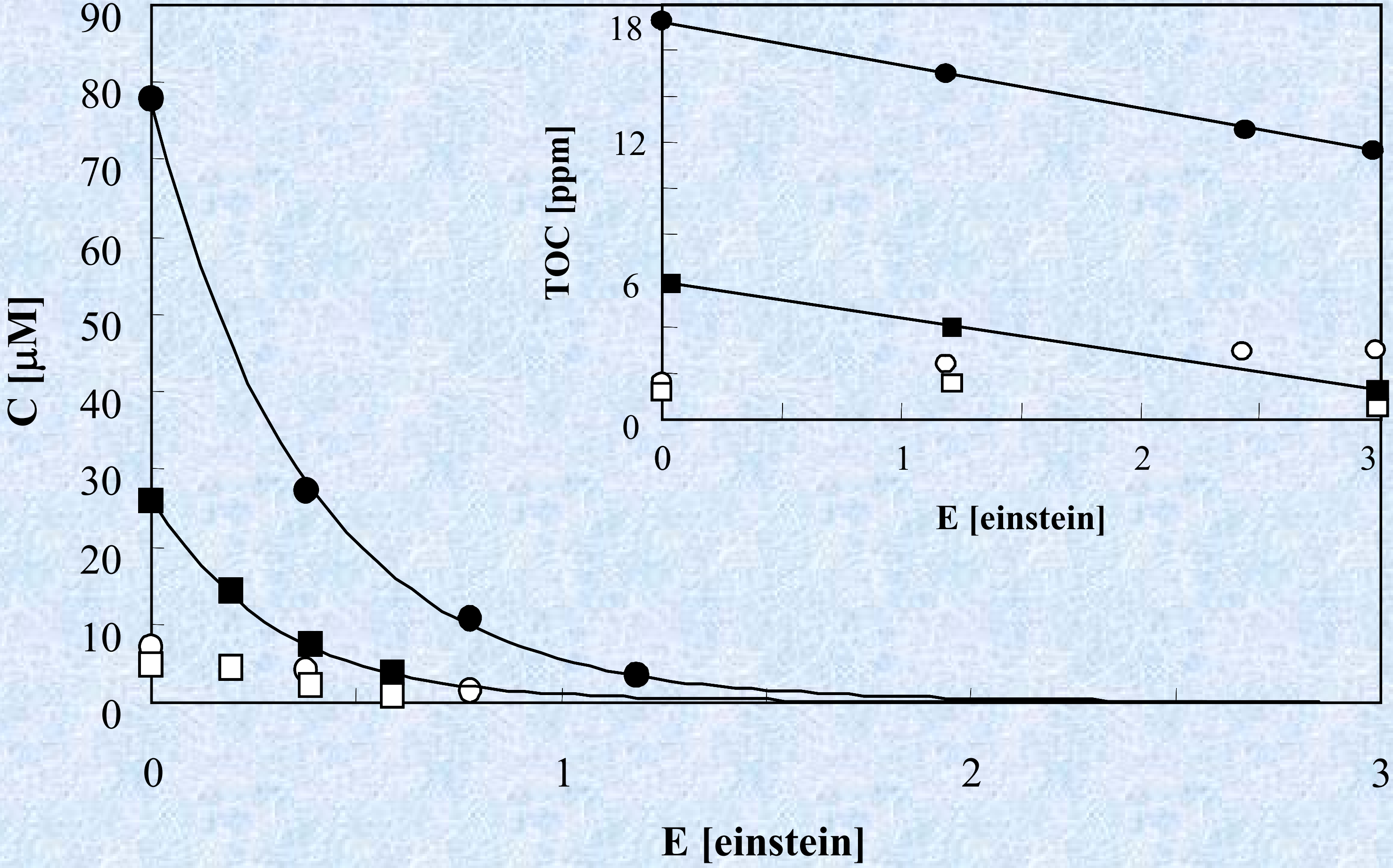
Scheme of the photoreacting continuous system



(A) switch valve;
(B) thermocouple;
(C) not-reacting tank;
(D) pump;
(E) regulation valve;
(F) manometer;
(G) membrane vessel;
(H) line under pressure;
(I) rotameter;
(L) feedtank;
(PFP) plug flow photoreactor.



