Integrated Advanced Technologies for the Remediation of Industrial Wastewaters. Case studies

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Industrial Wastewater remediation

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Possible treatments?

- Conventional processes are hampered by industrial wastewater recalcitrant nature.
- Advanced Oxidation Processes (AOPs) are efficient but they are not economically acceptable for application to large-scale effluents treatment.

Adequate remediation strategy?

- Integrated physic-chemical-biological techniques can ameliorate the drawbacks of individual processes and improve the overall treatment efficiency.

A **combined treatment line** for a particular industrial wastewater remediation must be investigated:

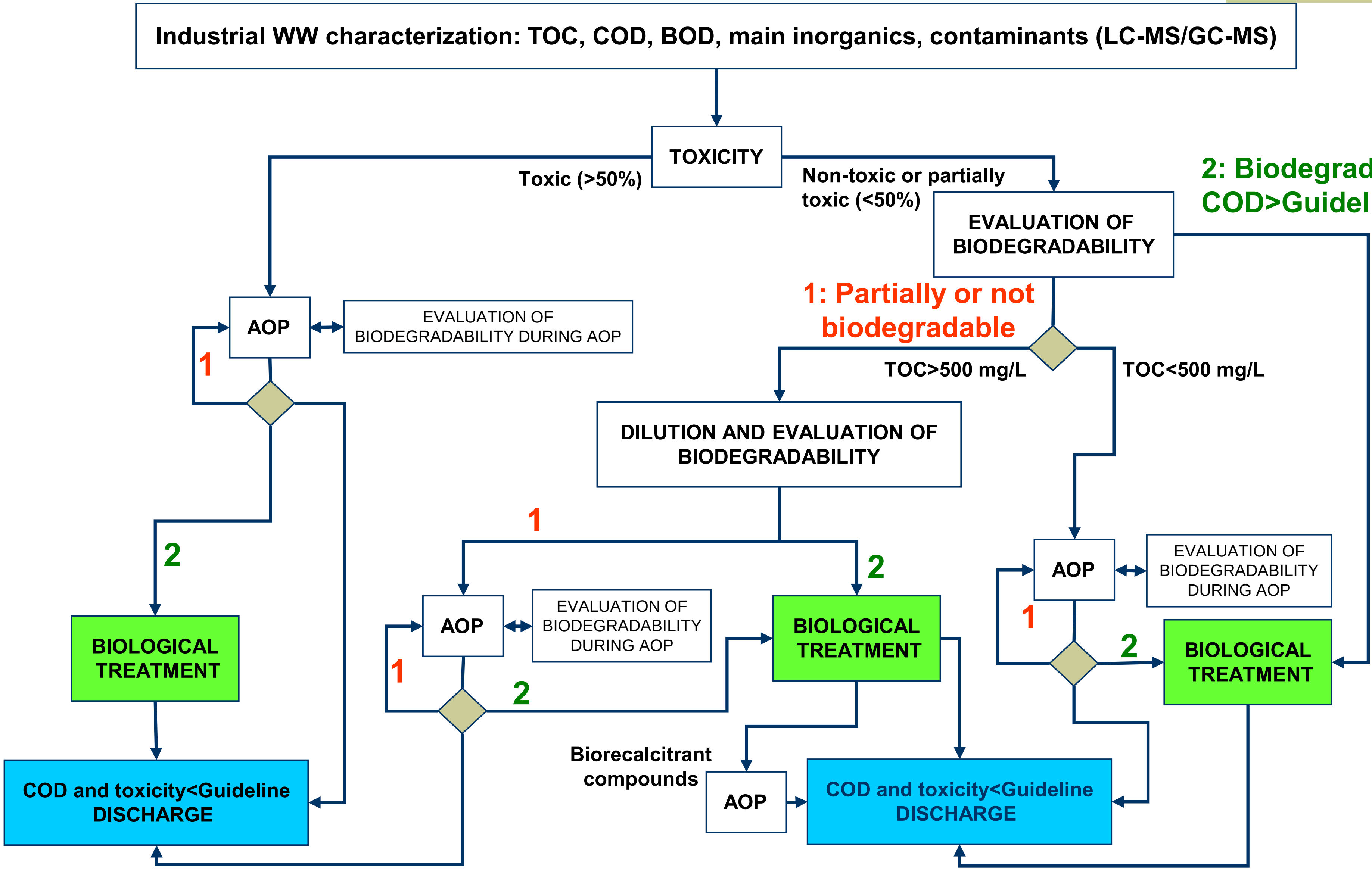
- Physic-chemical pre-treatment.
- Advanced Oxidation process (Solar photo-Fenton process or ozonation).
- Toxicity and biodegradability assessment.
- Combination with advanced biological treatment after biodegradability enhancement.

Finally a **economic evaluation** of the treatment line must be performed.

Solar AOPs for industrial wastewater remediation

- There is no sense in using solar photocatalytic processes for complete mineralization of recalcitrant industrial wastewaters containing hazardous non-biodegradable pollutants. **High operating and investment costs.**
- The use of photocatalysis as a pre-treatment can be justified if the intermediates resulting are readily degraded by microorganisms.
- The use of photocatalysis as a post-treatment is justified when industrial wastewater is not toxic and presents low biodegradability from the beginning.
- Toxicity and biodegradability tests are highly important for effluents partially treated by photocatalysis as more toxic or recalcitrant degradation products could be generated during the process.
- Highly confidence toxicity results will be obtained when using at least two different bioassays.

Solar AOPs for industrial wastewater remediation



Oller et al., Sci. Tot. Env. 409, 2011

Physic-chemical pre-treatment

Stabilize industrial wastewater and enhance the efficiency of the subsequent oxidation treatment

Lab scale assays performed in a Jar-test apparatus for optimization

Pre-treatment performed in pilot scale plant

Jar-test equipment with 6 positions (OVAN) for coagulation/flocculation assays at lab scale.

Designed to process 1 m^3/h of wastewater.

Sand filter (75 µm).

Two micro-filters (25 µm and 5 µm).

Toxicity and biodegradability tests

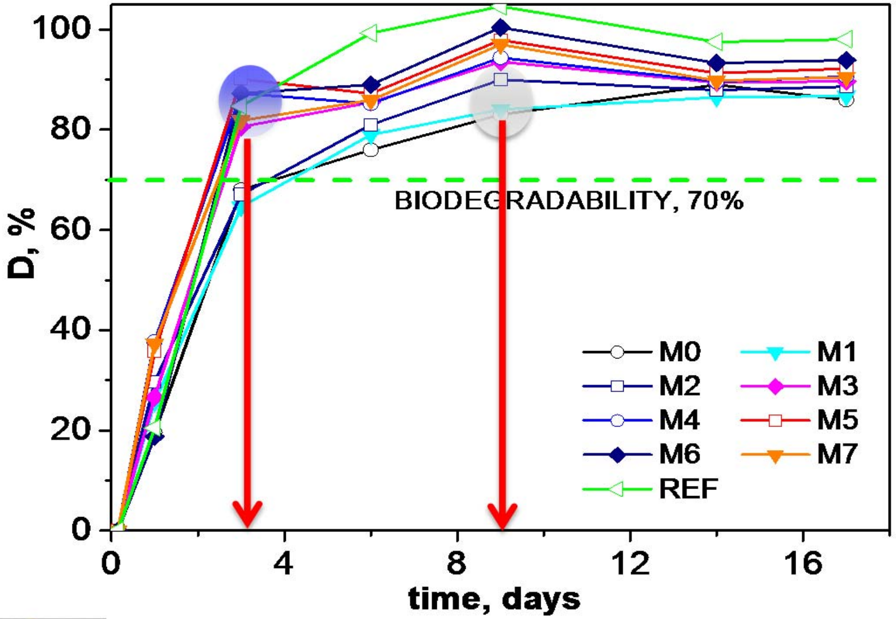
Respirometric tests

BM-T respirometer (Surcis S.L.):

- Acute toxicity and short term biodegradability assays on conventional activated sludge
- 1L capacity vessel.
- Temperature and pH control system.

Zahn-Wellens test

Long term biodegradability test:



$$D_t = \left[1 - \frac{C_t - C_B}{C_A - C_{BA}}\right] \times 100$$

Combination Chemical and biological oxidation. Pilot plants

Solar photo-Fenton at pilot plant scale

CPC solar photo-reactor.

- Irradiated surface = 3 m²
- V_T = 80 L; V_i = 44.6 L
- Batch mode operation.

Ozonation at pilot plant scale

10 L Ozonation system with a thermic ozone destructor (> 300ºC). Inlet and outlet detectors of O_3 in gas phase.

Operating conditions: 100 L/h air; 50% level of O_3 production: inlet concentration of 3.5 g/h O_3.

Immobilized Biomass Reactor (IBR) at pilot plant scale

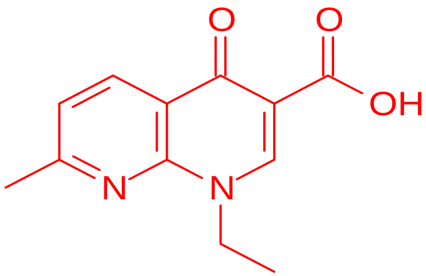
20L total volume .

Reception (200 L) and decantation (40 L) for continuous mode.

