Tratamiento de aguas conteniendo contaminantes orgánicos persistentes mediante combinación de procesos de oxidación avanzada y biológicos. Proyecto CADOX

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PLATAFORMA SOLAR DE ALMERÍA. CIEMAT-Ministerio de Educación y Ciencia. 04200 Tabernas, Almería

SOLAR SAFE WATER
14 al 17 de Octubre de 2005 - Iguazú - Misiones - República Argentina

MINISTERIO DE EDUCACION Y CIENCIA | Ciemat Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas | PSA

Programme for Research, Technological Development and Demonstration under the Fifth Framework Programme

Work Programme for Environment and Sustainable Development

Key Action 1: Sustainable Management and Quality of Water

CADOX: A coupled Advanced Oxidation - Biological Process for Recycling of Industrial Wastewater containing persistent organic contaminants.

http://www.psa.es/webeng/projects/cadox/index.html

February 2003-July 2006.

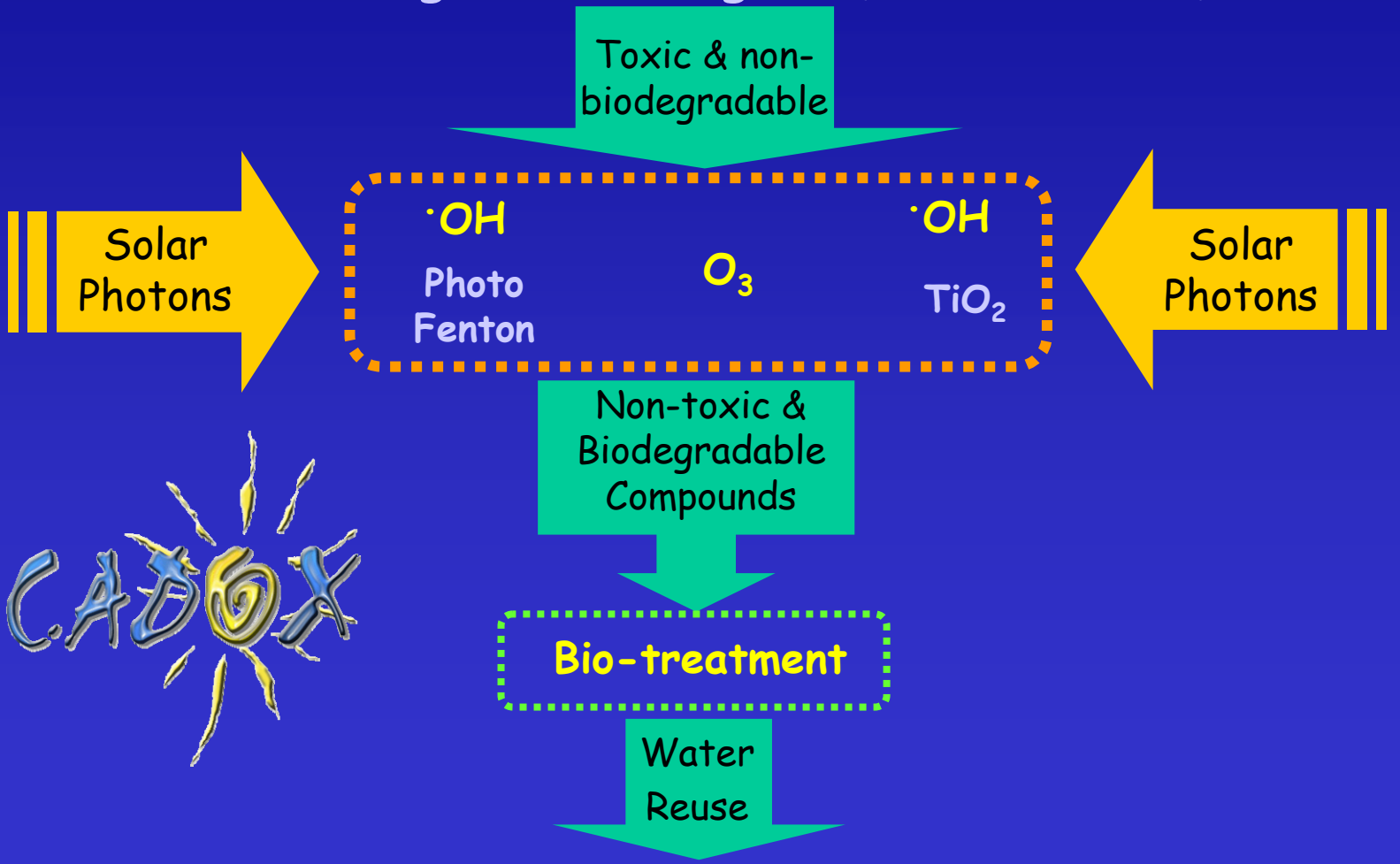
PARTNERS

- Research institution for energy and environment. COORDINATOR. Spain.
- Engineering. Turnkey treatment plants installation. Spain
- Manufacturer of solar collectors. Portugal
- Public university. Spain
- Research Institution. Portugal
- Manufacturer of ozone systems. France
- Agrochemical and pharmaceutical products manufacturing company. Belgium
- Public university. Switzerland
- Chemical industry with NBCS wastewaters. Spain

OVERVIEW

Industrial Wastewater (IPPC directive)

containing PS<500 mg/L (WF directive)



U1

MAIN OBJECTIVES

- ✓ Demonstrating that the coupling of AOPs and biodegradation is a suitable procedure for decontaminating wastewaters containing 7 medium/high soluble pesticides and NBCS.
- ✓ Treating other compounds as function of the final users (JANSSEN and DERETIL) necessities.
- ✓ Definition of new solar collectors for carrying out TiO_2 and Photo-Fenton photocatalysis.
- ✓ Construction of 2 small prototypes with the previous technologies including O_3. Coupling with aerobic biological treatment (fixed-bed activated sludge reactor).

OCTOBER 2005

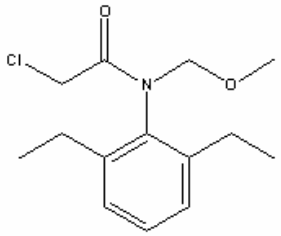
- ➢ Construction of a demonstration plant.
- ➢ Design and economic evaluation of a full size treatment plant.
- ➢ Detailed analysis of the applicability of this technology in Europe by determining sources of PS at low-medium concentration (<500 mg/L).

Diapositiva 5

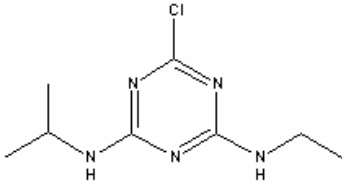
U1 Averiguar si pongo la fecha hasta la cual voy a contar experimentos junio 2005 o mejor septiembre 2005 porque esté más cerca de la fecha del congreso.

USUARIO; 06/10/2005

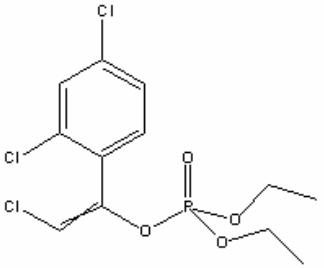
TARGET SUBSTANCES



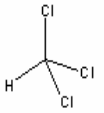
Alachlor



Atrazine

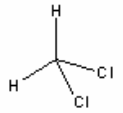


Chlorfenvinphos

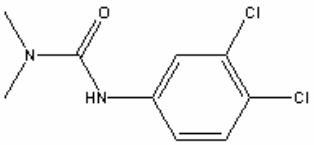


Chloroform

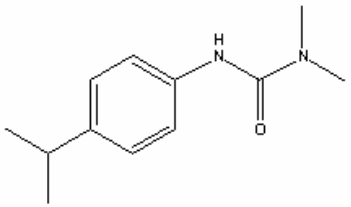
Dichloroethane



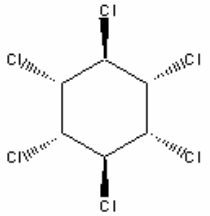
Dichloromethane



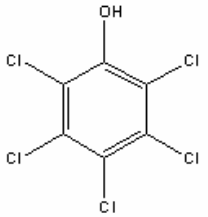
Diuron



Isoproturon



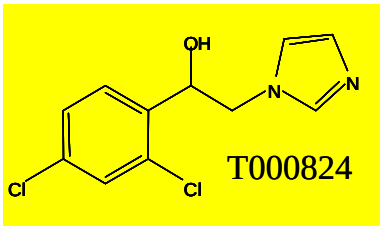
Lindane

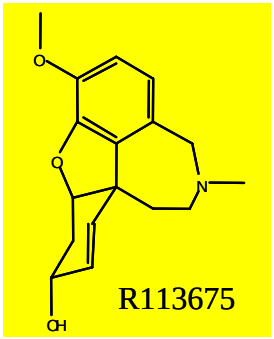


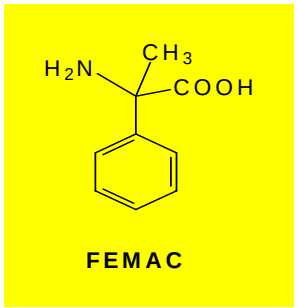
Pentachlorophenol

NBCS and "soluble" pesticides included in the list of priority substances in the field of water policy and amending Directive 2000/60/EC.

DECISION No 2455/2001/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 20 November 2001







Final users compounds

LAB TESTS

The first Tasks of the CADOX project have been designed for determining the main parameters related with the degradation of the target compounds by each method:

TiO_2 (INETI)

Photo-Fenton (PSA) 

Ozone (UAB)

Biological Degradation (EPFL)

50 mg/L (except for those of lower water solubility). Only Femac at 500 mg/L. Main parameters:

- ✓ Target compounds, TOC, COD.
- ✓ Cl-, NH4-N, NO3-N, pH.
- ✓ Biodegradability, Toxicity.
- ✓ Fe(II), Fe(III), H_2O_2, O_3.

PRELIMINARY CONCLUSIONS (I)

1. The pesticides show the same kind of reactivity in both systems (Fenton/photo-Fenton and heterogeneous photocatalysis).
2. For atrazine and phenylurea pesticides some residual TOC hardly to remove remains in solution, due to the stability of trazine ring and urea formed during degradation process, respectively.
3. Heterogeneous photocatalysis need more accumulation of energy (more irradiation times) to achieve the same degree of mineralization than Fenton/photo-Fenton process.

S. Malato, J. Cáceres, A. R. Fernández-Alba, L. Piedra, M. D. Hernando, A. Agüera, J. Vial. Photocatalytic treatment of diuron by solar photocatalysis: evaluation of main intermediates and toxicity. ***Env. Sci. Technol.,*** **37,** 2516-2524, 2003.
S. Malato, J. Blanco, A. Vidal, D. Alarcón, M. I. Maldonado, J. Cáceres, W. Gernjak. Applied studies in solar photocatalytic detoxification: an overview. ***Solar Energy, 75,*** 329-336, 2003.

PRELIMINARY CONCLUSIONS (II)

4. **Biodegradability is attained when practically total dechlorination is achieved.**
5. Ozonation gives low yields of pesticide mineralization and total dechlorination is very slowly attained.
6. **Mineralization of NBCS is readily achieved under photo-Fenton conditions, but hardly occurs with TiO_2. Coupling biological treatment with Fenton/photo-Fenton is not necessary.**
7. The elevated irradiation times required by TiO_2 to decrease TOC could produce severe NBCS losses by volatilization.

V. Sarria, S. Kenfack, O. Guillod, C. Pulgarin An innovative coupled solar-biological system at field pilot scale for the treatment of biorecalcitrant pollutants. ***J. Photochem. Photobiol. A: Chemistry 159,*** 89-99 2003.
M.I. Franch, J.A. Ayllón, J. Peral and X. Domènech. Fe(III)-photocatalysed degradation of low chain carboxylic acids. Implication of the iron salt. ***Applied Catalysis B: Environmental, 50,*** 89-99, 2004.
Maria José Farré, Maria Isabel Franch, Sixto Malato, José Antonio Ayllón, José Peral and Xavier Domènech. Degradation of some biorecalcitrant pesticides by Homogeneous and Heterogeneous Photocatalytic Ozonation. ***Chemosphere, 58,*** 1127-1133, 2005.

NEW CPCs DESIGN

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PSA

Definition of new solar collectors for carrying out TiO_2 and Photo-Fenton photocatalysis.

NEW CPCs DESIGN

An improved solution must permit:

- ✓ TiO_2 and Photo-Fenton.
- ✓ Smaller number of tubes, connections, etc per collector surface than in the collectors available previously to CADOX.
- ✓ Higher illuminated volume per collector surface, with a lower "dead-volume" in the overall photocatalytic plant.
- ✓ Smaller amount of catalyst.