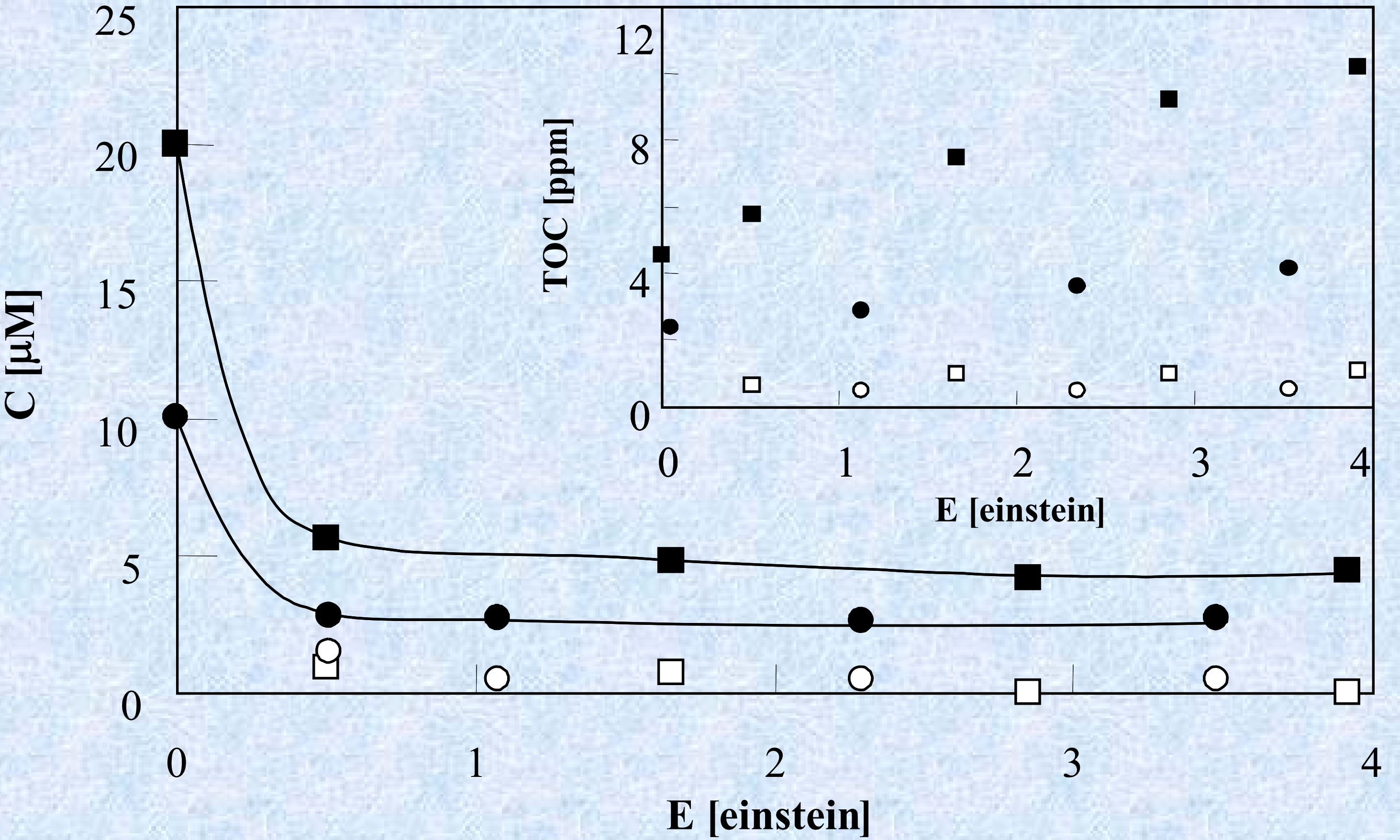
Lincomycin and TOC (in the inset) concentrations versus the cumulative photon energy, E, for runs carried out in total recirculation regimens by using the hybrid system with DK2540C membrane at different initial lincomycin concentrations. 75 mM: Retentate, ●; permeate, ○. 25 mM: Retentate, ■; permeate, □. Measurements error: ± 3%.[3]



Lincomycin and TOC (in the inset) concentrations versus the cumulative photon energy, E, for runs carried out in total recirculation regimens by using the hybrid system with DL2540C membrane at different initial lincomycin concentrations.

75 mM: Retentate, ●; permeate, ○.