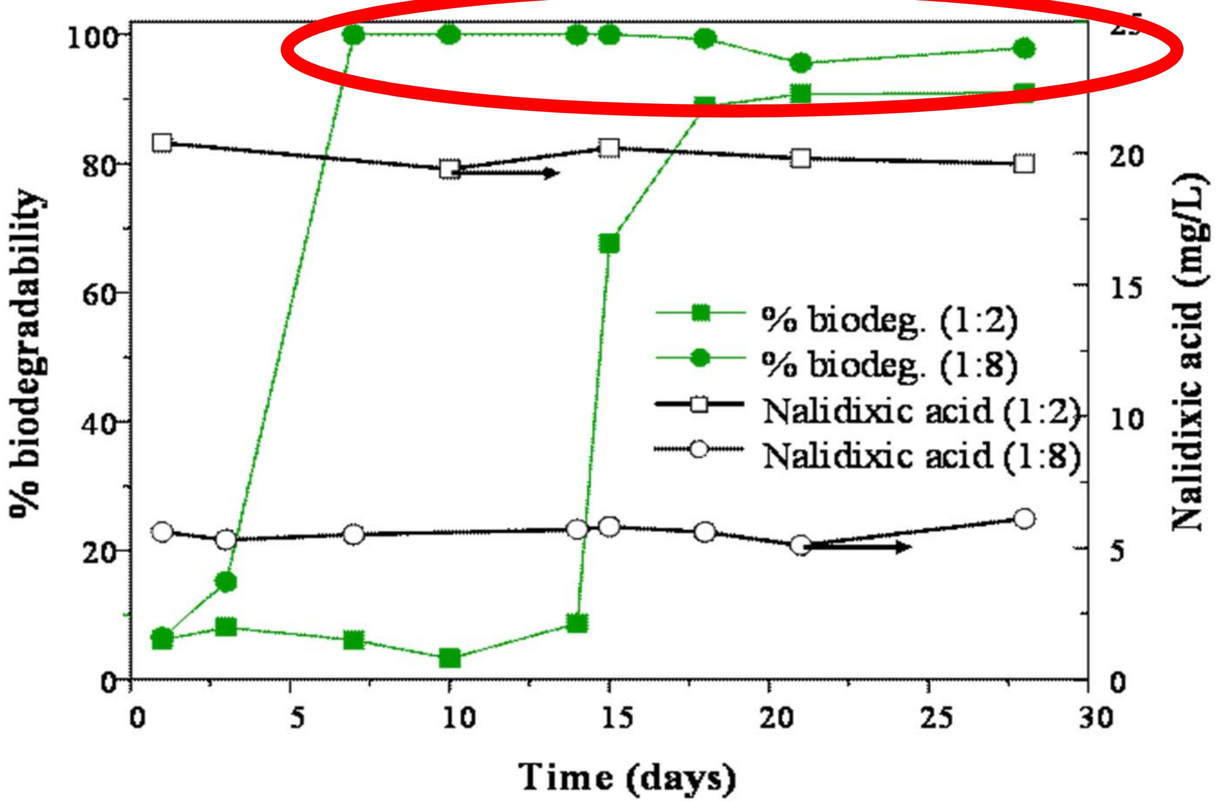
pH and oxygen dissolved automatic control systems.

Data acquisition and monitoring by a SCADA system.

Remediation of industrial WW containing pharmaceuticals. IBR-AOP



Parameter	Amount
pH	3.98
Conductivity	7 $mS.cm^{-1}$
TOC	775 $mg.L^{-1}$
COD	3420 $mg.L^{-1}$
Nalidixic acid	45 $mg.L^{-1}$
TSS	0.407 $g.L^{-1}$
Cl^-	2.8 $g.L^{-1}$
PO_4^{3-}	0.01 $g.L^{-1}$
SO_4^{2-}	0.16 $g.L^{-1}$
Na^+	2 $g.L^{-1}$
Ca^{2+}	0.02 $g.L^{-1}$



Remediation of industrial WW containing pharmaceuticals. IBR-AOP

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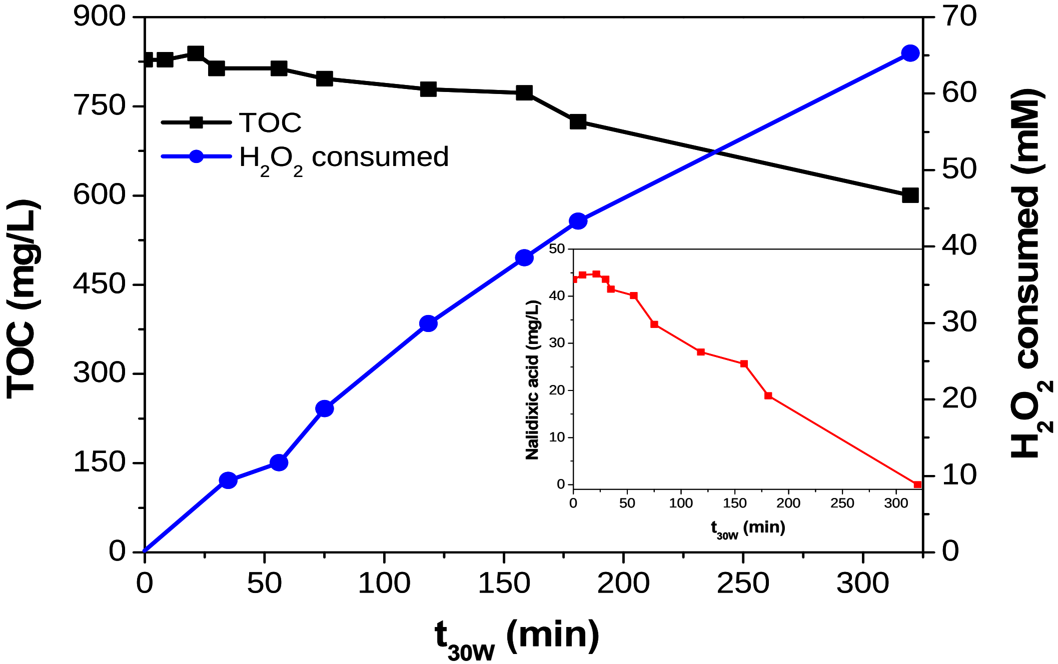
INITIAL CONDITIONS (solar photo-Fenton)

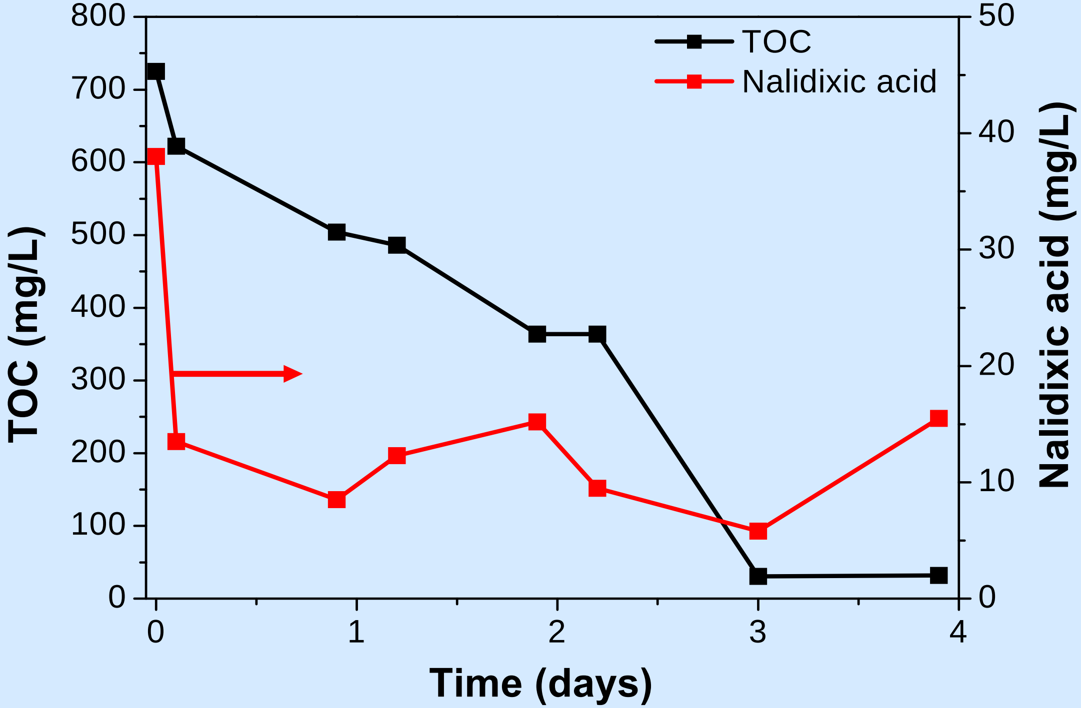
- Nalidixic acid: 39 mg/L
- Initial TOC: 822 mg/L
- [NaCl]: 6.5 g/L



- **Total degradation of the nalidixic acid at 350 minutes (illumination time) (65 mM H_2O_2)**
- **28% of the initial TOC was removed**

INITIAL CONDITIONS (Biotreatment)

- Nalidixic acid: 38 mg/L
- Initial TOC: 725 mg/L
- [NaCl] : 4.3 g/L
- NH_4^+ : <0.1 mg/L
- NO_3^- : <0.1 mg/L
- pH: 6.6



- **96% of the initial TOC was removed**
- **Nalidixic acid persists after biological treatment (~15 mg/L)**