NEW CPCs DESIGN

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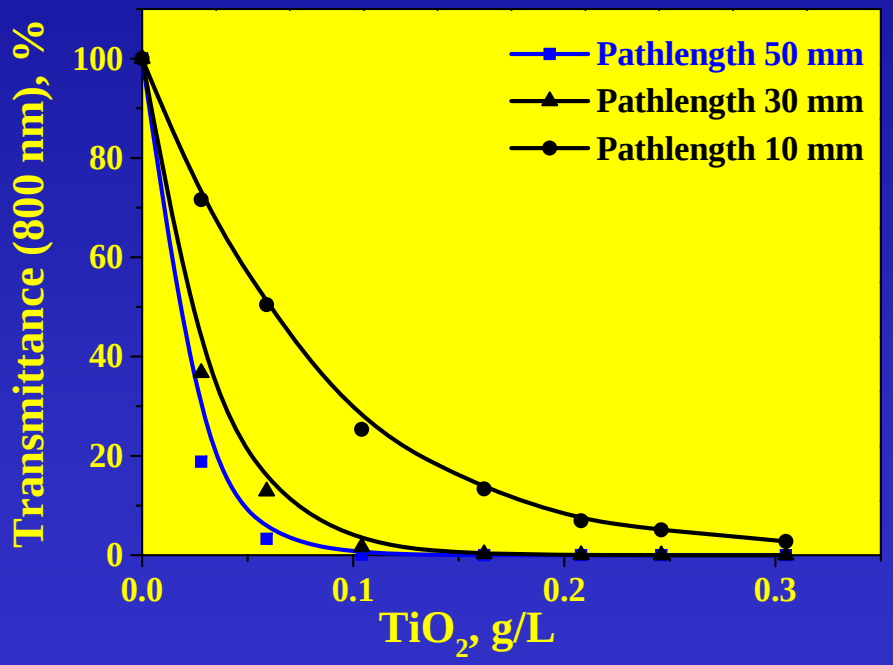
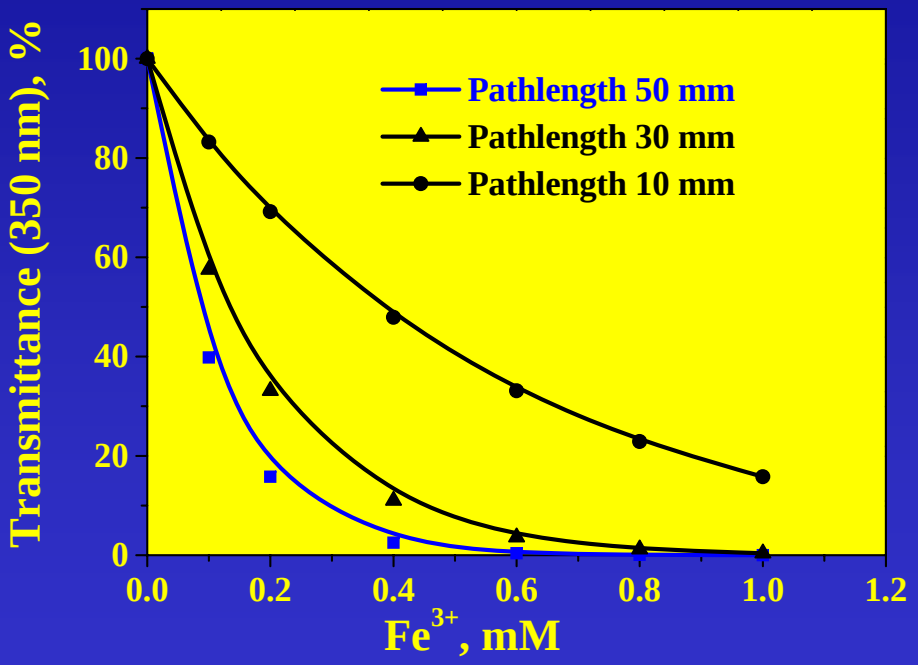
Objective: Minimum transmittance (Max. absorption of photons) at minimum concentration of photocatalyst





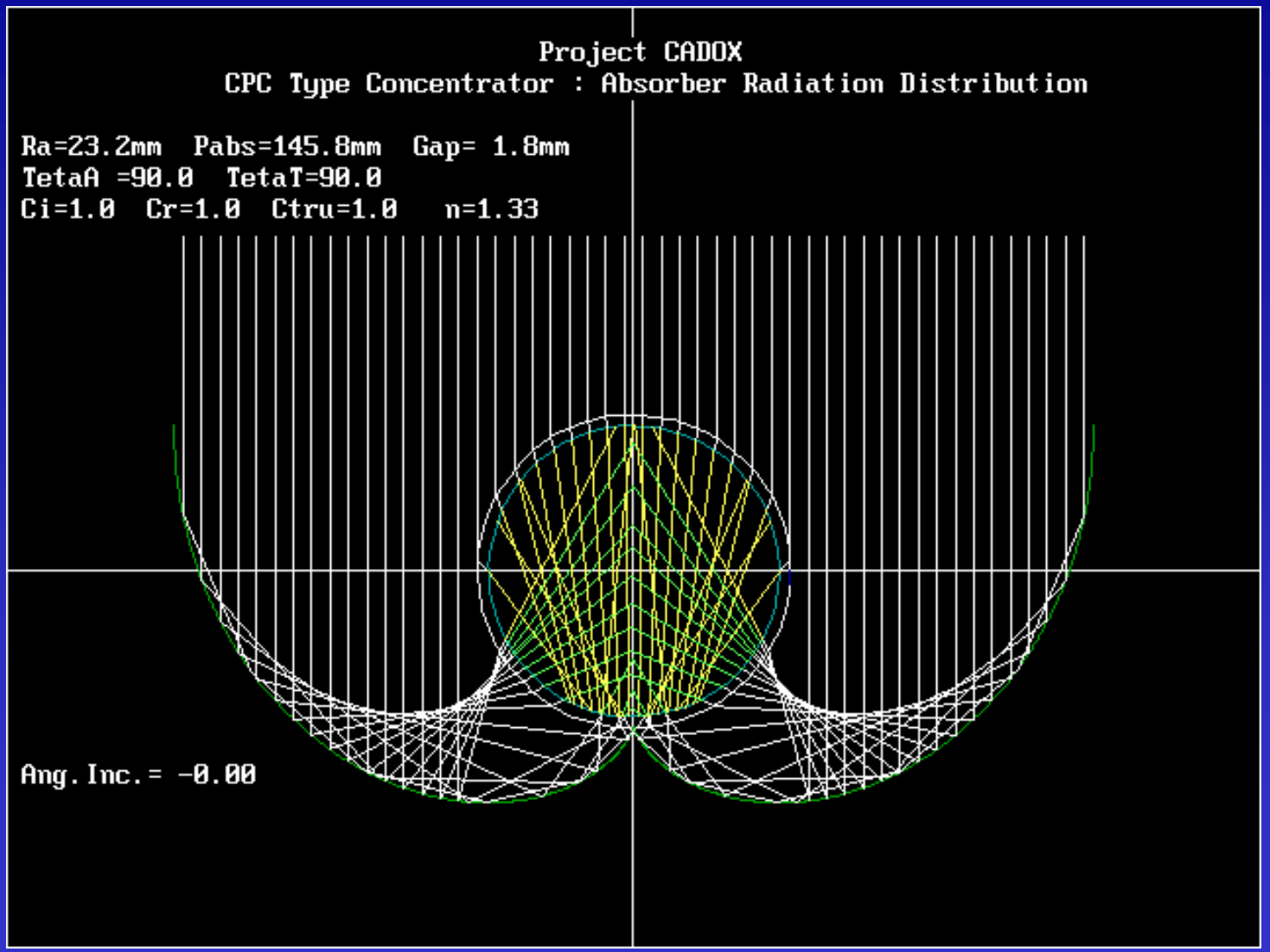
NEW CPCs DESIGN

The study for the CPC profile shows that a 50mm O.D. reactor seems to be a better solution because:

- ✓ Former CPCs were not suitable for photo-Fenton at low iron concentration.
- ✓ It could permit less catalyst loading and/or enhance light absorption.
- ✓ Tubes will be in a smaller number, thereby reducing the probability of breakage and of leaks.
- ✓ The larger diameter will allow for a more precise fabrication of the curved mirrors and for a greater ease of automation of manufacture.

S. Malato Rodríguez, J. Blanco Gálvez, M.I. Maldonado Rubio, P. Fernández Ibáñez, D. Alarcón Padilla, M. Collares Pereira, J. Farinha Mendes, J. Correia de Oliveira. Engineering of solar photocatalytic collectors. ***Solar Energy, 77,*** 513-524, 2004

NEW CPCs DESIGN



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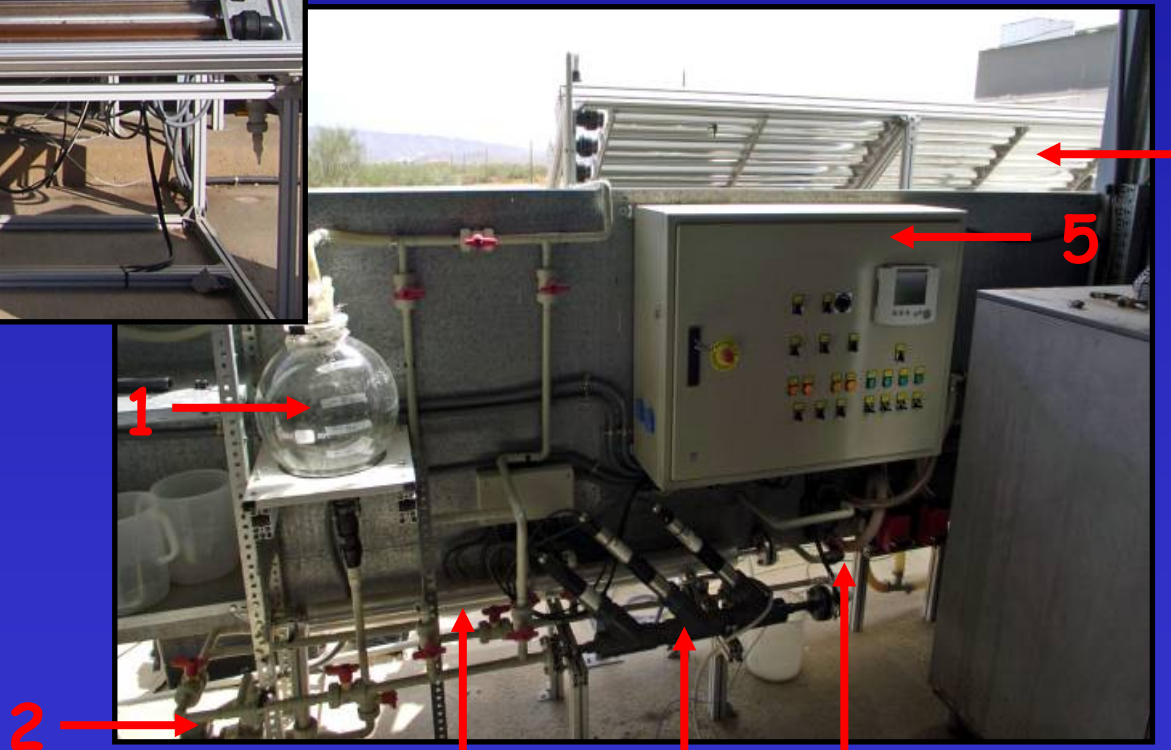
PSA

Guiding the Al mirrors and fixing the tubes

NEW CPCs

NEW PILOT PLANT

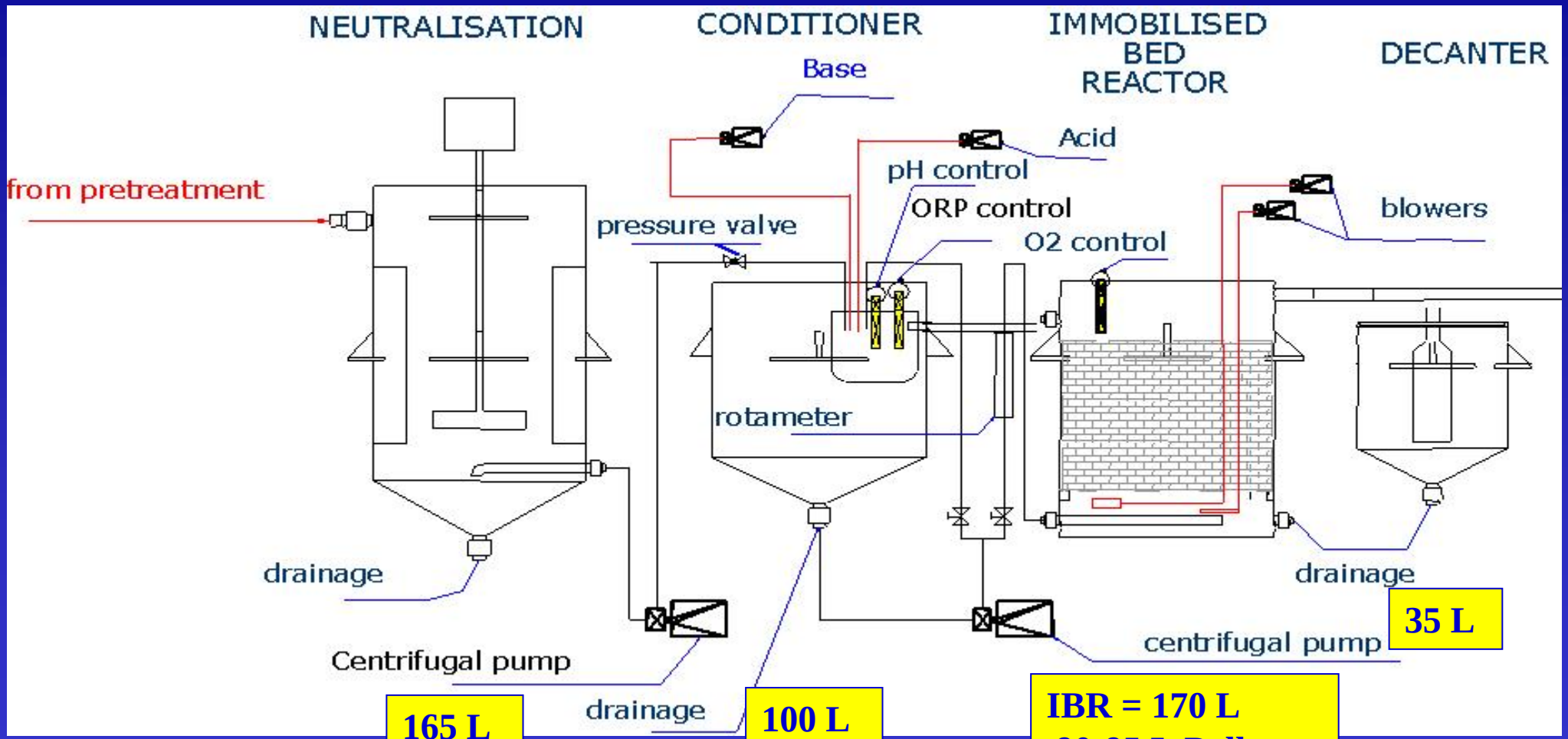


1. Tank
2. Recirculation pump
3. Sensors
4. Heat exchangers
   (a:heating,b:cooling)
5. Instrument panel
6. Solar collector