25 mM: Retentate, ■; permeate, □. (Measurements error: ± 3%.)[3]

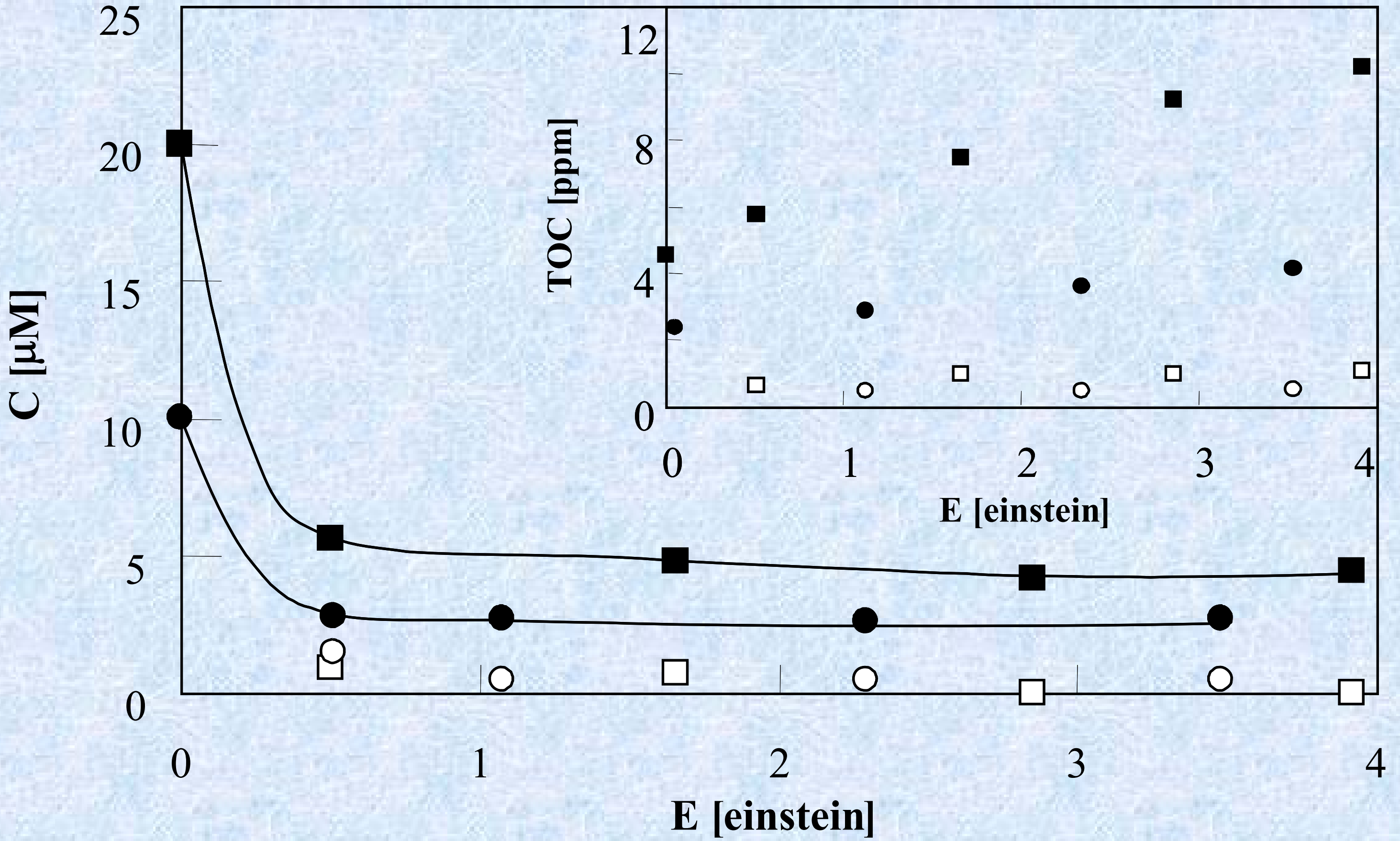


Lincomycin and TOC (in the inset) concentrations versus the cumulative photon energy, E, for runs carried out in continuous regimen by using the hybrid system at different initial lincomycin concentrations.

DK2540C membrane, 10 mM: Retentate, ●; permeate, ○.

DL2540C membrane, 25 mM: Retentate, ■; permeate, □.

(Measurements error: ± 3%.)[3]



It can be noticed a total organic carbon accumulation in the reacting volume. This feature can be explained by considering that under the experimental conditions used, the amount of photons entering the system per unit time are not sufficient to mineralise the organic carbon fed in the photoreactor per unit time.