Remediation of industrial WW containing pharmaceuticals. IBR-AOP

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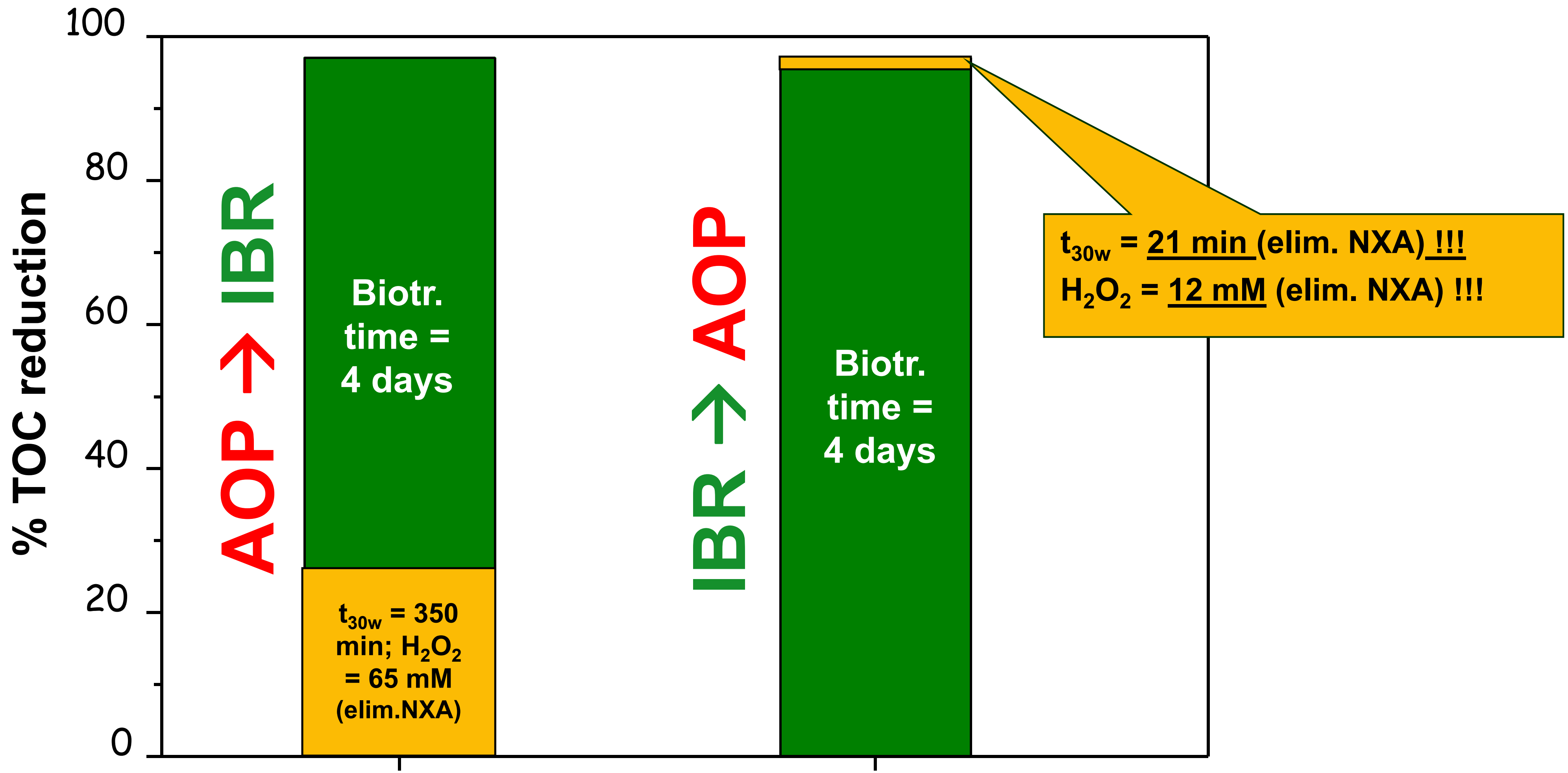

Remediation of industrial WW containing pharmaceuticals. IBR-AOP

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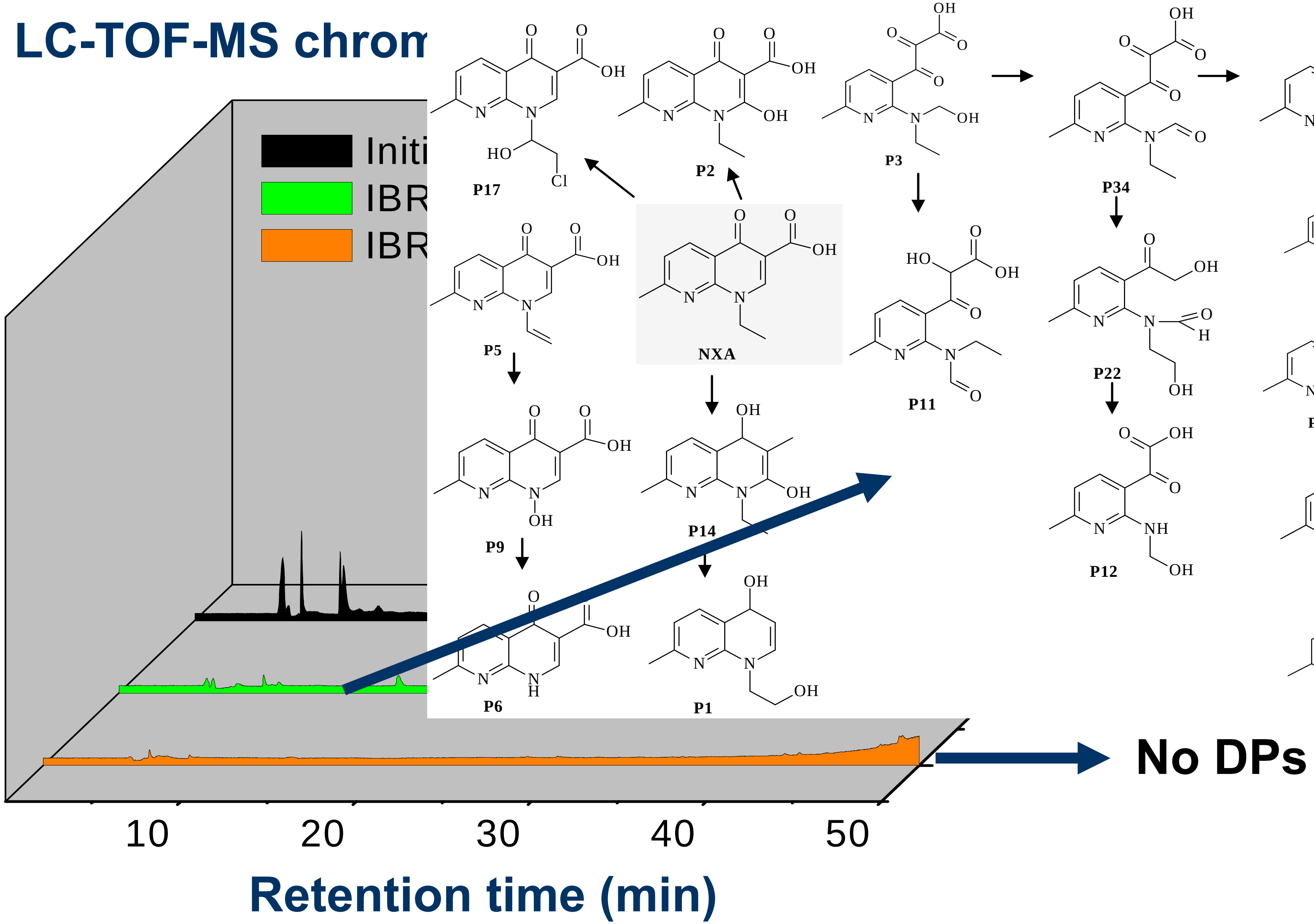
LC-TOF-MS chrom



Remediation of industrial WW containing pesticides. AOP-IBR demo scale

Non-biodegradable pesticides

Biodegradable compounds

Industrial wastewater

DOC_0:

480 mg/L

Solar Photo-Fenton

- 20 mg/L Fe^{2+} / pH: 2.8
- 44 % mineralization.
- DOC_f: 270 mg/L
- 21 mM H_2O_2 consumed.