NEW PILOT PLANT

1. Ozone generator
2. Contact column
3. Pump
4. Oxygen bottle
5. Ozone analyser
6. Rotameter
7. Ozone destructor

NEW PILOT PLANT



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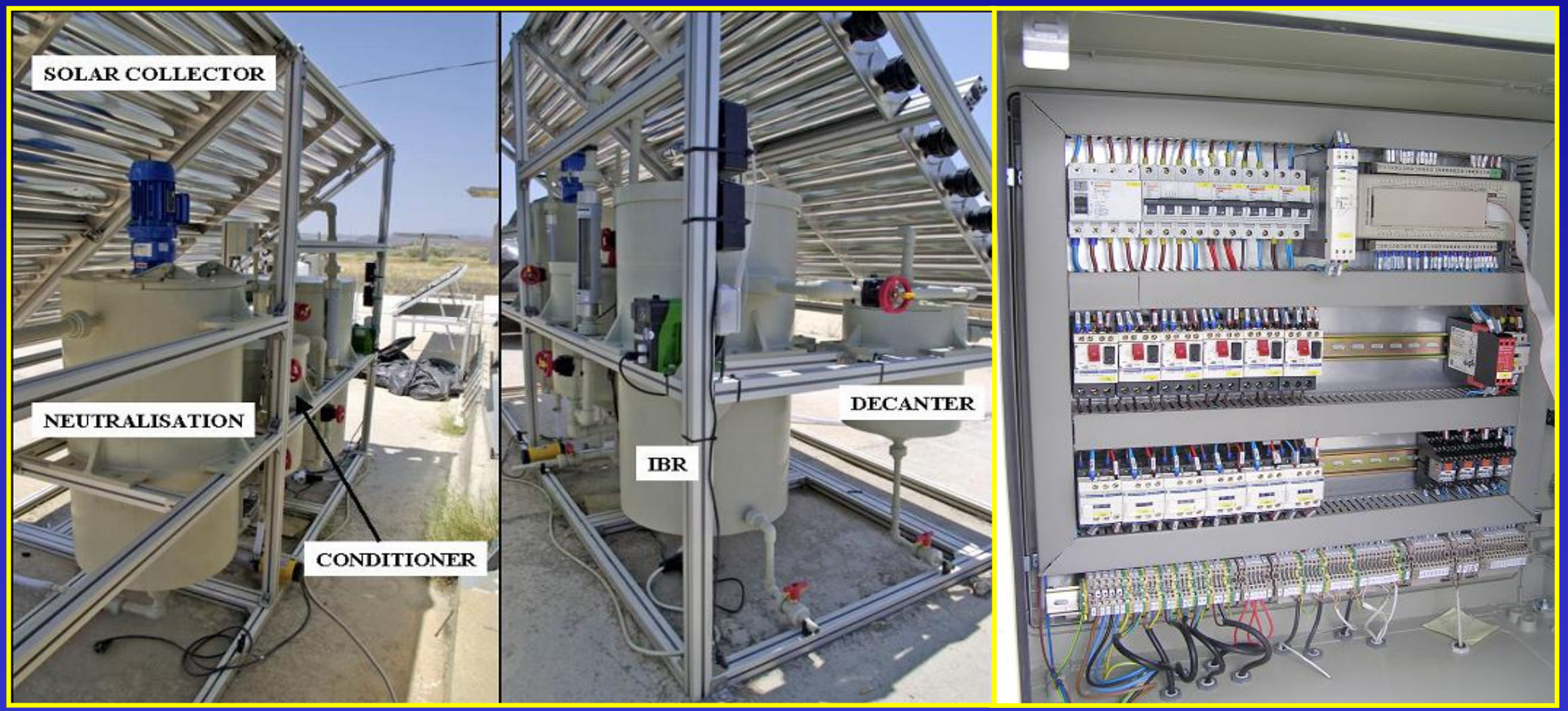
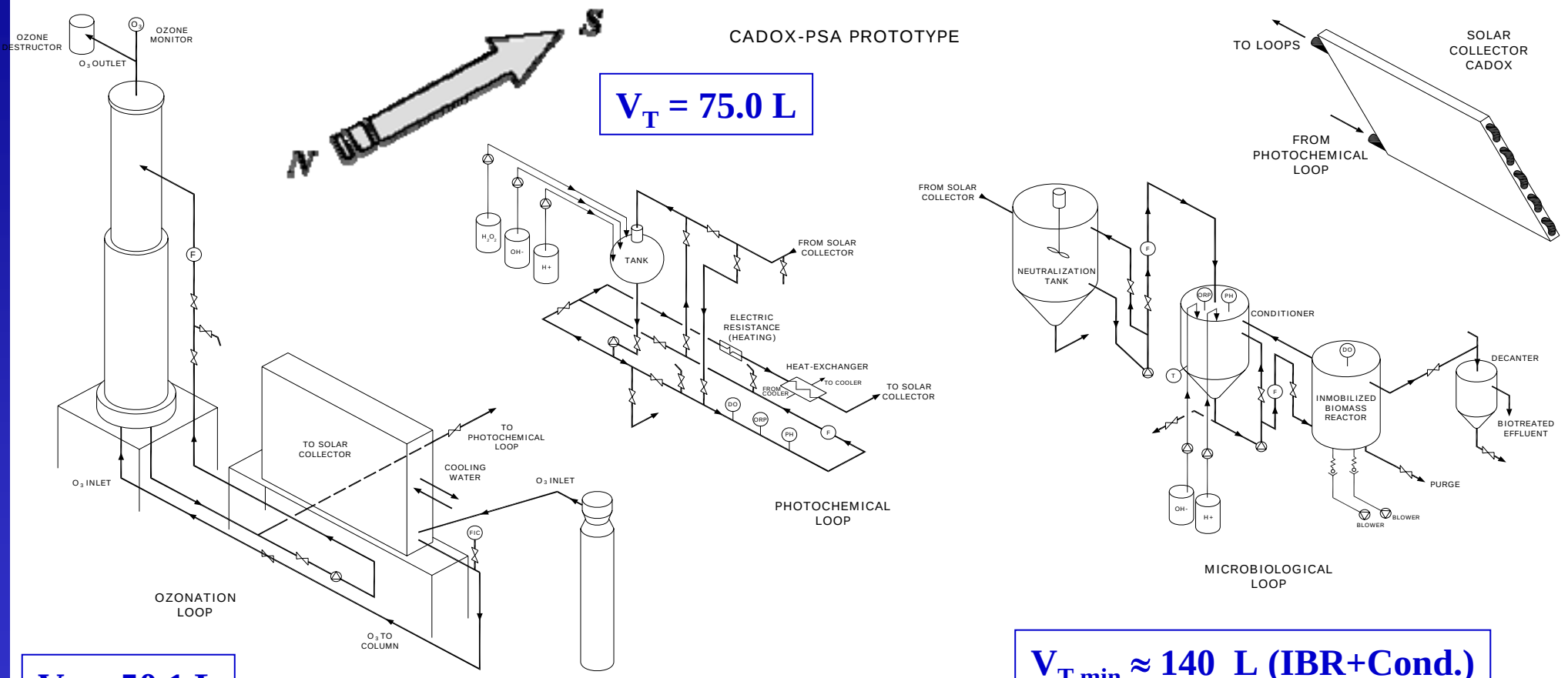


NEW PILOT PLANT

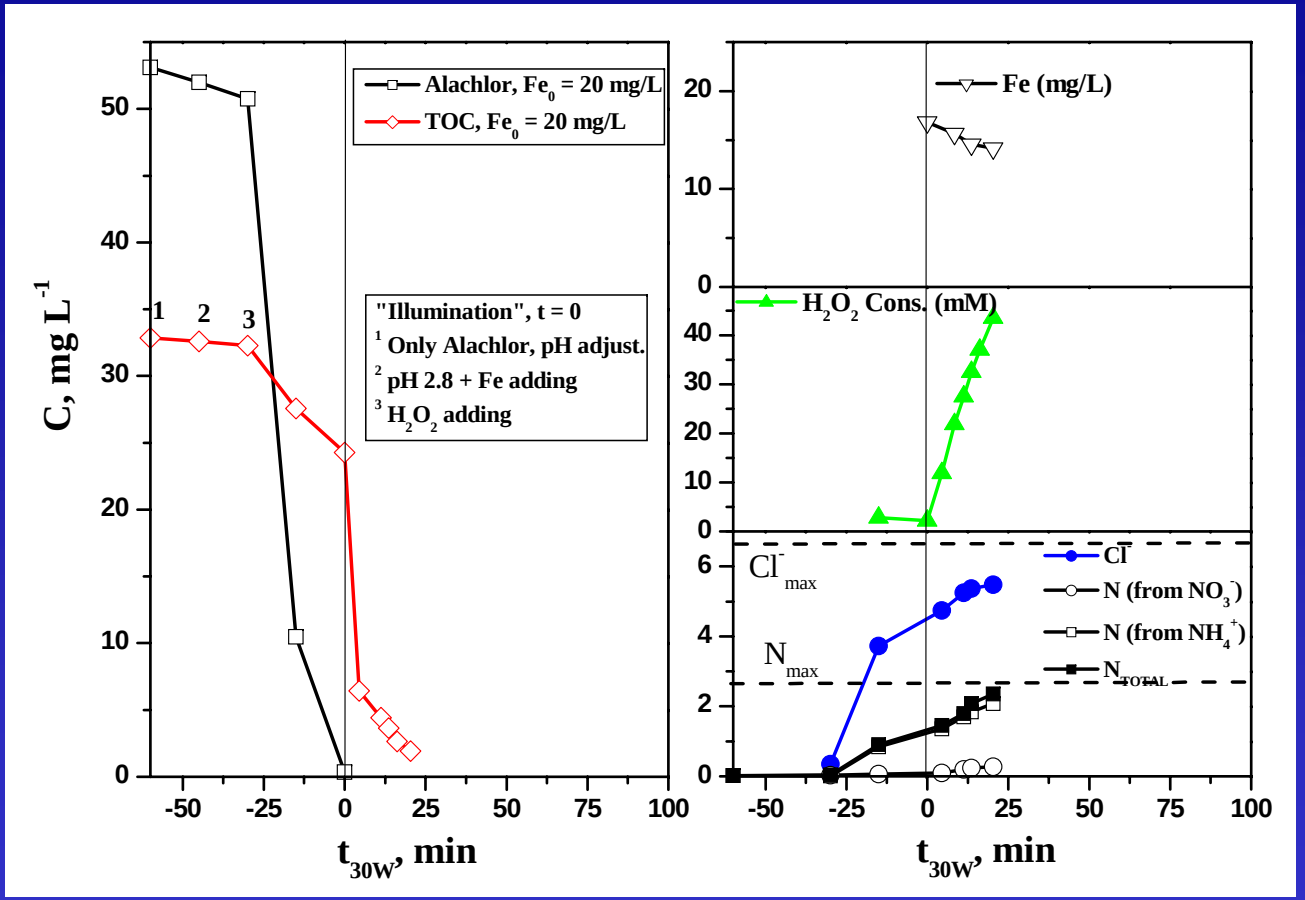


W. Gernjak, M. Fuerhacker, P. Fernández-Ibañez, J. Blanco, S. Malato. Solar Photo-Fenton treatment – Process Parameters and Process Control. ***Appl. Catal. B: Environ., accepted.***

J.D. Álvarez, W. Gernjak, S. Malato, M. Berenguel, M. Fuerhacker and L.J. Yebra. Dynamic Models for Hydrogen Peroxide Control in Solar Photo-Fenton Systems. ***J. Solar Energy Eng., accepted.***

Testing the new pilot plant

PHOTO - FENTON (I)



Alachlor, Atrazine, Chlorfenvinphos, Isoproturon, Diuron, Pentachlorophenol, Lindane

- Total degradation.
- Total mineralisation.
- Total dechlorination.