Integrated processes: Photocatalysis (PC) + Pervaporation (PV)

- ⇨ It has been demonstrated that the integration of **Photocatalysis (PC)** with a membrane separation process, i.e. **Pervaporation (PV),** is a very promising method to improve the efficiency of the detoxification of water streams containing organic pollutants at low concentration.
- ⇨ The commercial pervaporation membranes are **organophilic** so that most of the organic compounds permeate preferentially with respect to water.
- ⇨ 4-Chlorophenol has been used as a probe molecule and the disappearance rate (transformation in HQ and BQ) was highly improved.[1]

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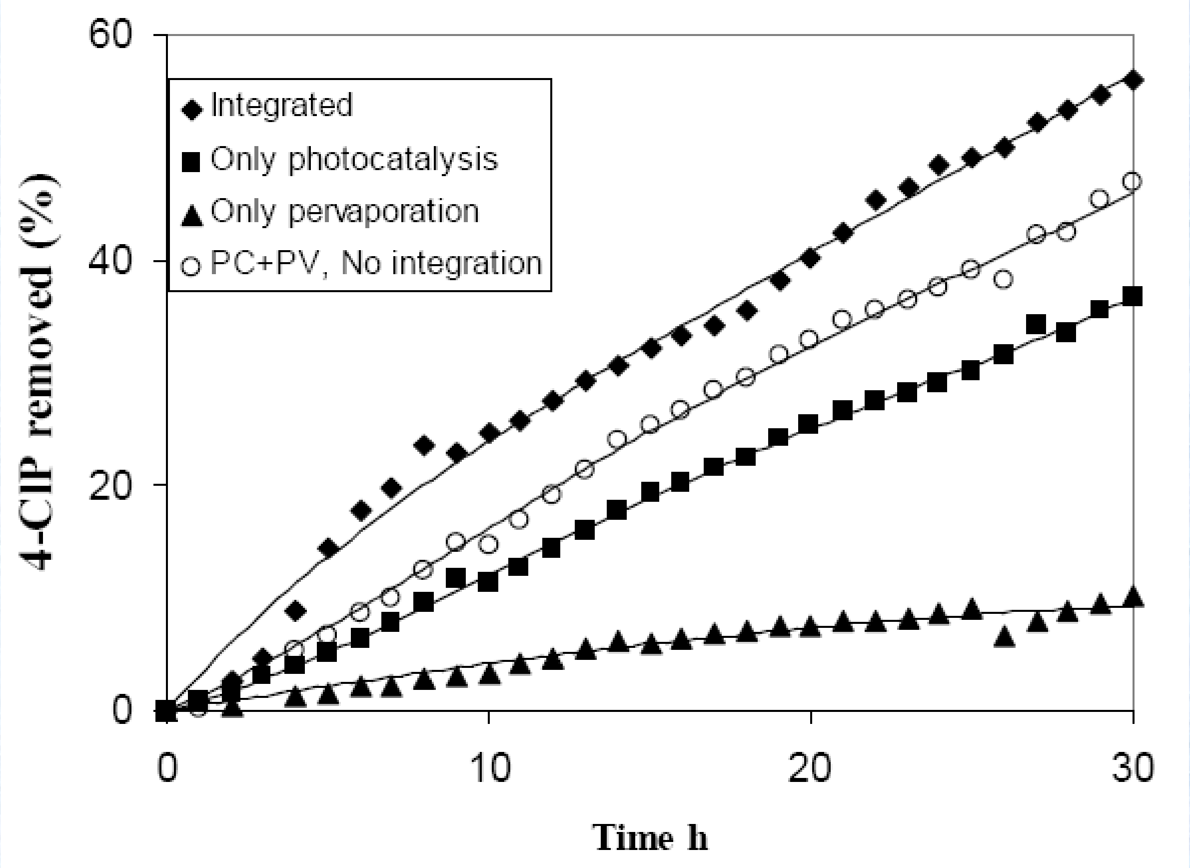
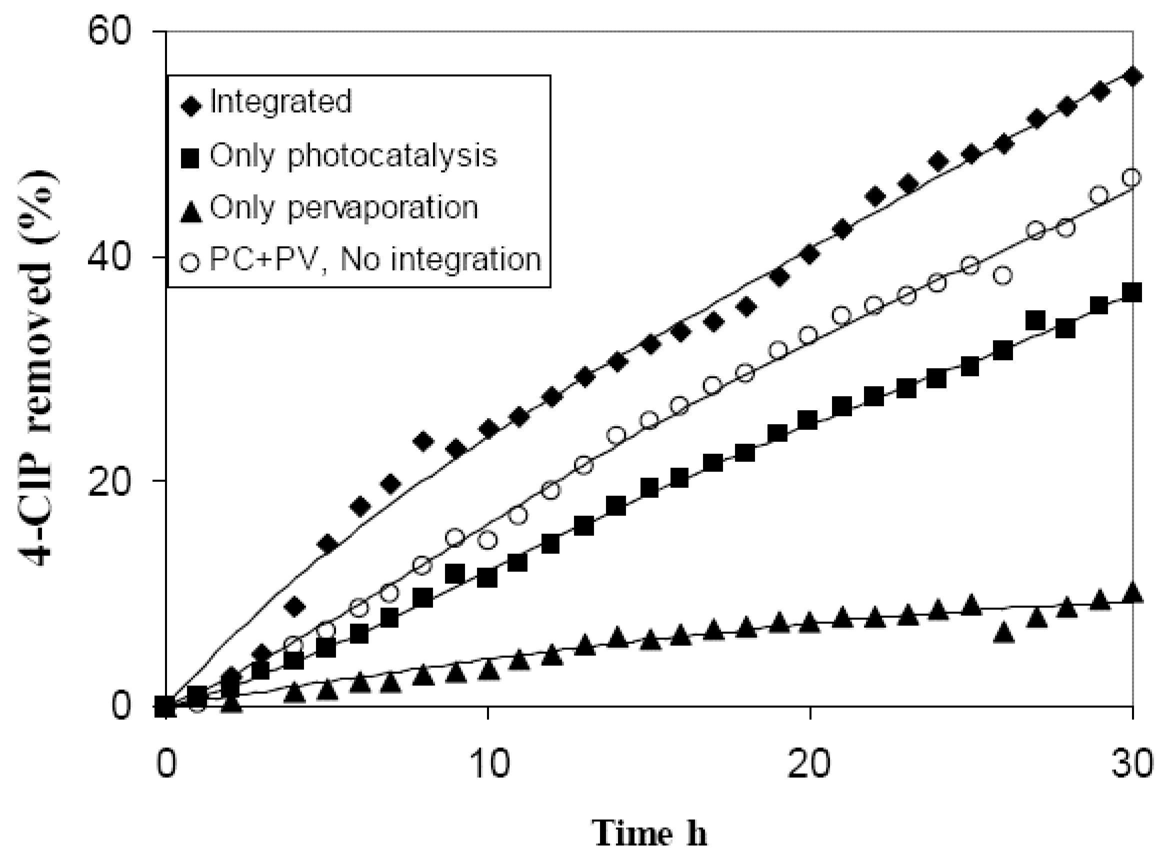
1. C. Roda, F. Santarelli, Proc. “*Engineering with Membranes*”, Granada (Spain), June 3-6 (2001), vol. I, pp. 334-339.