Biological treatment (IBR)

- DOC_0: 300 mg/L
- 1.5 days of biotreatment.
- 75 % mineralization.
- $DOC_{residual}$: 75 mg/L

Decontaminated water

DOC: 75 mg/L

Remediation of WW from agro-food industry. IBR-AOP

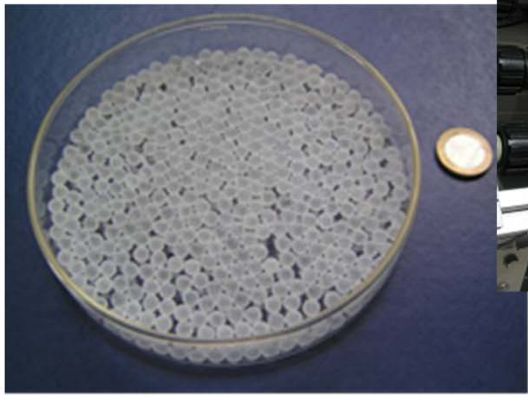
Agro-food WW characterization (citrus processing plant)

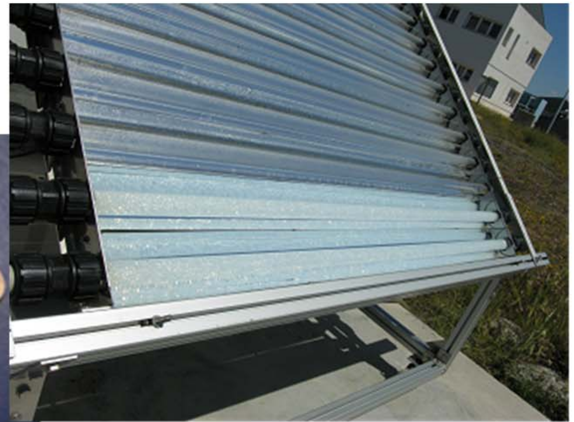
DOC: 1.2 to 2.3 mg L^{-1}

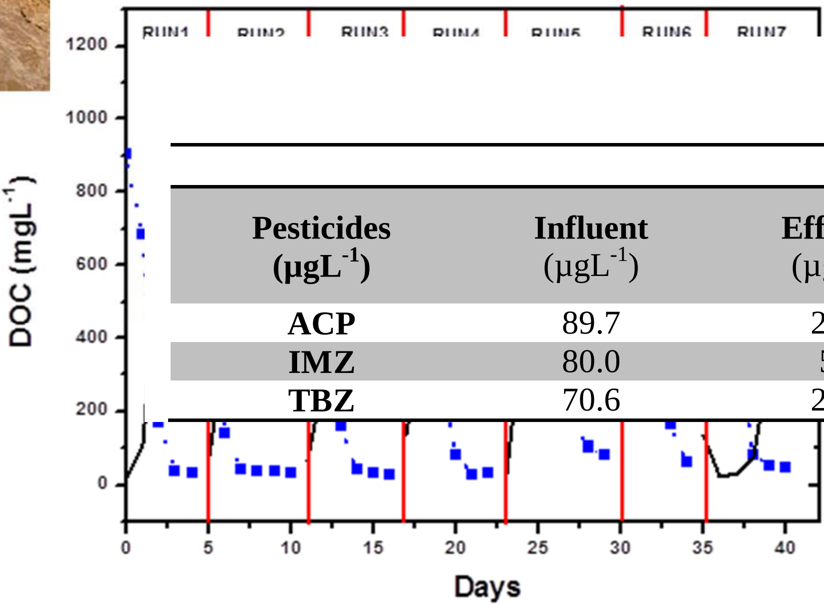
COD: 2.4 to 4.7 g L^{-1}

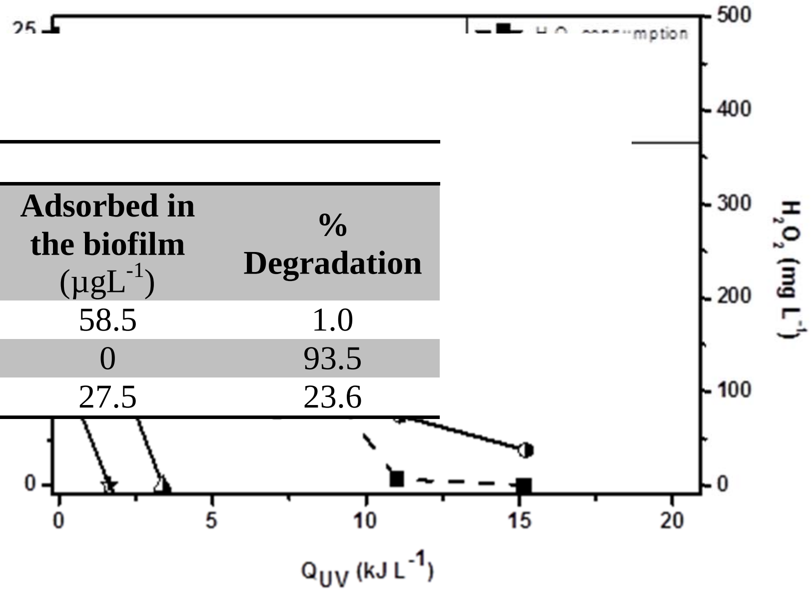
Total Nitrogen: 3.5 to 163 mg L^{-1}

Turbidity: 397-719 NTU









Pesticides (μgL^{-1})	Influent (μgL^{-1})	Effluent (μgL^{-1})	Adsorbed in the biofilm (μgL^{-1})	% Degradation
ACP	89.7	29.8	58.5	1.0
IMZ	80.0	5.2	0	93.5
TBZ	70.6	26.4	27.5	23.6

Landfill Leachate treatment

- Landfilling is the most widespread method for municipal solid waste (MSW) disposal (95% solid residues worldwide).
- Results from percolation of rainfall, degradation of the organic fraction and other compounds transfer.
- Complex nature which depends of age, precipitation, seasonal weather variation, waste type and surrounding population.
- Is a great threat to environment and human health.

Landfill leachate: Physic-chemical pre-treatment

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pH adjustment (final pH=5)

H_2SO_4 (96%)

Fe^{3+} dosage ($FeCl_3 \cdot 6H_2O$)

$[Fe]_{final}$=56 mg/L

Coagulation/Flocculation

Settling

pH adjustment (final pH=3)

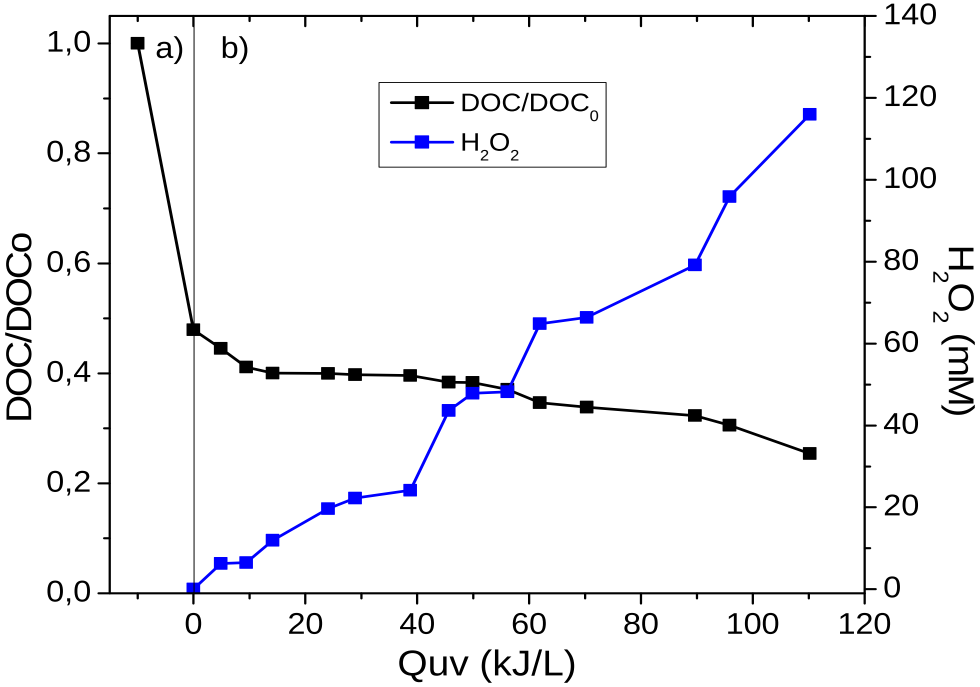
H_2SO_4 (96%)

LL before and after pre-treatment		
pH	7.8	5
Turbidity (NTU)	140	24
COD (mg/L)	5700	2120
DOC (mg/L)	2390	1209
[Fe]t final (mg/L)	7	57
Biodegradability	0.01	0.01
Toxicity(%I)	0%	11.2%

Landfill leachate: Solar photo-Fenton treatment

a) Physic-chemical pre-treatment step.

b) Solar photo-Fenton process.



70% of DOC removal after 700 min of irradiation time.

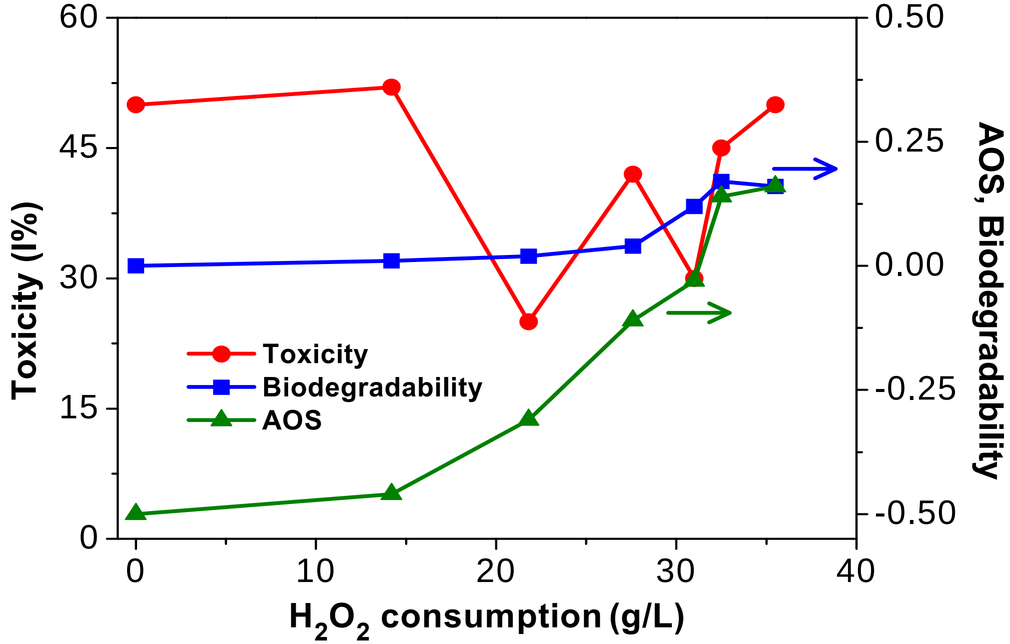
Total H_2O_2 consumption of 120 mM (4 g/L).