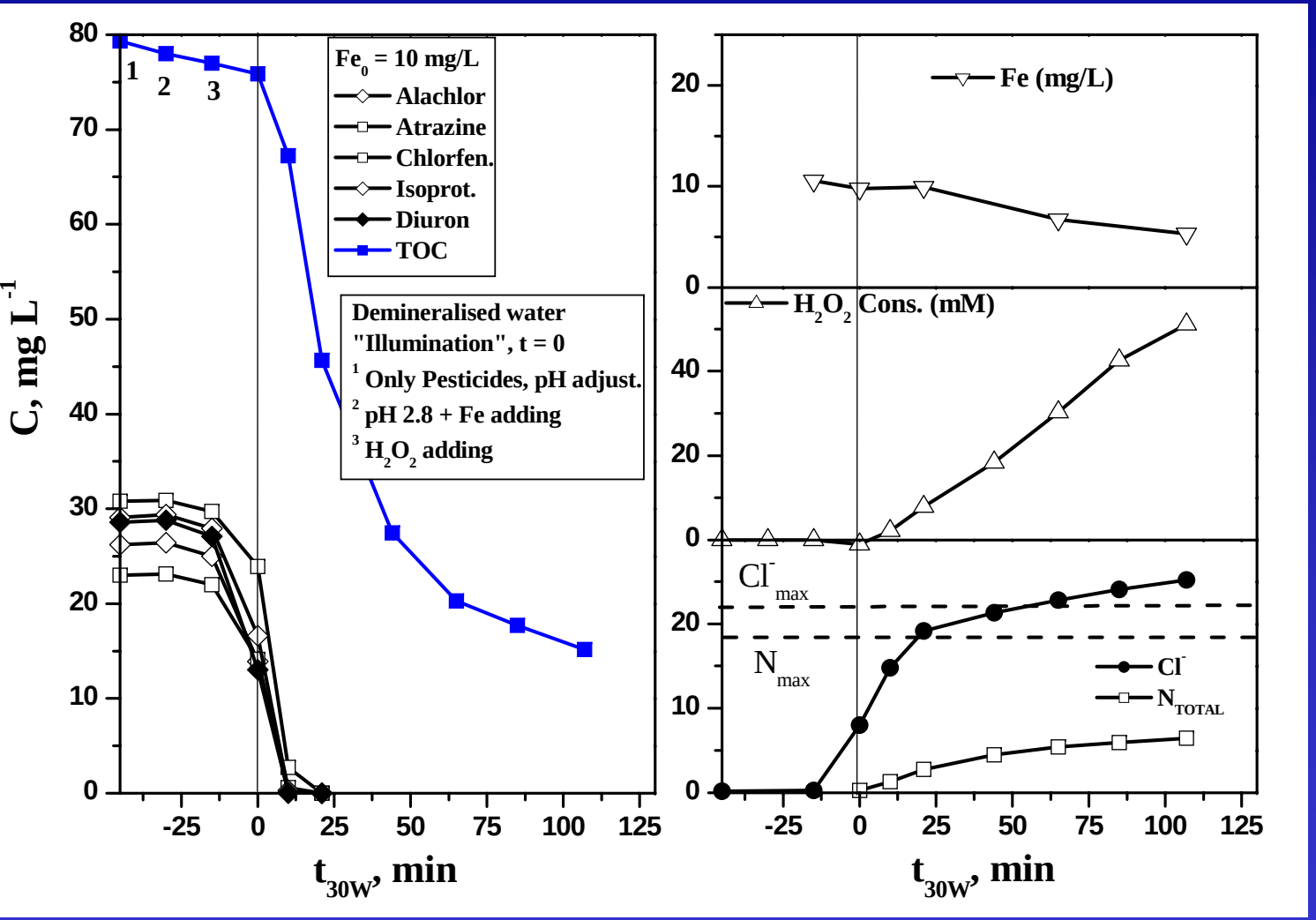
NBCS non tested in photo-Fenton prototype:

- Completely mineralised.
- No stable intermediates.
- No necessity of Coupling with biological.

M. I. Maldonado, W. Gernjak, I. Oller, J. Blanco, P. Fernández-Ibáñez and S. Malato. Photo-Fenton degradation of Alachlor, Atrazine, Chlorfenvinphos, Diuron, Isoproturon and Pentachlorophenol at Solar Pilot Plant. ***Journal of Environmental Pollution. in press.***

S. Malato Rodríguez, J. Blanco Gálvez, Manuel I. Maldonado Rubio, P. Fernández Ibáñez, W. Gernjak, I. Oller Alberola. Treatment of Chlorinated Solvents by TiO2 Photocatalysis and Photo-Fenton: Influence of Operating Conditions in a Solar Pilot Plant. ***Chemosphere, 58,*** 391-398, 2005.

PHOTO - FENTON (II)



Tested mixtures

10 mg/L each

30 mg/L each

Distilled water

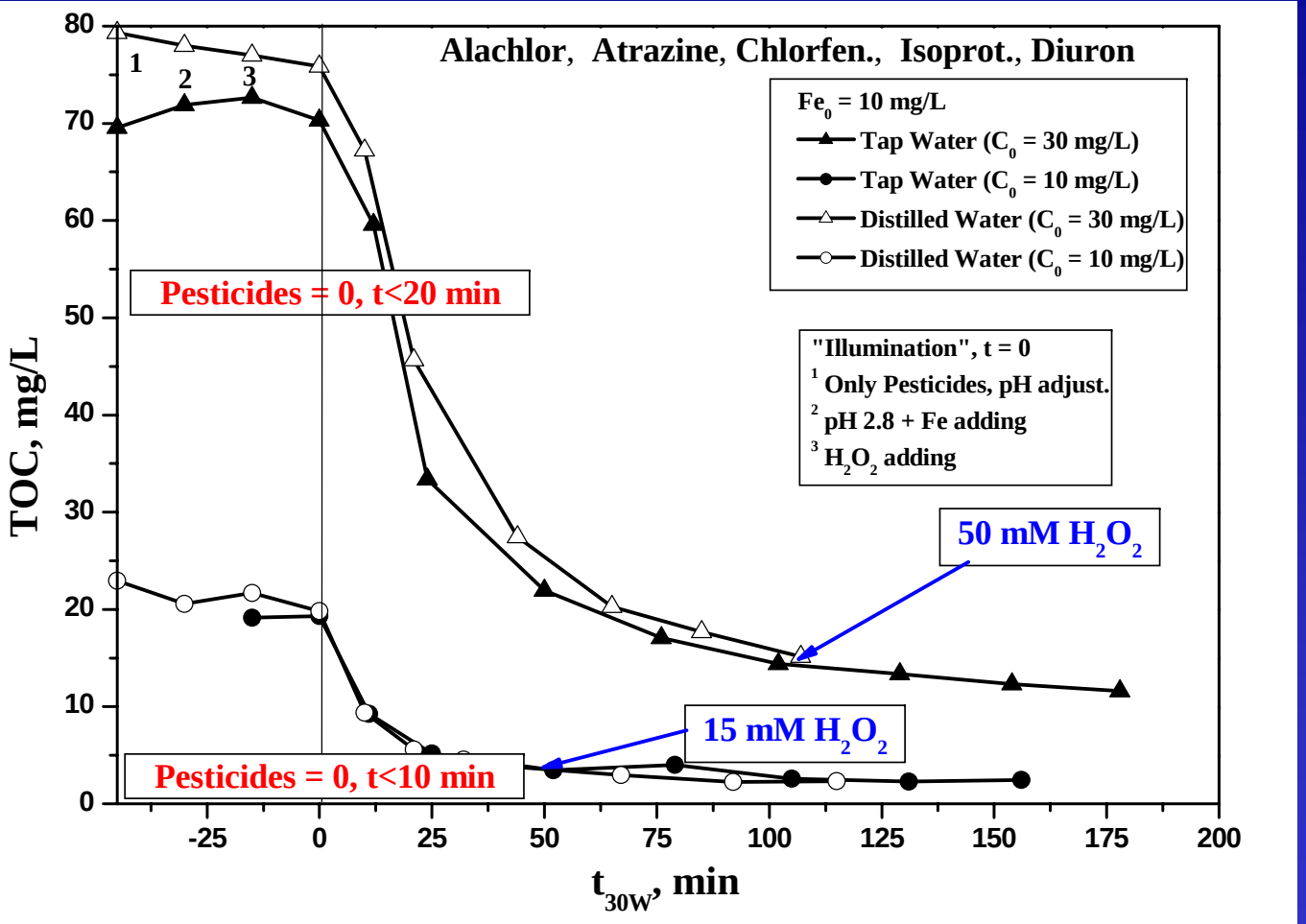
Tap water

$A = 4\ m^2$, $V_{TOT} = 75\ L$

M. Hincapié, M.I. Maldonado, I. Oller, W. Gernjak, J. A. Sánchez-Pérez, M. M. Ballesteros, and S. Malato. Solar photocatalytic degradation and detoxification of EU priority substances. ***Catalysis Today, 101,*** 203-210, 2005.

Margarita Hincapié Pérez, Gustavo Peñuela, Manuel I. Maldonado, Pilar Fernández-Ibáñez, Isabel Oller, Wolfgang Gernjak and Sixto Malato. Degradation of pesticides in water using solar advanced oxidation processes. ***Appl. Catal. B: Environ., accepted.***

PHOTO - FENTON (III)



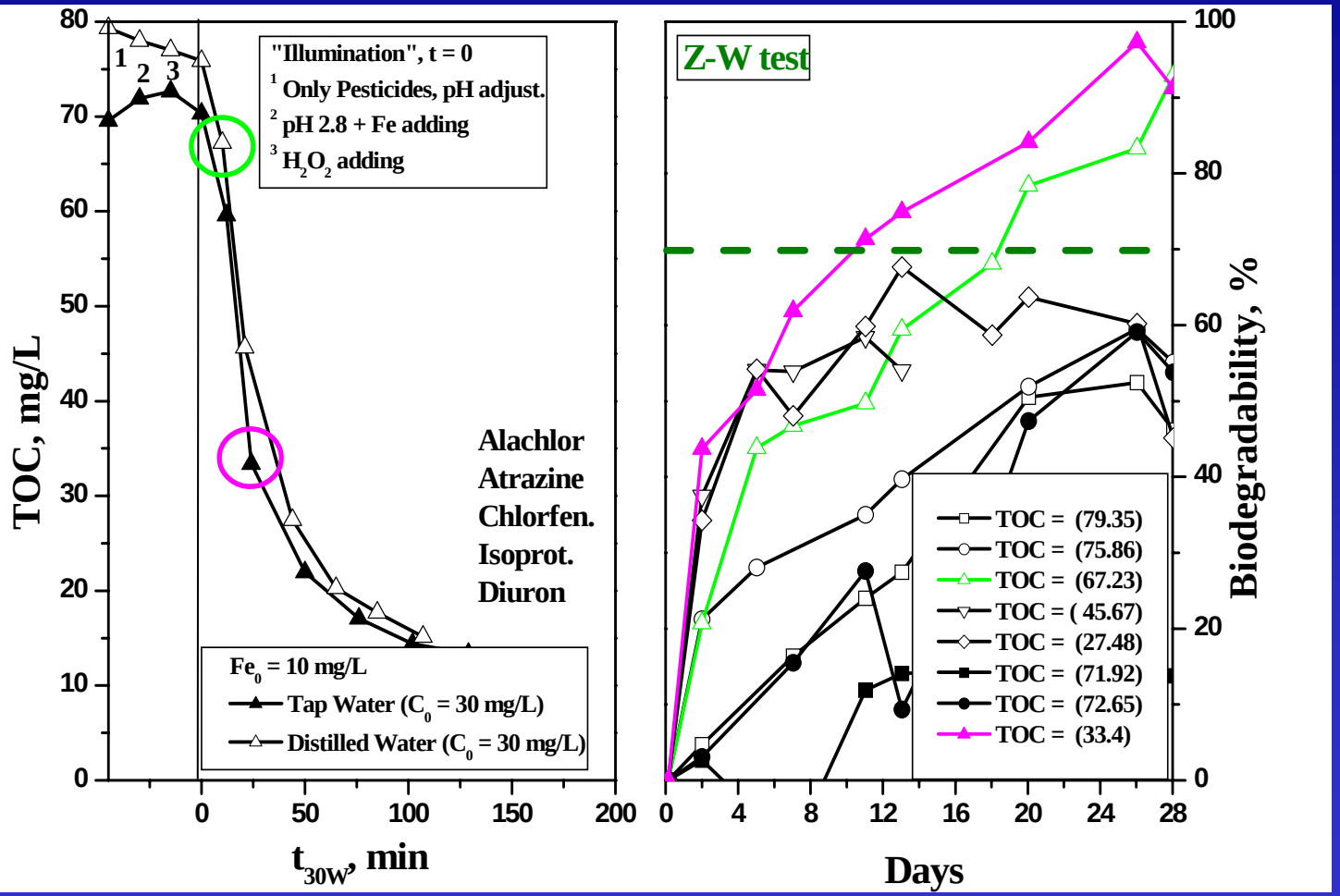
Pesticide mixture, 10 mg/L and 30 mg/L each one

- Total degradation.
- 80 % mineralisation.
- Total dechlorination.

Diapositiva 25

U2 Explicar porqué para la mezcla de plaguicidas se ha usado Fe 10 mg/L en lugar de 20 mg/L.
USUARIO; 09/10/2005

PHOTO-FENTON / BIODEGRADABILITY

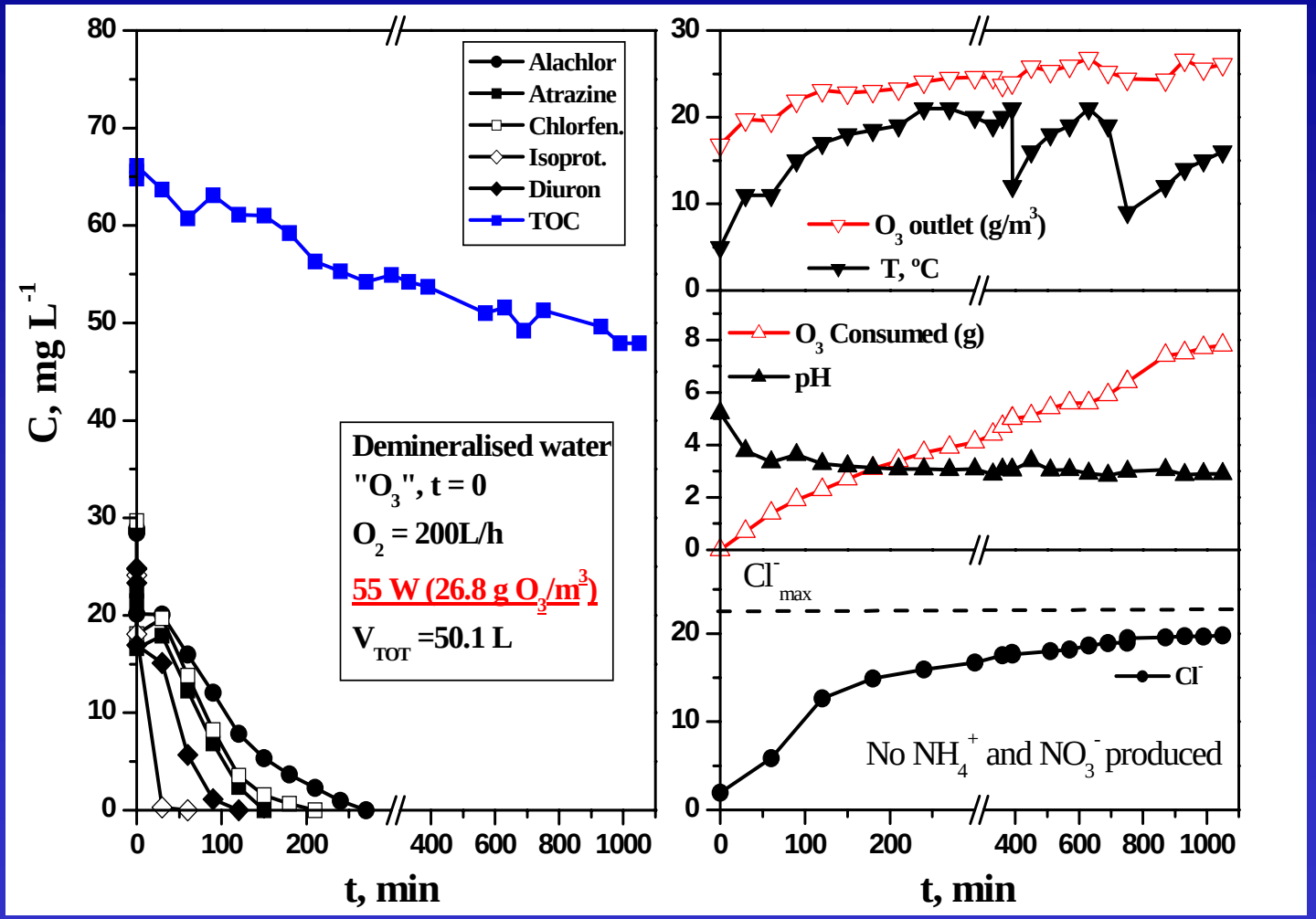


Zahn-Wellens test: EC protocol (Directive 88/302/EEC)

- Biodegradability enhanced.
- Biodegradable after total dechlorination.
- TOC = 67,23 mg/L, 70% biodegradability after 18 days. Best coupling point.