PC + PV, no integration represents the arithmetic sum of the removals of PC and PV acting alone. The plot overestimates the performances of the two processes operating in series, without integration, because the second process of the series would in any case work with a smaller driving force (proportional to the 4-ClP concentration).

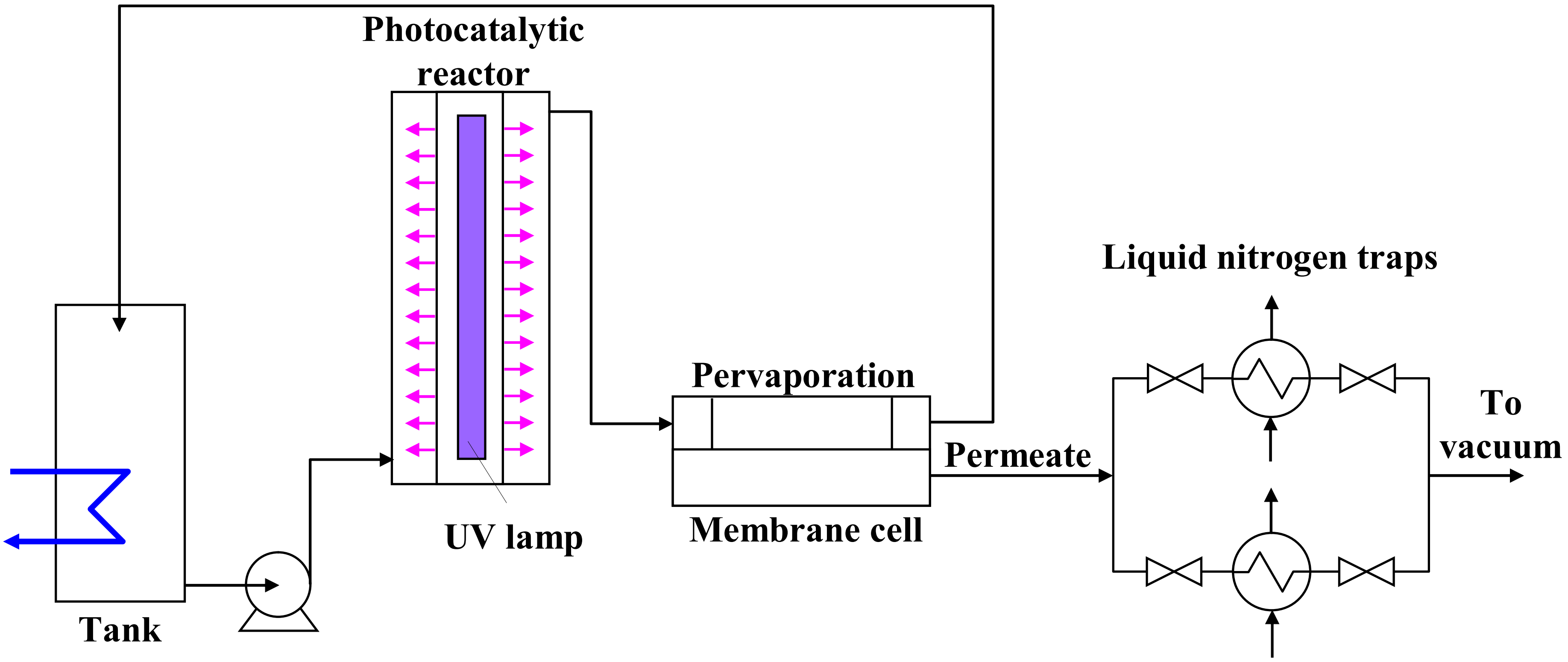
The optimistic sum is everywhere lower than the plot representing the operation of the integrated process.



Some synergy exists because PC is favoured by the continuous subtraction by PV of the intermediates that hinder the photocatalytic reaction competing with 4-ClP.

Also PV takes advantage of PC that transforms a poorly permeable compound (4-ClP) into highly permeable compounds (HQ and especially BQ).

It is worth noting that in the integrated process the quantity of permeate stream collected is very small on respect to the initial volume of water to be purified.


Photocatalytic reactor
Liquid nitrogen traps
Pervaporation
To vacuum
Permeate
UV lamp
Membrane cell
Tank

Summary

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Integrate Microwave – UV sources for photocatalytic reaction

- Microwave assisted chemistry is performed using special reactors of dielectric materials placed inside a microwave oven fed with high voltage magnetron sources emitting continuous or pulsed power (ca. 2450 MHz).[1-3]
- This technique has been used both in **gas-solid system** for the photodegradation of many organic molecules (carboxylic acids, aldehydes, phenolic substrates, etc.) adsorbed on TiO_2 (T=20÷200°C) and in **liquid-solid systems** for the photo-degradation of cationic rodhanine-B in aqueous TiO_2 dispersion.
- CNR (Italian National Centre of Research) took patents of new devices consisting of microwave-UV integrated electrodeless sources.[4]

1. I.H. Tseng, W.C. Chang, J.C.S. Wu, *Appl. Catal. B: Environ.* **37** (2002) 37.
2. Z.H. Ai, P. Yang, X.H. Lu, *Fresenius Environ. Bull.* **13** (2004) 550.
3. S. Horikoshi, F. Hojo, H. Hidaka, N. E. Serpone, *Environ. Sci. Tech.* **38** (2004) 2198
4. I. Longo, A. Ricci, N. Tosoratti, *Proc. of XVI National Congress of Industrial Chemistry*, 2005, 113.