Required accumulative energy was 110 kJ/L.

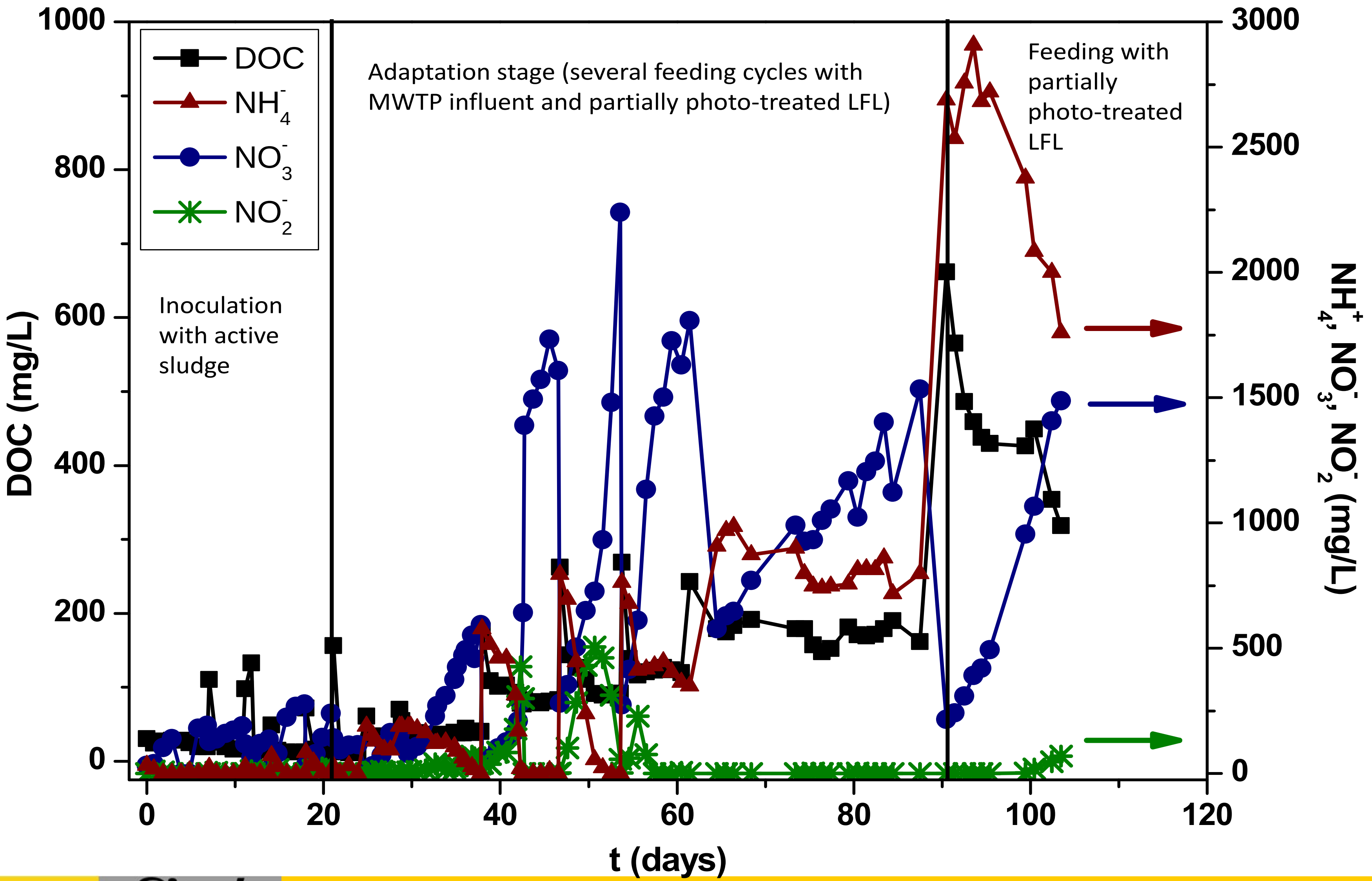
Is solar photo-Fenton process able to improve biodegradability?

Acute toxicity (I%= 40).

Good biodegradability was reached for 40% mineralization (consumption of 35.5 g H_2O_2/L).



Landfill leachate post-treatment by IBR



Landfill leachate treatment: Economic assessment

Preliminary economic assessment:

- In solar-driven systems the most important investment cost is the CPC field.
- Solar photo-Fenton **design point**: mineralization degree of 27% (final DOC=8.3 g/L).
- Q_{UV}=137 kJ/L → CPC collector surface of 6850 m².
- Leachate design flow of 40 m^3/day (365 days/year of operation)
- Industrial grade reagents.

	Operating costs	% over total costs
	€/m^3	%
Total reagents consumption	31.4	72.2
Electricity consumption	0.1	0.2
Labour requirement	1.4	3.2
CPC solar field and auxiliary facilities	10.5	24.2
Total costs	**43.4**	**100**

Cork boiling wastewater remediation

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- Processing of cork slabs includes a boiling ste chemical characteristics.
- High water consumption: 400 L/ton of cork.
- 6-30 boiling cycles per batch of water.

Cork boiling wastewater characterization

Parameter	Value (mg L^{-1})
pH	7.2
Conductivity (mS cm^{-1})	1.1
Turbidity (NTU)	163
TSS	290
COD	1240
DOC	586
Total nitrogen	27.8
Total iron	3.3
Na^+	60.1
NH_4^+	15.1
K^+	224.6
Mg^{2+}	20.3
Ca^{2+}	99.3
Cl^-	134
SO_4^{2-}	4.9
PO_4^{3-}	<DL
NO_3^-	<DL
Biodegradability	0.13 (Slightly biodegradable)
Toxicity	8.6% (Non-toxic)

Biodegradability=(CODb/COD)

DL= detection limit

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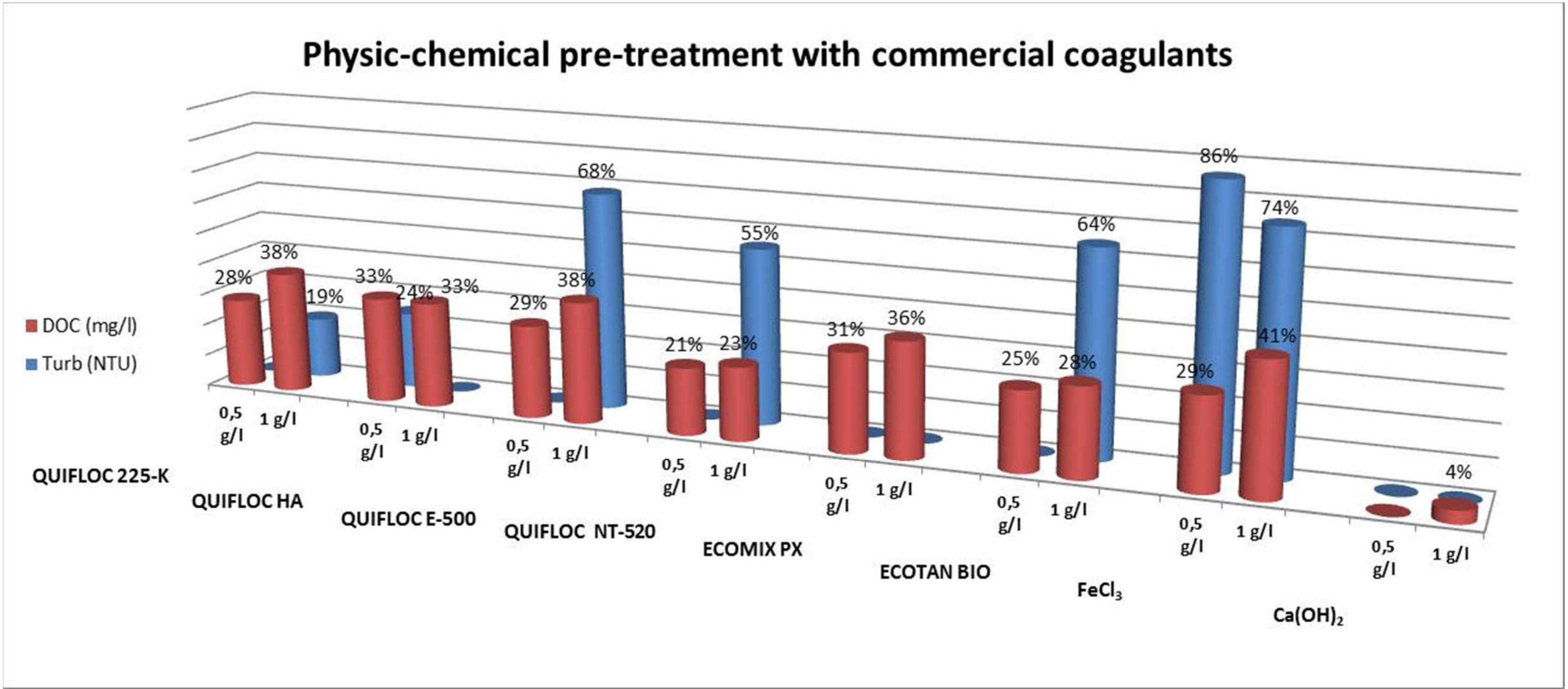
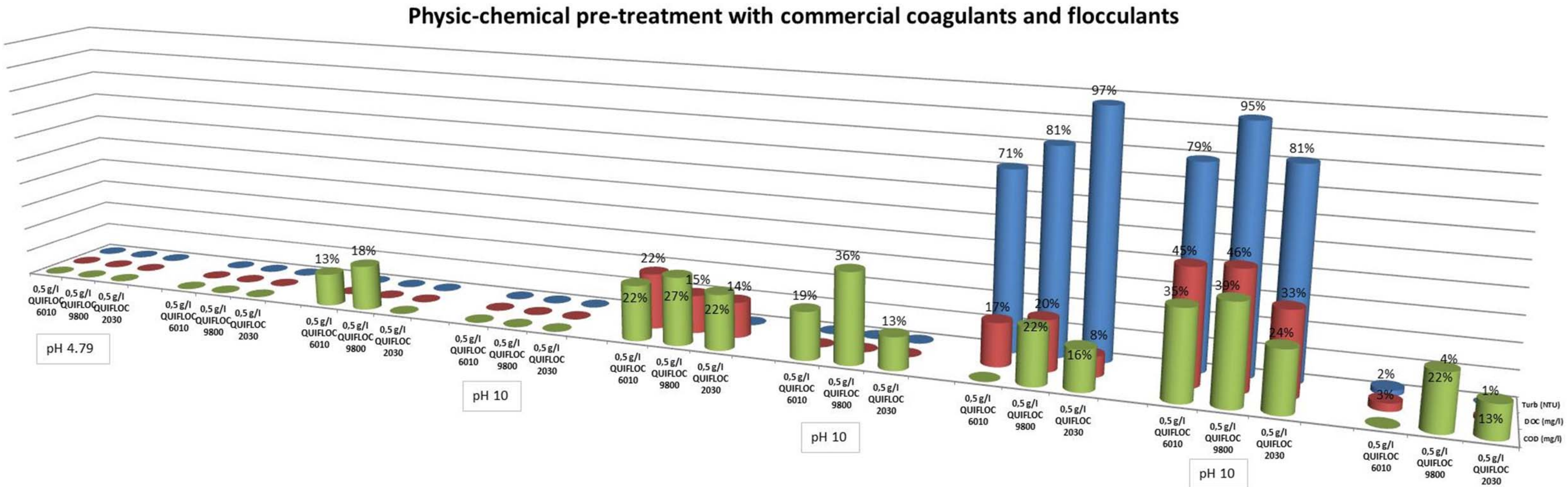
ate