Milena Lapertot, César Pulgarín, Pilar Fernández-Ibáñez, Manuel I. Maldonado, Leonidas Pérez-Estrada, Isabel Oller, Wolfgang Gernjak and Sixto Malato. Enhancing biodegradability of priority substances (pesticides) by solar photo-Fenton. *Wat. Res., accepted*

OZONATION PROCESS



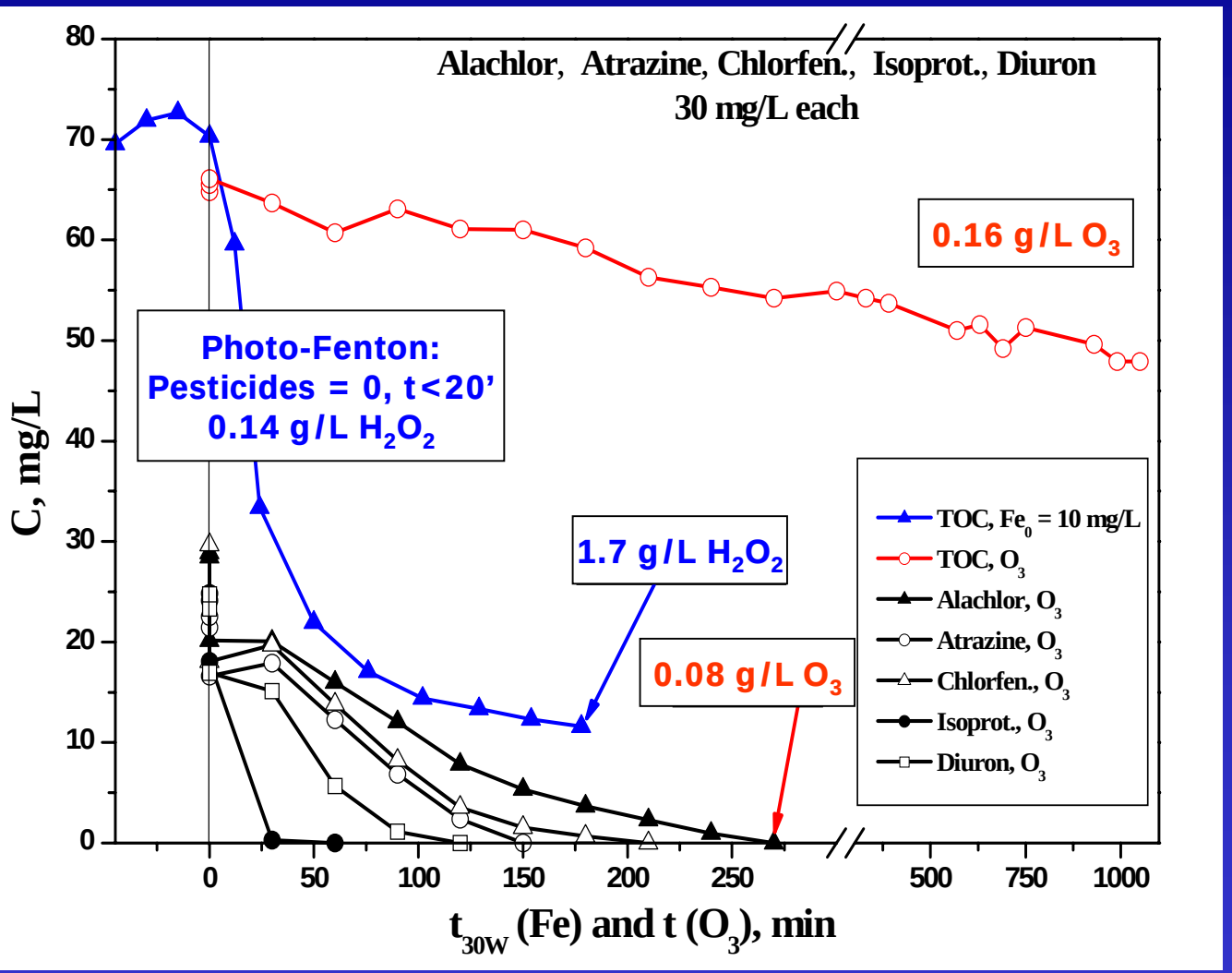
Pesticide mixture, 30 mg/L each one

- Total degradation.
- 25 % mineralisation.
- Total dechlorination.

M.I. Franch, J.A, Ayllón, J. Peral and X. Domènech. Enhanced photocatalytic degradation of maleic acid by Fe(III) adsorption onto the TiO2 surface. ***Catalysis Today, 101,*** 245-252, 2005.

Ivan Muñoz, Joan Rieradevall, Francesc Torrades, José Peral and Xavier Doménech. Environmental Assessment of Different Solar Driven Advanced Oxidation Processes. ***Solar Energy, 79,*** 369-375, 2005.

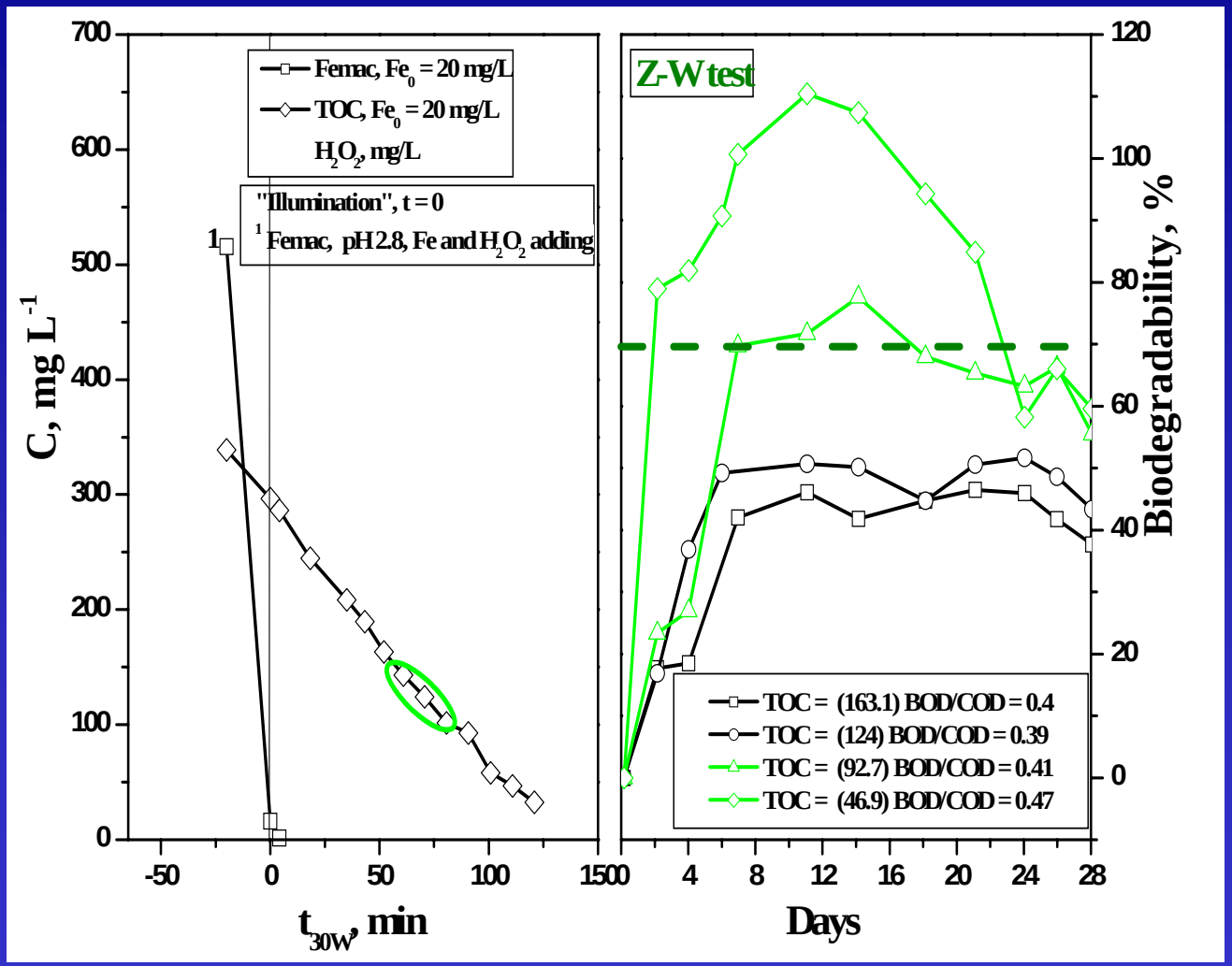
PHOTO-FENTON vs. OZONATION



Comparison Photo-Fenton & O_3 Pesticide mixture, 30 mg/L each one

- Photo-Fenton faster.
- Photo-Fenton much more mineralisation.
- O_3 low consumption.
- O_3 mineralisation and dechlorination very slow.

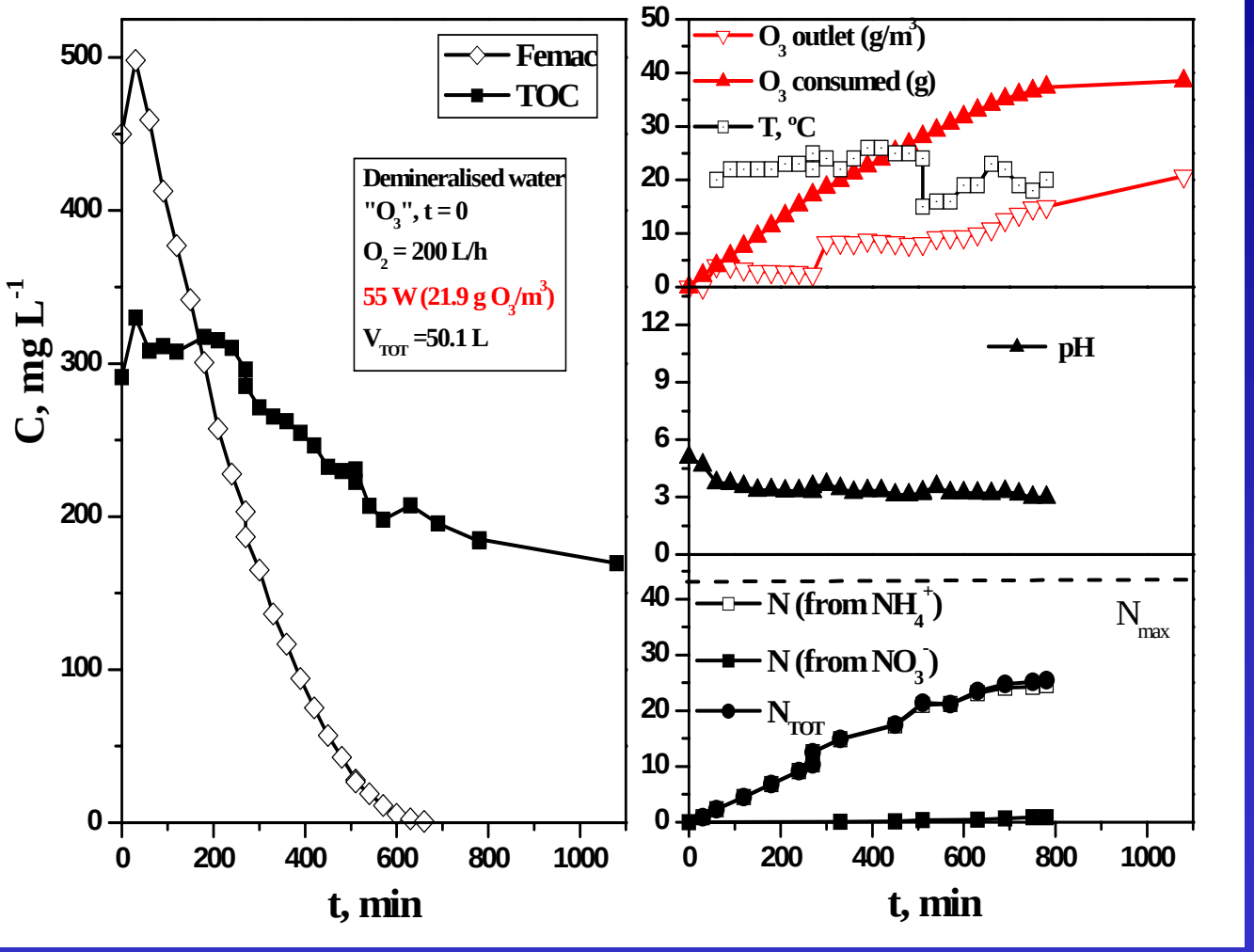
PHOTO-FENTON (FEMAC) / BIODEGRADABILITY TESTS



Zahn-Wellens test: EC protocol (Directive 88/302/EEC)

- Biodegradability enhanced.
- Biodegradable after 50-70% of TOC mineralised.
- TOC = 92.7 mg/L, 70% biodegradability after 7 days. Best coupling point.