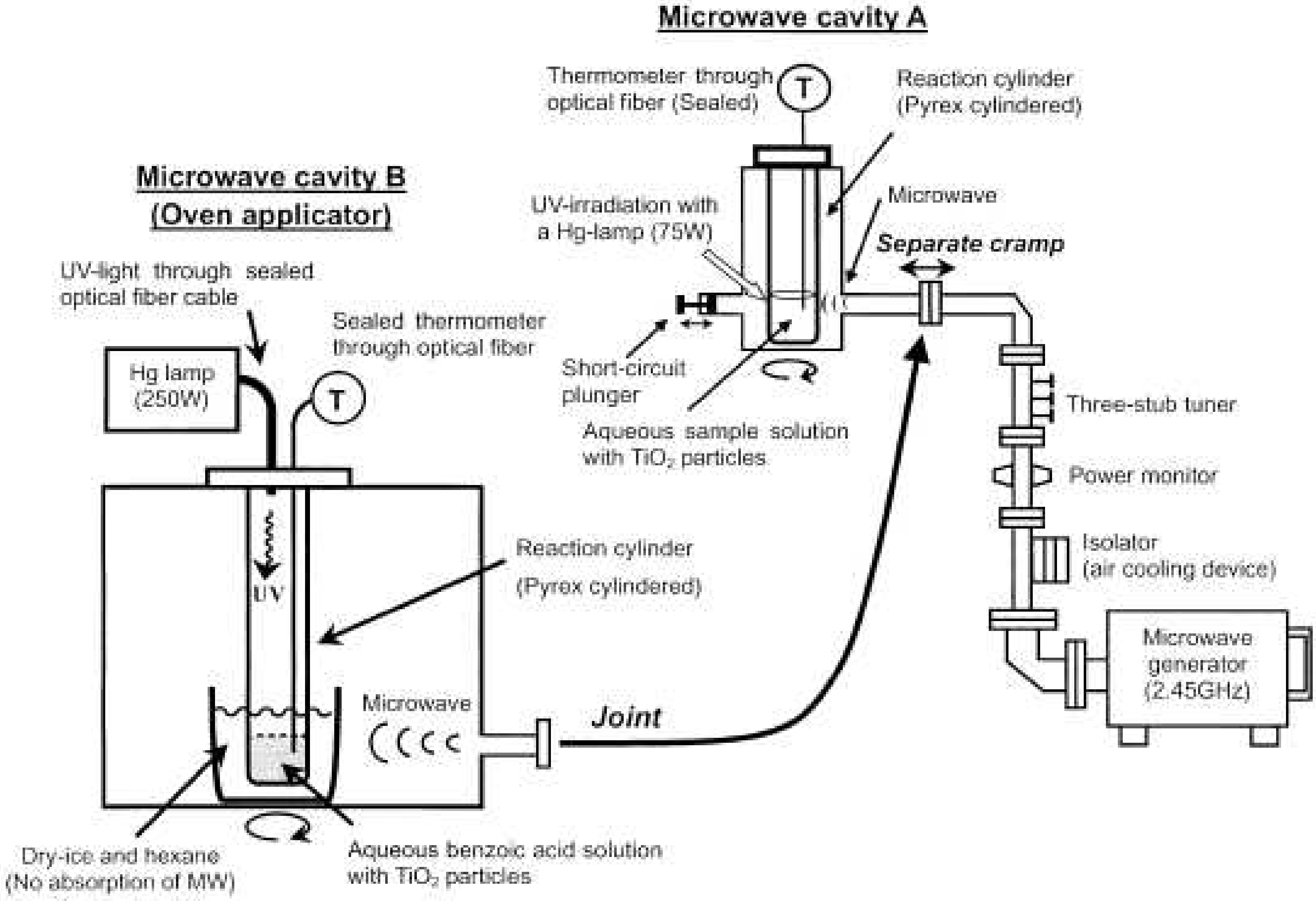

FIGURE 1. Experimental setup used for the UV and MW irradiation of the contents in the cylindrical reactor system employing a single-mode resonant cavity (A) and a multiple-mode applicator (B).[3]