- Wastewater containing: corkwood extracts (p chlorophenol, tannic fraction), suspended sol
- Low efficiency of conventional treatments.

Cork boiling wastewater physic-chemical pre-treatment



Cork boiling wastewater physic-chemical pre-treatment

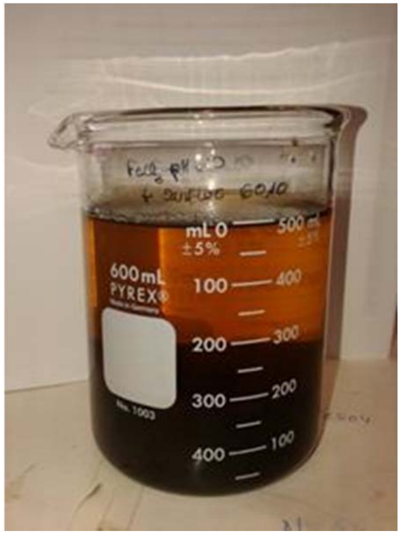


	Acute toxicity (% inhibition)	Short term biodegradability (DQOb/DQO)
Raw wastewater	63.0 %	0.08
Pre-treated with $FeCl_3$ 0.5 g L^{-1} + pH 10	58.6 %	0.30
Pre-treated with $FeCl_3$ 0.75 g L^{-1} + pH 10 + QUIFLOC 9800 0.5 g L^{-1}	61.3 %	0.12
Pre-treated with $FeCl_3$ 0.75 g L^{-1}+ pH 10 + QUIFLOC 6010 0.5 g L^{-1}	50.7 %	0.16
Pre-treated with $Ca(OH)_2$ 0.75 g L^{-1}	60.3 %	0.14

Cork boiling WW: Solar photo-Fenton compared to ozonation post-treatment

70 % DOC elimination

	Solar photo-Fenton process	O_3(raw pH 5.6)	O_3(pH 12)	O_3(pH 12)/H_2O_2
O_3 consumed (g/L)	-	1.11	2,08	2.07
H_2O_2 consumed (g/L)	2.51	-	-	1.40
Toxicity (%Inhibition)	96	76	94	90



Cork boiling wastewater: post-treatment by IBR

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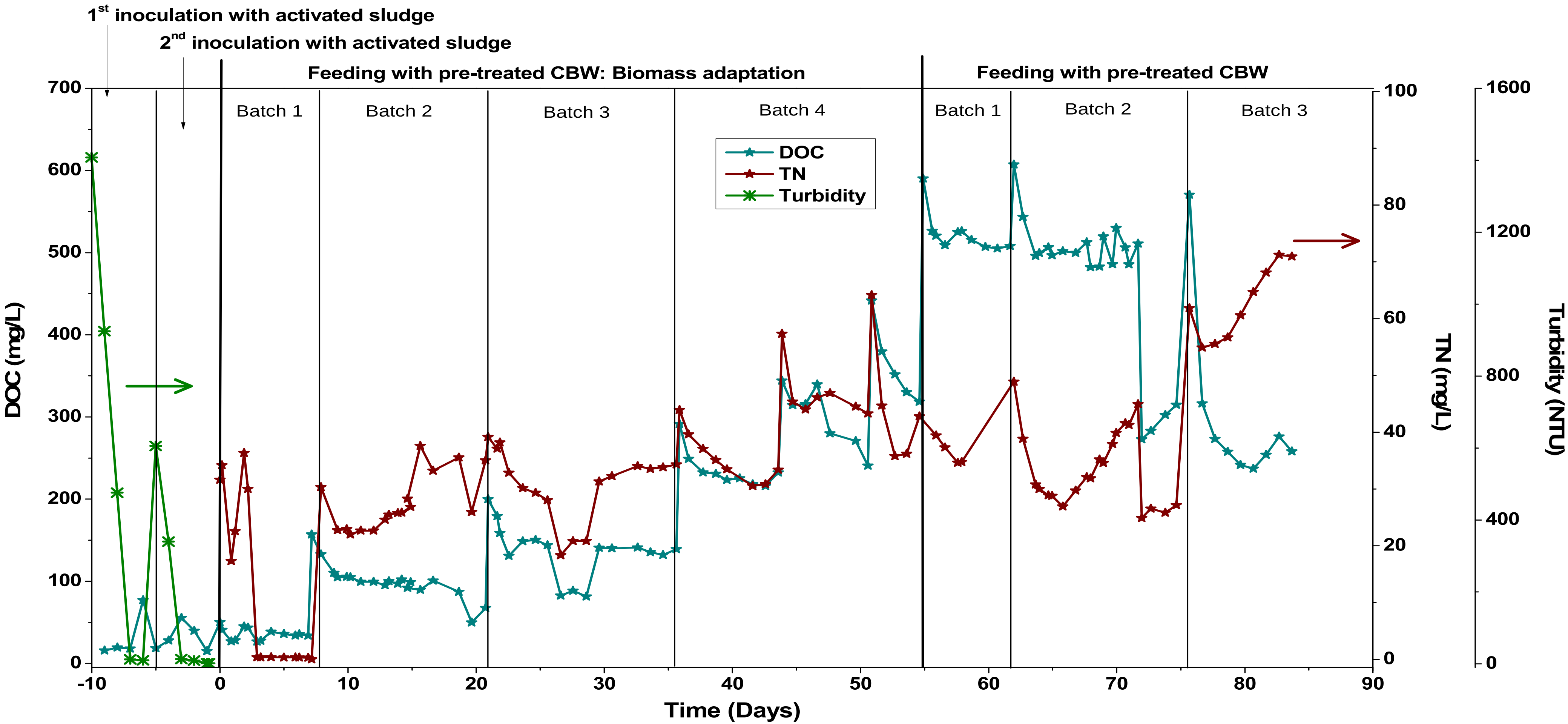


Adaptation phase: Pre-treated Cork Boiling Wastewater (COD=50 – 300 mg/L) + MWWTP influent (COD_{end} = 50 mg/L).

Feeding: Pre-treated Cork Boiling Wastewater (600 mg/L).