OZONATION (FEMAC)

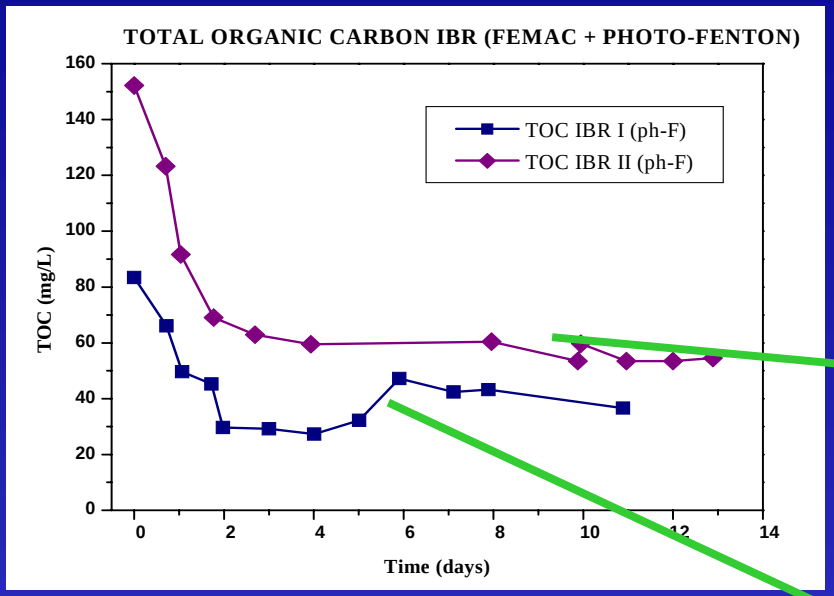


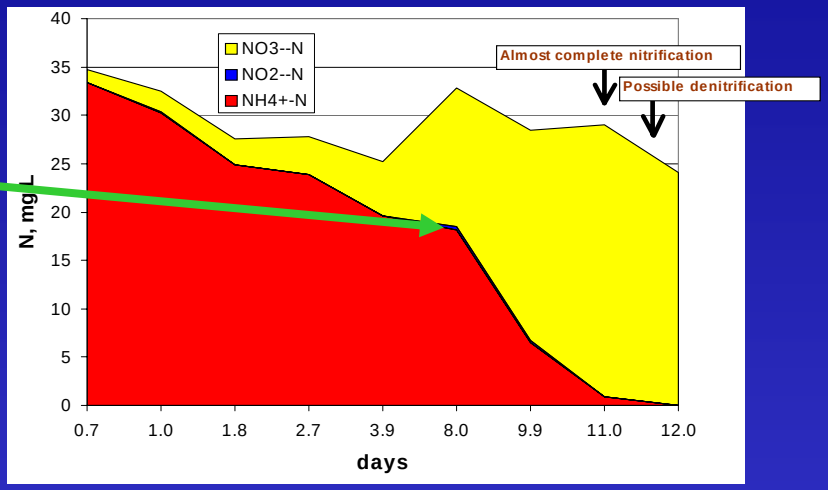
Femac concentration 500 mg/L

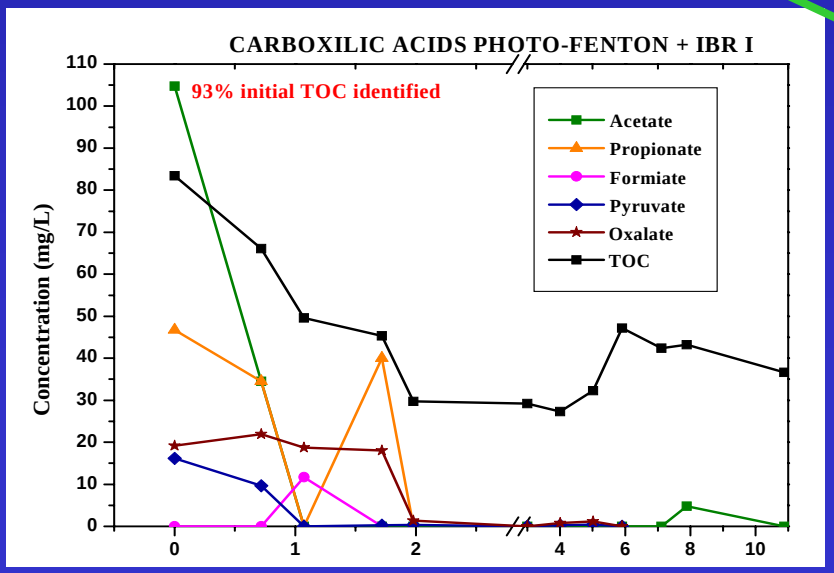
- Almost no mineralisation. near 30 mg/L of TOC (6.5 hours).
- Incomplete nitrogen mineralisation to ammonium.
- O_3 outlet concentration rises, specially after Femac conversion.

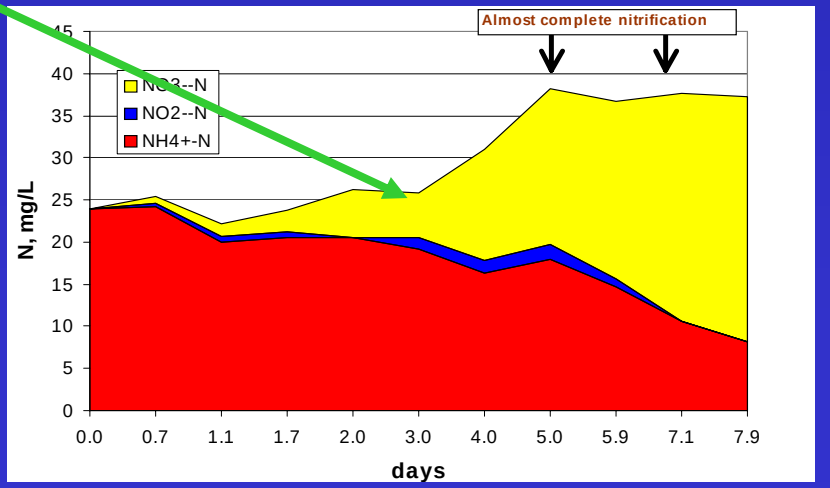
BIOTREATMENT (FEMAC I)

V_T = 138 L (from 3 photo-Fenton tests)
Complete nitrification. No mineral medium.
SIMILAR RESULTS WITH O_3









PILOT PLANT CONCLUSION (I)

PESTICIDES

- ✓ Fe = 10 mg/L is enough for reaching complete mineralisation.
- ✓ Longer treatment time with O_3 than photo-Fenton for achieving pesticides degradation. Almost no TOC degradation with O3 .
- ✓ Zahn-Wellens tests useful for determining optimal TOC range at which wastewater become biodegradable.
- ✓ Biodegradability increase very significant after short photo-Fenton treatment times.

PILOT PLANT CONCLUSION (II)

FEMAC

- ✓ Photo-Fenton and ozonation processes are suitable for degrading Femac. Mineralisation higher with photo-Fenton than with ozone.
- ✓ Z-W test predicts the correct value for coupling AOP/ Biotreatment in a TOC range between 150-90 mg/L (Femac completely disappeared).
- ✓ Complete nitrification clearly detected both after Photo-Fenton and O_3 treatments.
- ✓ TOC decreased from around 150 mg/L to <30 mg/L in IBR.

TESTING REAL WASTEWATERS

REAL WASTEWATER WITH FEMAC

- Treatment of real saline wastewater containing Femac, from a final user (DERETIL, CADOX project partner). Sea water employed in the industry process lines.
- Main characteristics of the industrial wastewater: COD=200-400 mg/L, TOC=100-200 mg/L, NH_4^+=0-40 mg/L, NO_3^-=200-600 mg/L in seawater and Femac=500 mg/L.
- Inoculation of the Immobilised Biomass Reactor with activated sludge coming from WWTP of DERETIL. Fixed bacteria adapted to sea water.