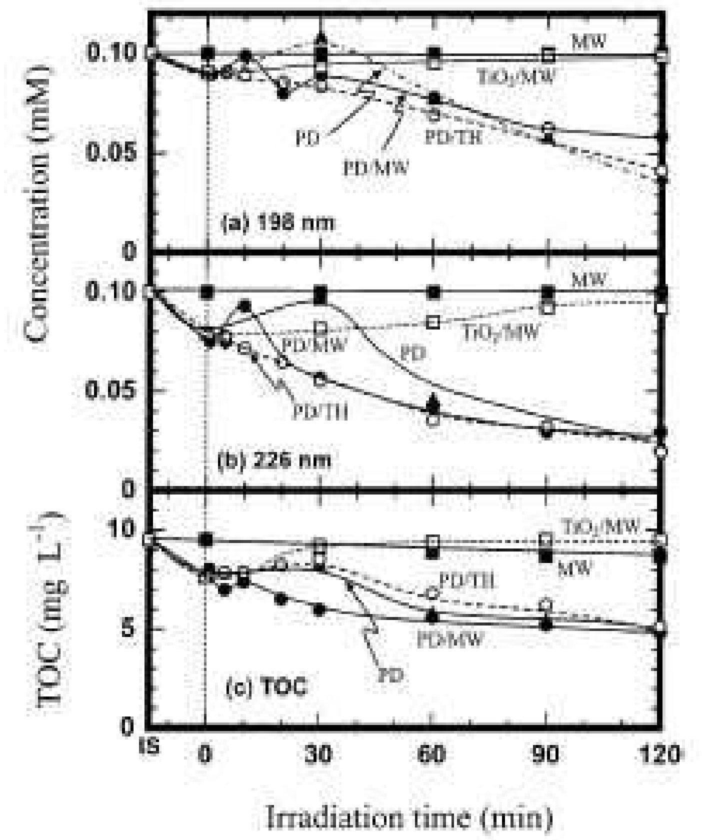

FIGURE 2. Temporal decrease of the UV absorption at 198 nm (a) and 226 nm (b), and the temporal disappearance of TOC during the degradation of a benzoic acid solution by microwave irradiation (MW), photocatalyzed reaction under microwave and dark conditions (TiO_2/MW), photocatalyzed oxidation (PD) at TiO_2 loadings of 60 mg, thermally assisted photocatalyzed oxidation (PD/TH), and integrated microwave-assisted photocatalyzed degradation (PD/MW) (IS = initial solution).[3]

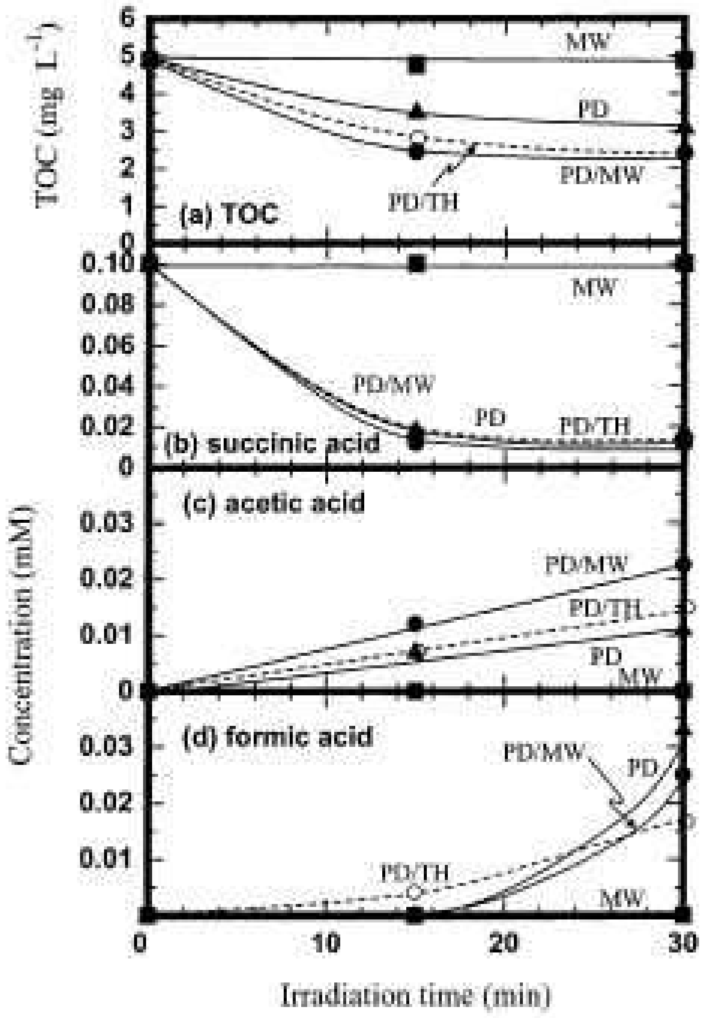

FIGURE 4. Decrease of TOC and succinic acid, and formation of acetic acid and formic acid intermediates in the degradation of succinic acid (30 mL, 0.1 mM) in the presence of TiO_2 (60 mg).[3]

CONCLUSIONS

- In contrast with the gas-solid systems (many applications) heterogeneous photocatalysis in liquid-solid system can be used alone only in some specific cases.

- A more useful perspective is to couple heterogeneous photocatalysis with other technologies.

- Coupling with biological, electrochemical, ozone, membrane technologies appear promising.

- The use of sunlight is very intriguing but it should follow a systematic investigation on bench scale by using artificial light to have a better knowledge of the influence of some parameter on the photoreactivity.

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