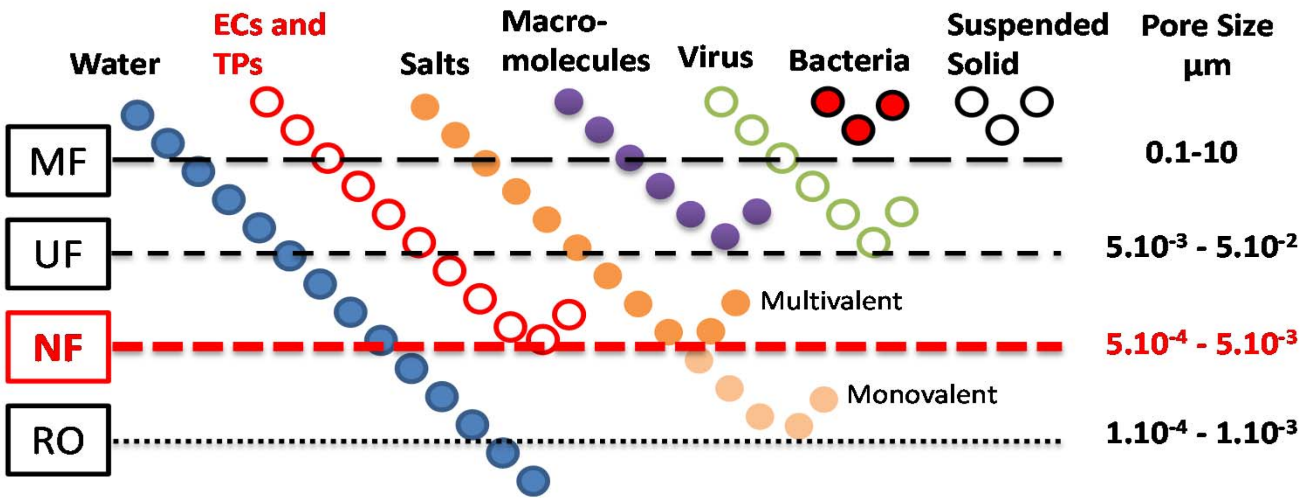
Cork boiling wastewater: post-treatment by IBR

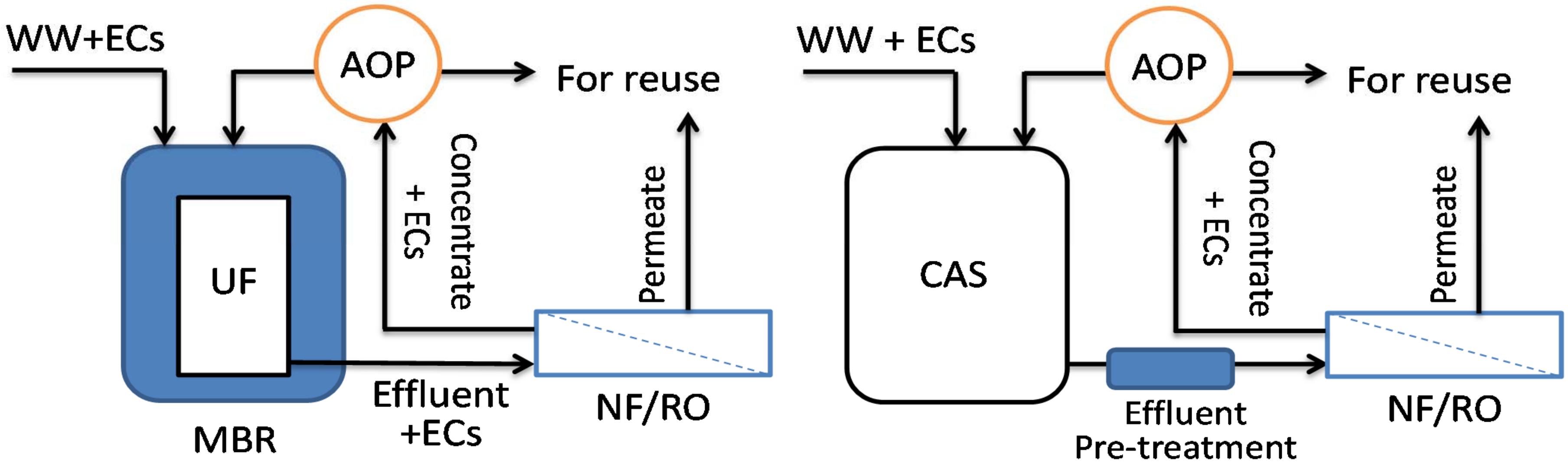
Lab-scale assays for chronic toxicity evaluation on activated sludge from MWWTP

- Two flaks (900 mL activated sludge + 100 mL de pre-treated cork boiling WW) under continues agitation and aeration through several days.
- Assessment of the activated sludge activity by means of the oxygen uptake rate, OUR.

	Day	Flask 1	Flask 2
DOC (mg L^{-1})	0	82.2	79.6
	1	51.0	57.8
	2	-	47.2
	6	-	31.3
	10	-	-
OUR (mg $L^{-1}\cdot h^{-1}$)	End of assay	1.55	1.24
DQO_b (mg L^{-1})	End of assay	34.2	21.5

Combination NF/AOPs



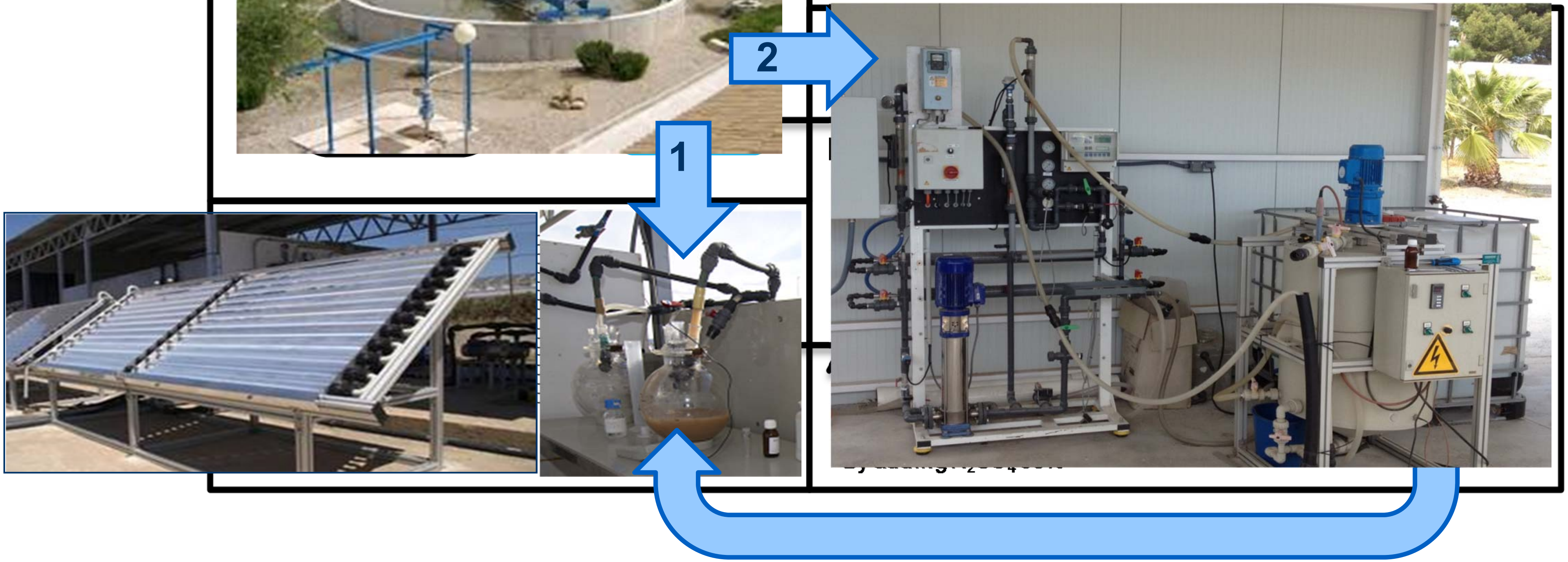


Combination NF/AOPs

Two alternatives:

1 Direct treatment, CF=1

2 Concentrate treatment, CF=4 or 10

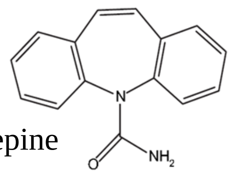


Combination NF/AOPs

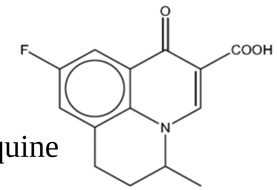
$r = kC$

Model compounds at different "realistic" C_0 in <u>natural water.</u>

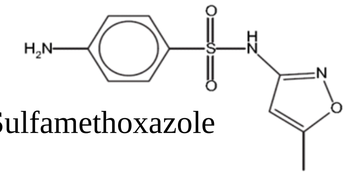
Fe (II), 0.1 mM, H_2O_2, 25 mg L^{-1}, natural pH