PHOTO-FENTON vs. OZONATION

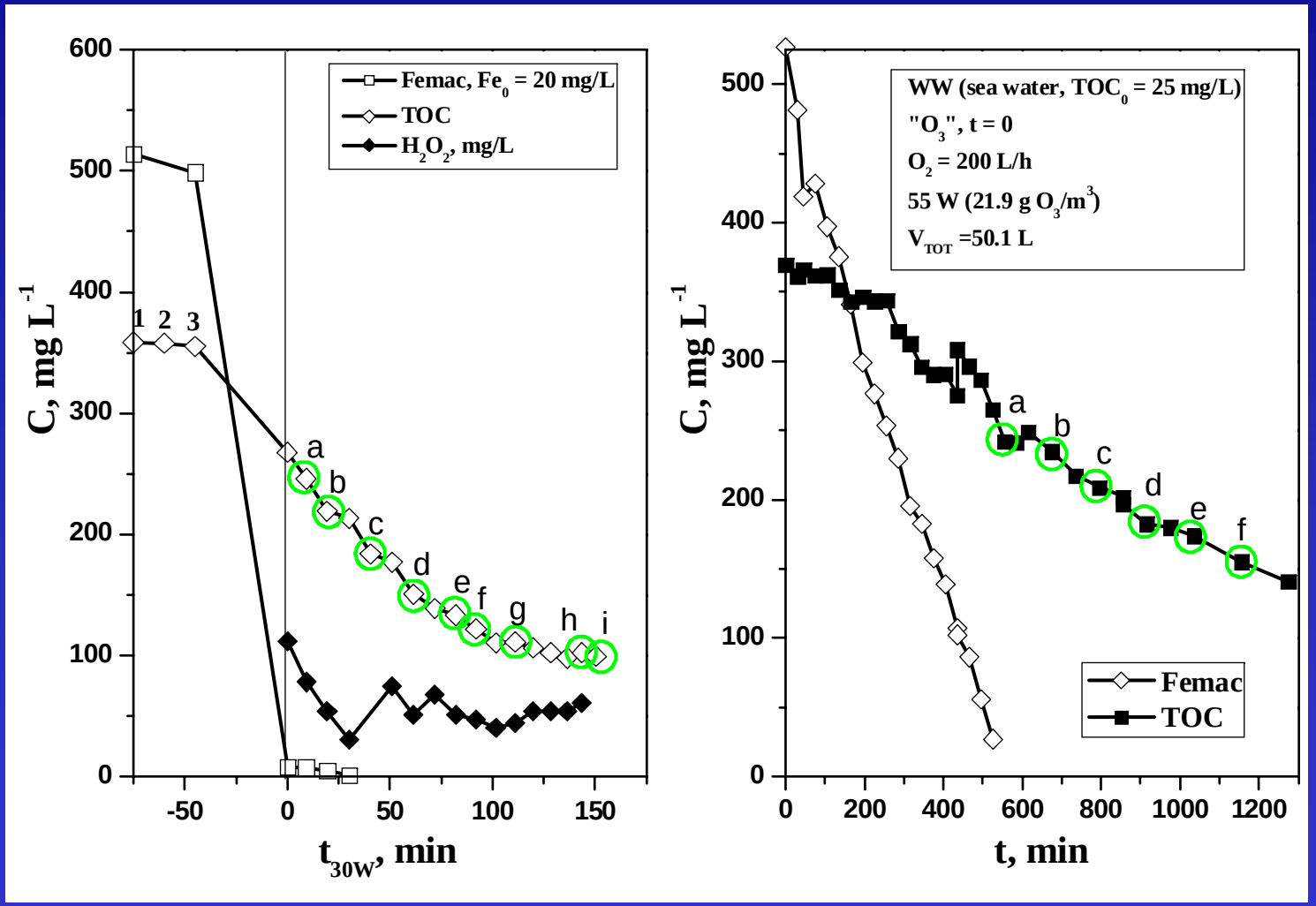
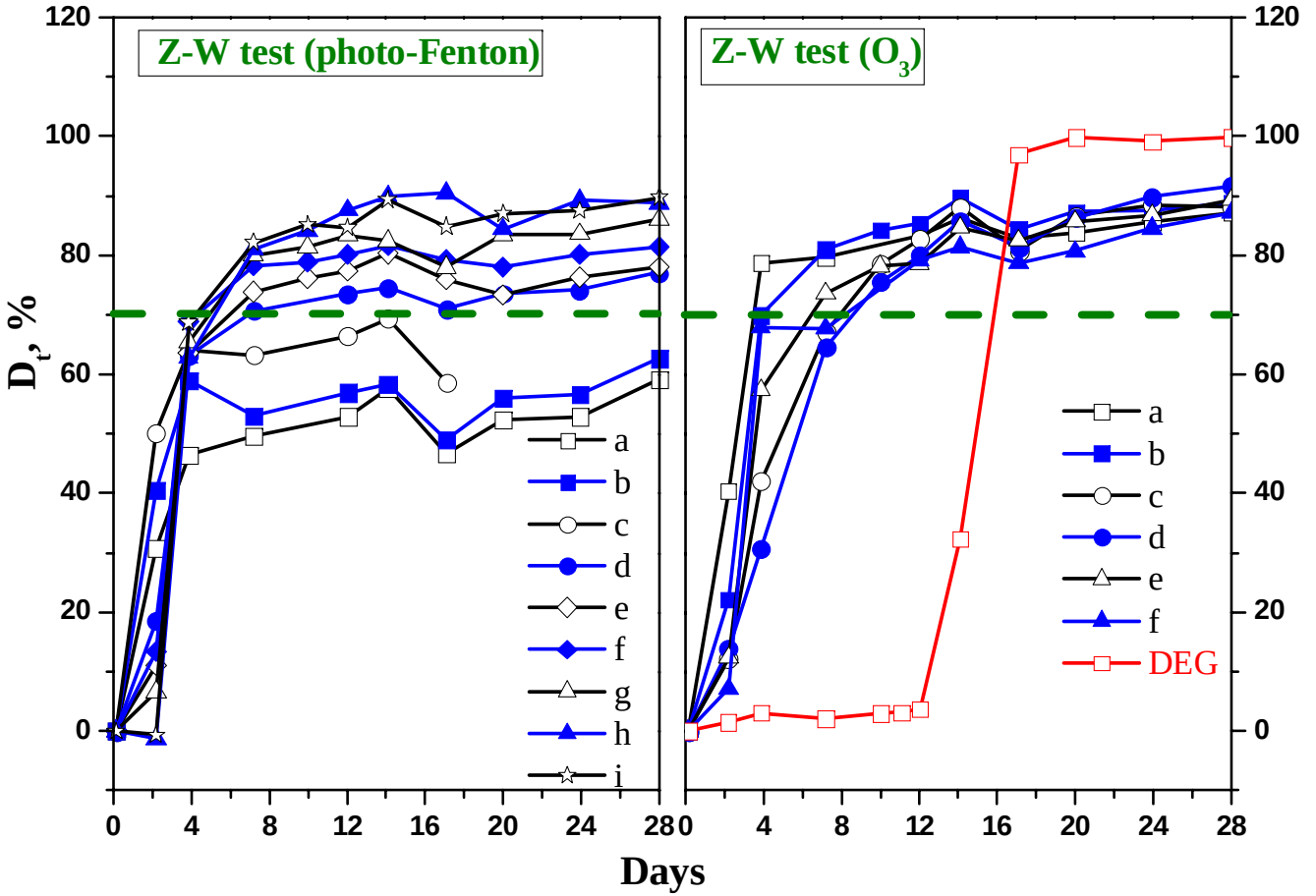
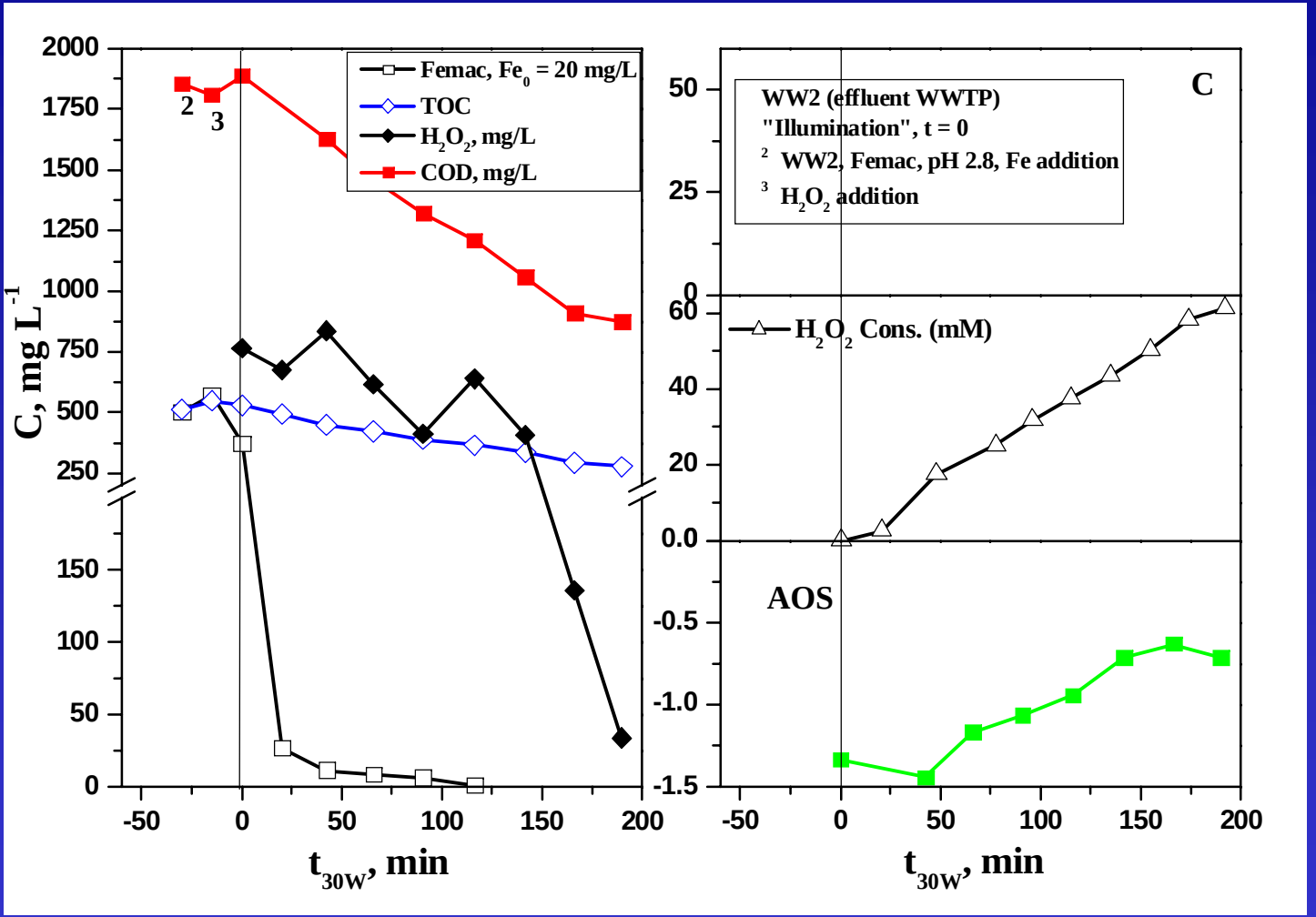


PHOTO-FENTON vs. OZONATION



- Biodegradability enhanced in both treatments.
- Biodegradable after Femac completely disappearance.
- 70% biodegradability in 4 days.
- Higher biodegradability as more pronounced photo-Fenton is. No difference in ozone samples.

PHOTO-FENTON (AOS)

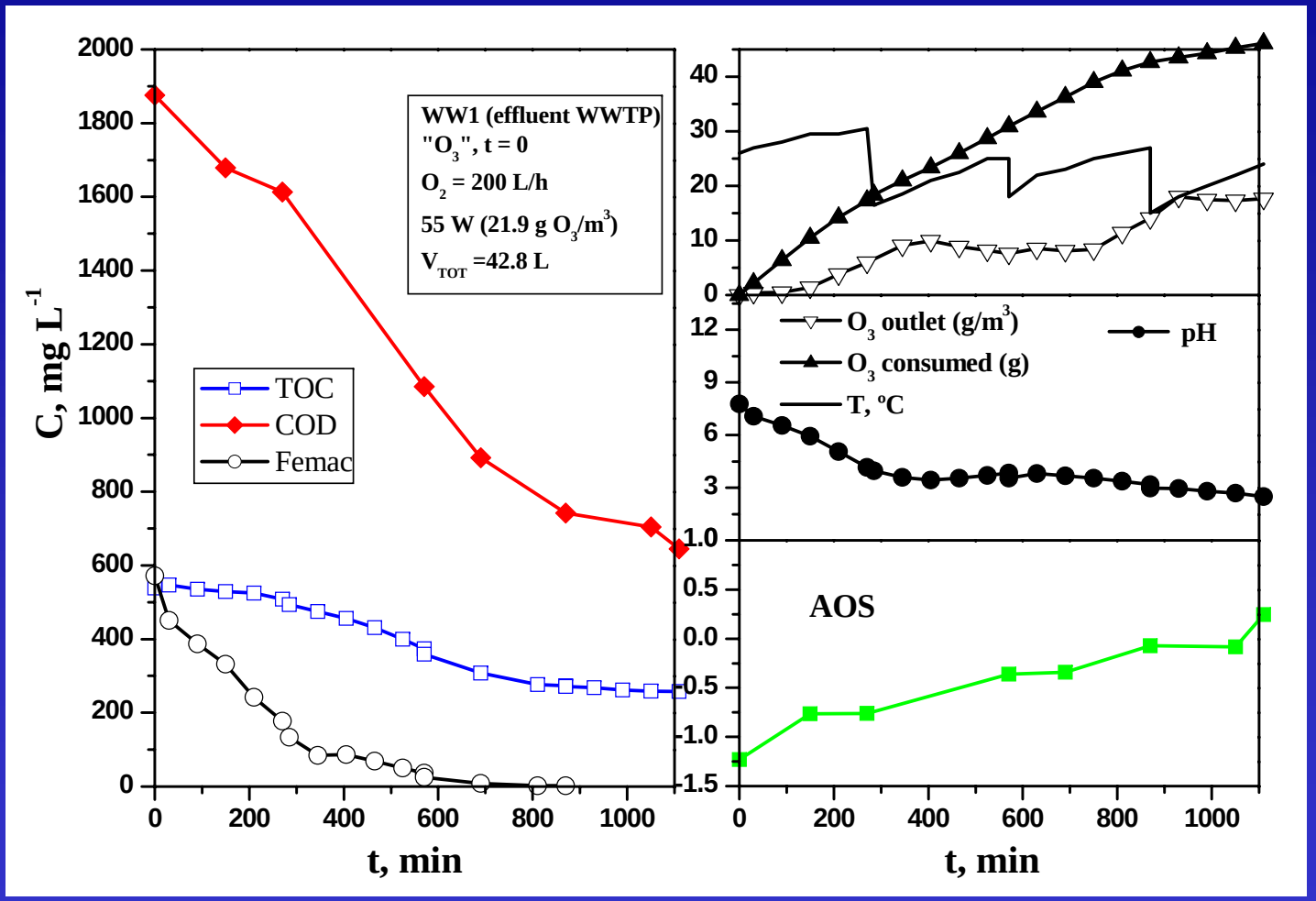


Advanced Oxidation State (*AOS*):

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

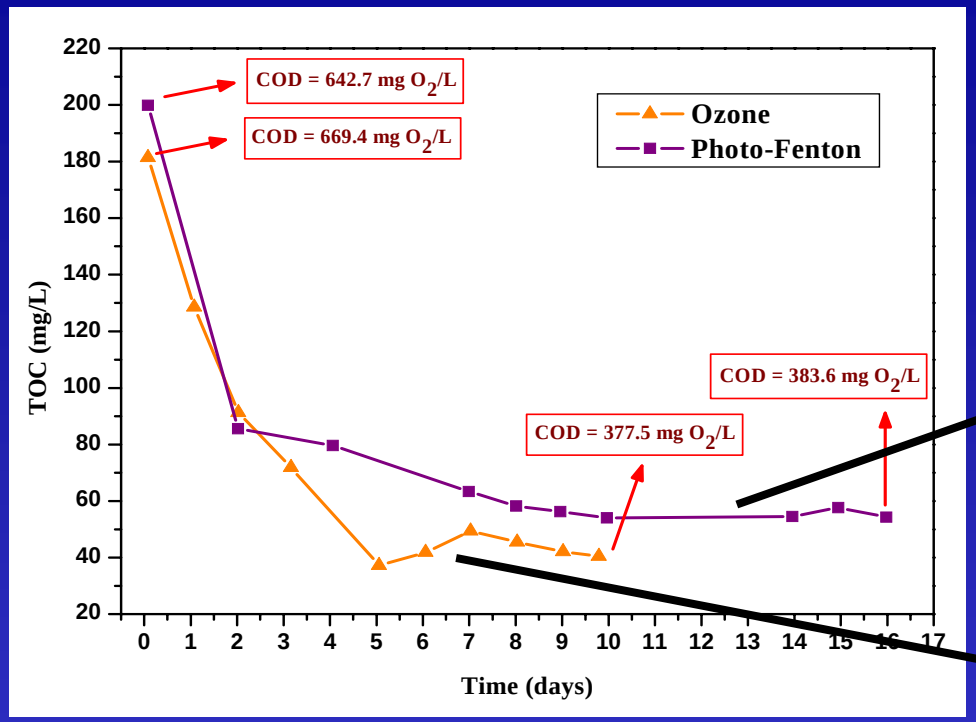
- Total degradation (100 min).
- Final TOC=330 mg/L. H_2O_2 consumed=1.5 g/L.
- *AOS* constant at 150 min. Biodegradable intermediates.
- Consistent with ZW results.
- Coupling with biotreatment 50 min after Femac=0 mg/L.

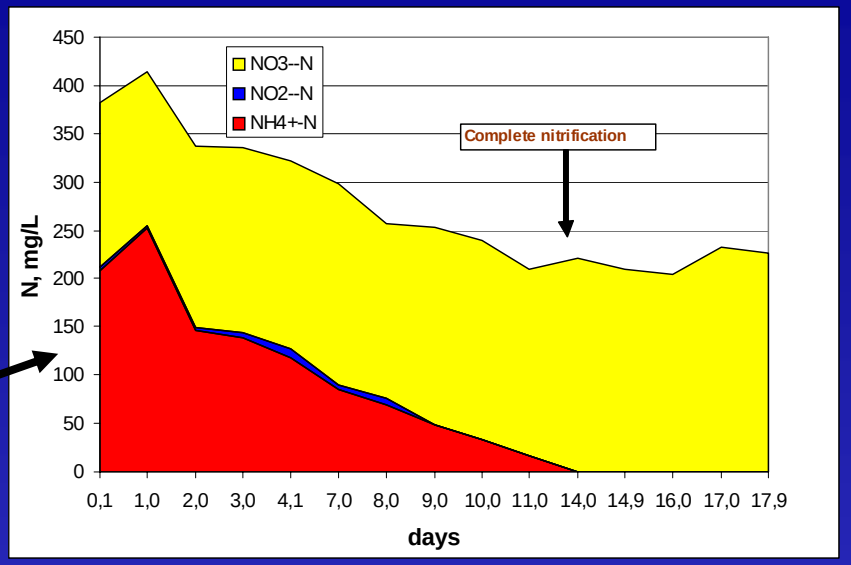
OZONATION (AOS)

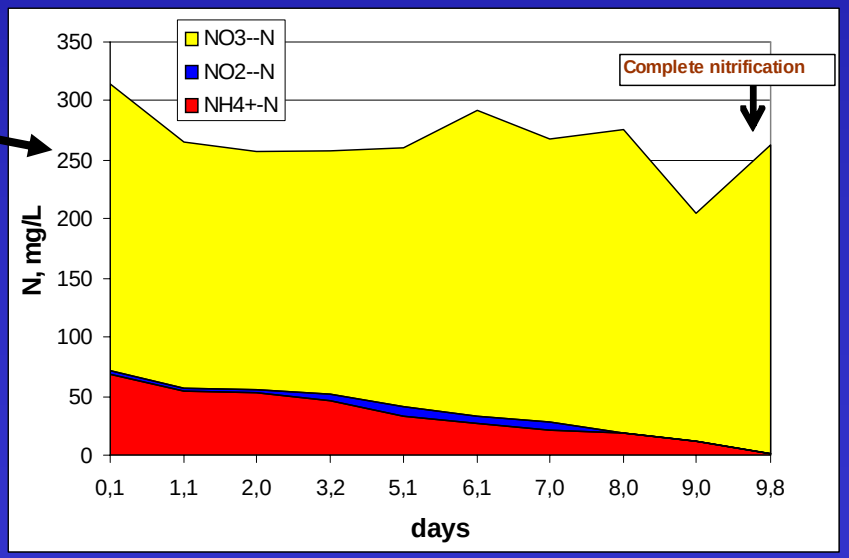


- Total degradation (700 min).
- Final TOC=270 mg/L.
- O_3 consumed=1.0 g/L.
- *AOS* constant at 600-800 min. Biodegradable intermediates.
- Consistent with ZW results.
- Coupling with biotreatment just when Femac=0 mg/L.

AOP / BIOLOGICAL PROCESS (SEA WATER)







V_T ≈ 138 L from 2 photo-Fenton tests and 3 ozone tests respectively

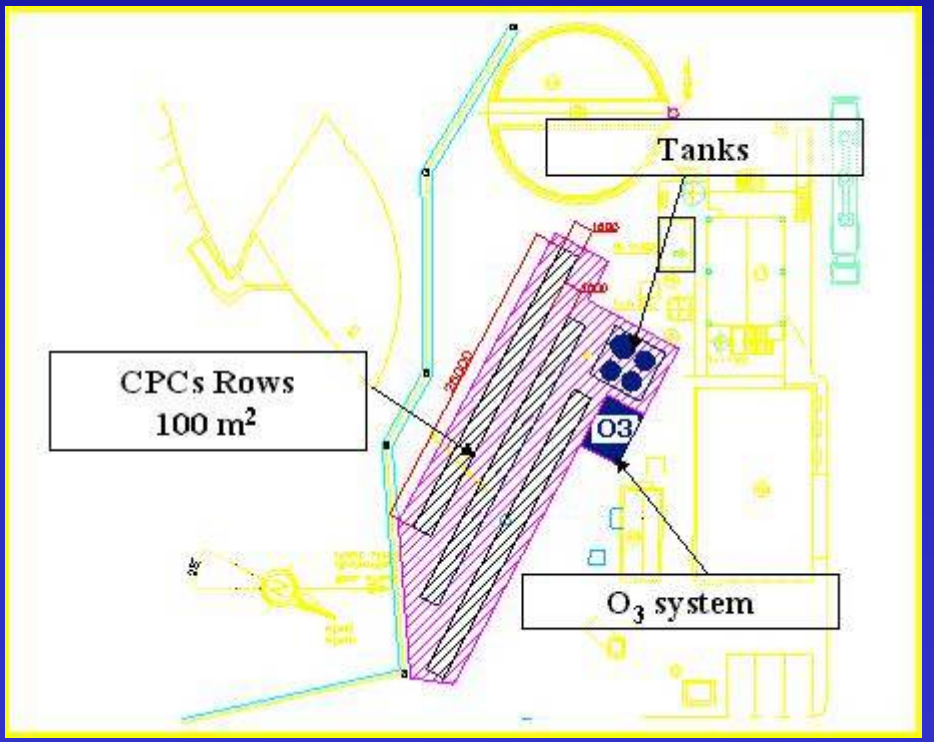
- Complete nitrification but slower than TOC decrease.

DEMONSTRATION PLANT DESIGN

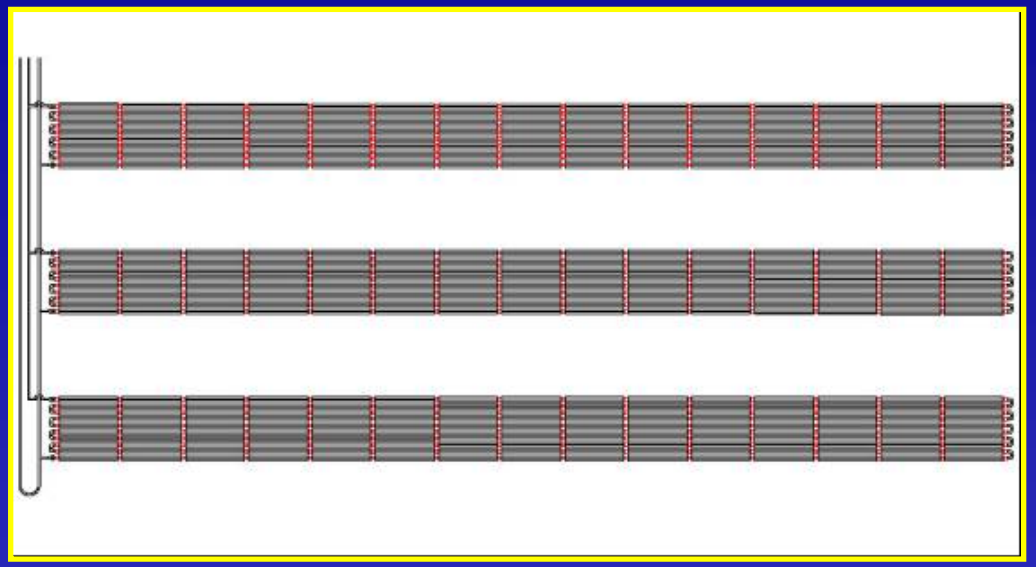
DEMONSTRATION PLANT DESIGN (I)

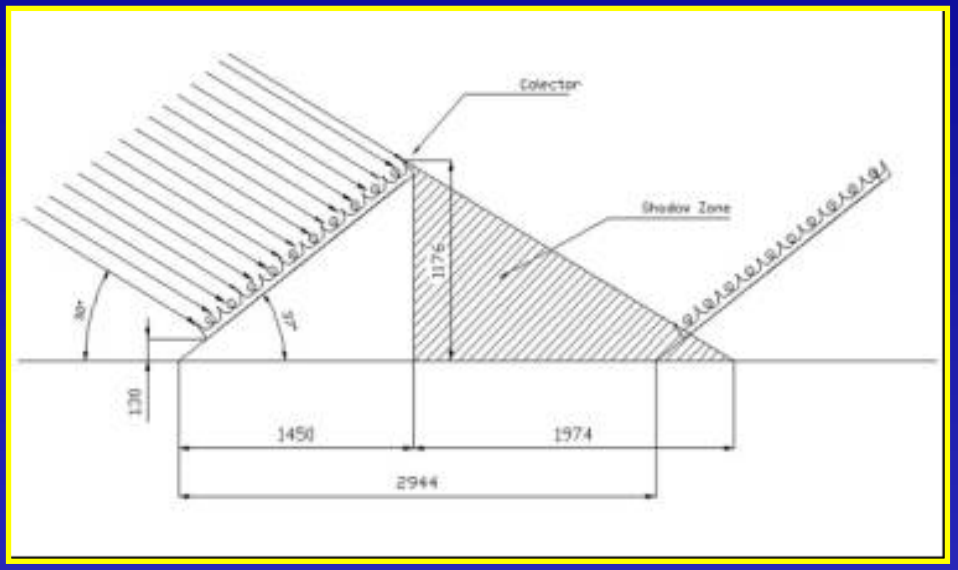
CADOX demonstration plant location at DERETIL instalations. Aereral picture.

Distribution of the equipment in-site.



DEMONSTRATION PLANT DESIGN (II)



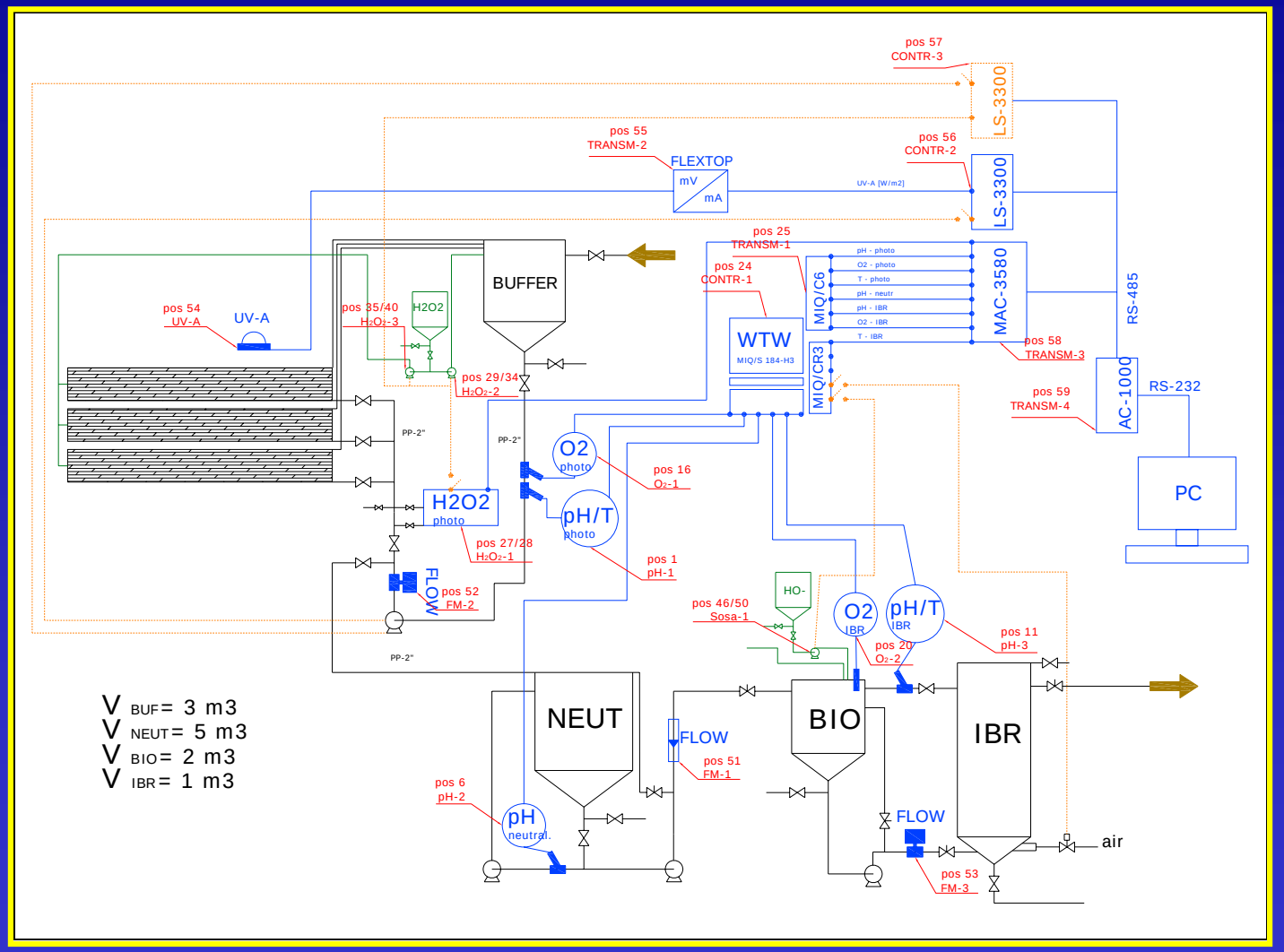


Collector field:

- 3 parallel rows of collectors.
- Each row with 15 modules, 25.5 m length.
- 101.5 m^2 of total aperture area.

Distance of eah row to prevent the shadow in the collectors.

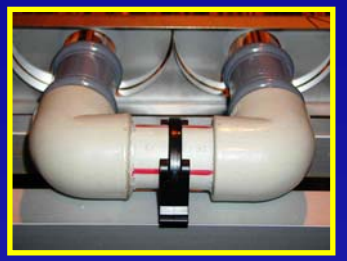
DEMONSTRATION PLANT DESIGN (III)



Control flow-sheet of solar photo-Fenton pre-treatment and subsequent biotreatment.

DEMONSTRATION PLANT DESIGN (IV)

Ozonation system constructed by TRAILIGAZ



- First prototype on a rectangular aluminium profile.
- Tubes from each module connected with PVC unions and propylene elbows on the conrners.

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