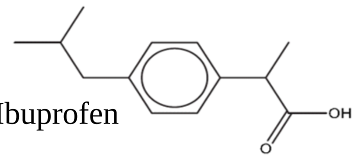
Carbamazepine



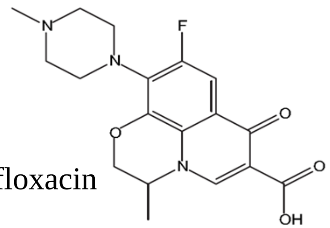
Flumequine



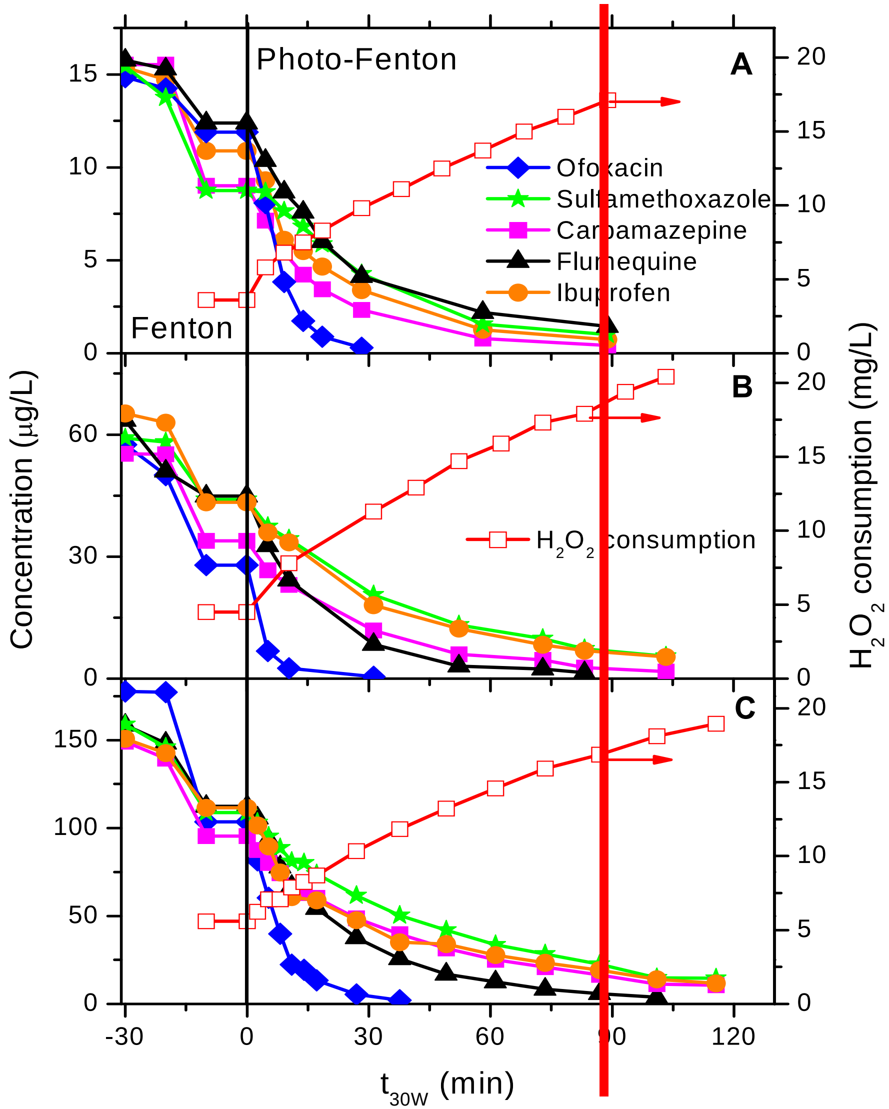
Sulfamethoxazole



Ibuprofen



Ofloxacin



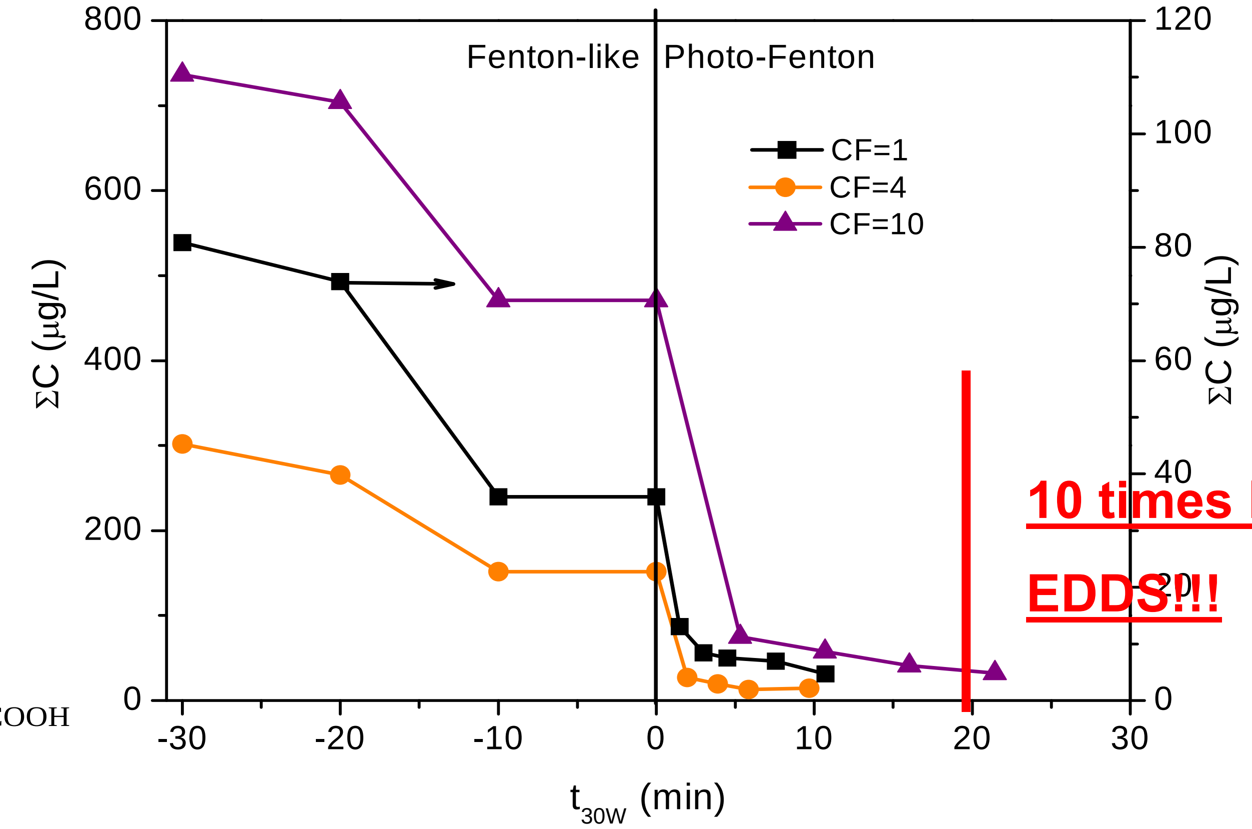
Combination NF/AOPs

Fe (II), 0.1 mM

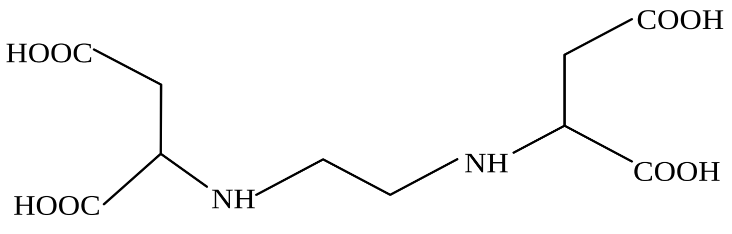
0.2 mM EDDS

H_2O_2, 25 mg L^{-1}

Natural pH



10 times less with EDDS!!!



Ethylenediamine-N,N'-disuccinic acid (EDDS)

$Fe(III)\text{-}L + h\nu \rightarrow [Fe(III)\text{-}L]^* \rightarrow Fe(II) + L^{\bullet}$

Combination NF/AOPs

Operational requirements for attaining *95% of pharmaceuticals degradation* present in NF concentrates (CF=4 and 10) when solar photo-Fenton and photo-Fenton like Fe(III)-EDDS complex were applied. CF=1 no NF.

	CF	1	4	10
Solar photo-Fenton	H_2O_2 consumed ($g m^{-3}$) Q_{uv} ($kJ\ L^{-1}$) t(min) / CPC surface[1]	17.0 22.5 90/100	4.4 5.1 120/22.6	1.9 2.8 110/12.4
Solar photo-Fenton like Fe (III)-EDDS complex	H_2O_2 consumed ($g m^{-3}$) Q_{uv} ($kJ\ L^{-1}$) t(min) / CPC surface[1]	24.9 2.7 14/15	6.2 0.6 10/3.3	2.5 0.5 19/2.7

Concluding remarks

After physic-chemical pre-treatment…

- Physic-chemical pre-treatment usually improves significantly industrial wastewater characteristics for facing its complete remediation and possible reuse.
- Best results are usually provided by Fe^{3+}.

After ozonation treatment…

- Toxicity should show slight decrease.
- Better results in biodegradability enhancement.
- Possible combination with advanced biological treatment for complete wastewater remediation.

After solar photo-Fenton process…

- Pre-treatment step did not improve photo-treatment´s efficiency for cork boiling wastewater.
- Toxicity reduction and biodegradability enhancement allow its combination with a subsequent advanced biological treatment.

Advanced biological treatment before or after chemical oxidation step…

- Specific industrial wastewater showing low toxicity levels and partially biodegradable could face an advanced biological treatment as the first step. Normally for those wastewater with high organic load and containing small concentrations of recalcitrant pollutants.

Concluding remarks (II)

The current lack of data for comparison of solar photocatalysis with other technologies definitely presents an obstacle towards an industrial application. Therefore, it is necessary:

- ✓ Give sound examples of techno-economic studies.
- ✓ Assessment of the environmental impact: life cycle analysis (LCA).
- ✓ To lead their application on industry it will be critical processes can be developed up to a stage, where the technology:
  - can be compared to other processes.
  - can demonstrate its robustness, i.e. small to moderate changes to the wastewater inlet stream do not affect the plant's efficiency and operability strongly.
  - is predictable, i.e. process design and up-scaling can be done reliably.
  - gives additional benefit to the industry interested on this technology application (e.g. giving the company the image of being "green").

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Acknowledgments

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http://www.psa.es/webeng/areas/tsa/index.php