BIORECALCITRANT INDUSTRIAL WASTEWATER TREATMENT BY INTEGRATING ADVANCED OXIDATION AND BIOLOGICAL PROCESSES

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Biodegradable substances:

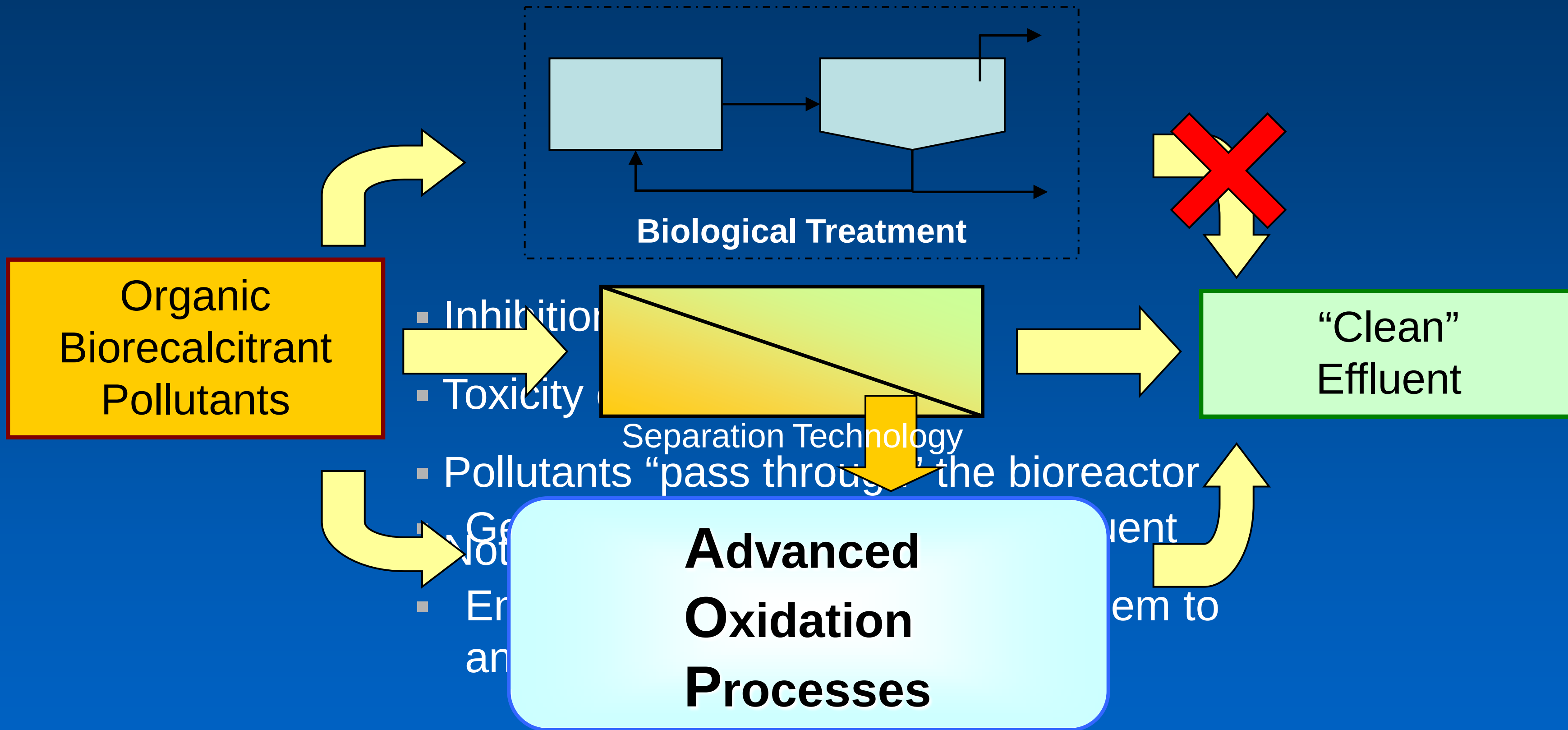
- Biofilter treatment/ activated sludge treatment /MBRs

Non-biodegradable substances can show

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

Alternative treatment

Integration of AOPs as part of a treatment train



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

Advanced Oxidation Processes (AOP)

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

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

Advanced Oxidation Processes (AOP)

H_2O_2/UV

$$H_2O_2 \xrightarrow{h\nu} 2OH^\bullet$$

Fenton

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

TiO_2/hν/O_2 (Photocatalysis)

$$TiO_2 \xrightarrow{h\nu} e^- + h^+$$

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

O_3/ H_2O_2

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

$$HO_2^- + O_3 \rightarrow HO_2^\bullet + O_3^{\bullet -}$$

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

$$O_2^{\bullet -} + O_3 \rightarrow O_2 + O_3^{\bullet -}$$

$$O_3^{\bullet -} + H^+ \rightarrow HO_3^\bullet$$

$$HO_3^\bullet \rightarrow HO^\bullet + O_2$$

Photo-Fenton

$$Fe^{3+} \xrightarrow{h\nu} Fe^{2+} + HO^\bullet$$

- **AOPs** may be used for **decontamination** of water containing organic pollutants, classified as bio-recalcitrant, and/or for **disinfection** removing current and emerging pathogens.
- The overarching goal for the future of **reclamation and re-use** of water is to capture water directly from non-traditional sources such as **industrial or municipal wastewaters** and restore it.
- Futuristic direct re-use systems envisioned involve only two steps: a single-stage MBR with an immersed nanofiltration membrane, followed by a **photocatalytic reactor to provide an absolute barrier** to pathogens and to destroy organic contaminants that may pass the nanofiltration barrier.

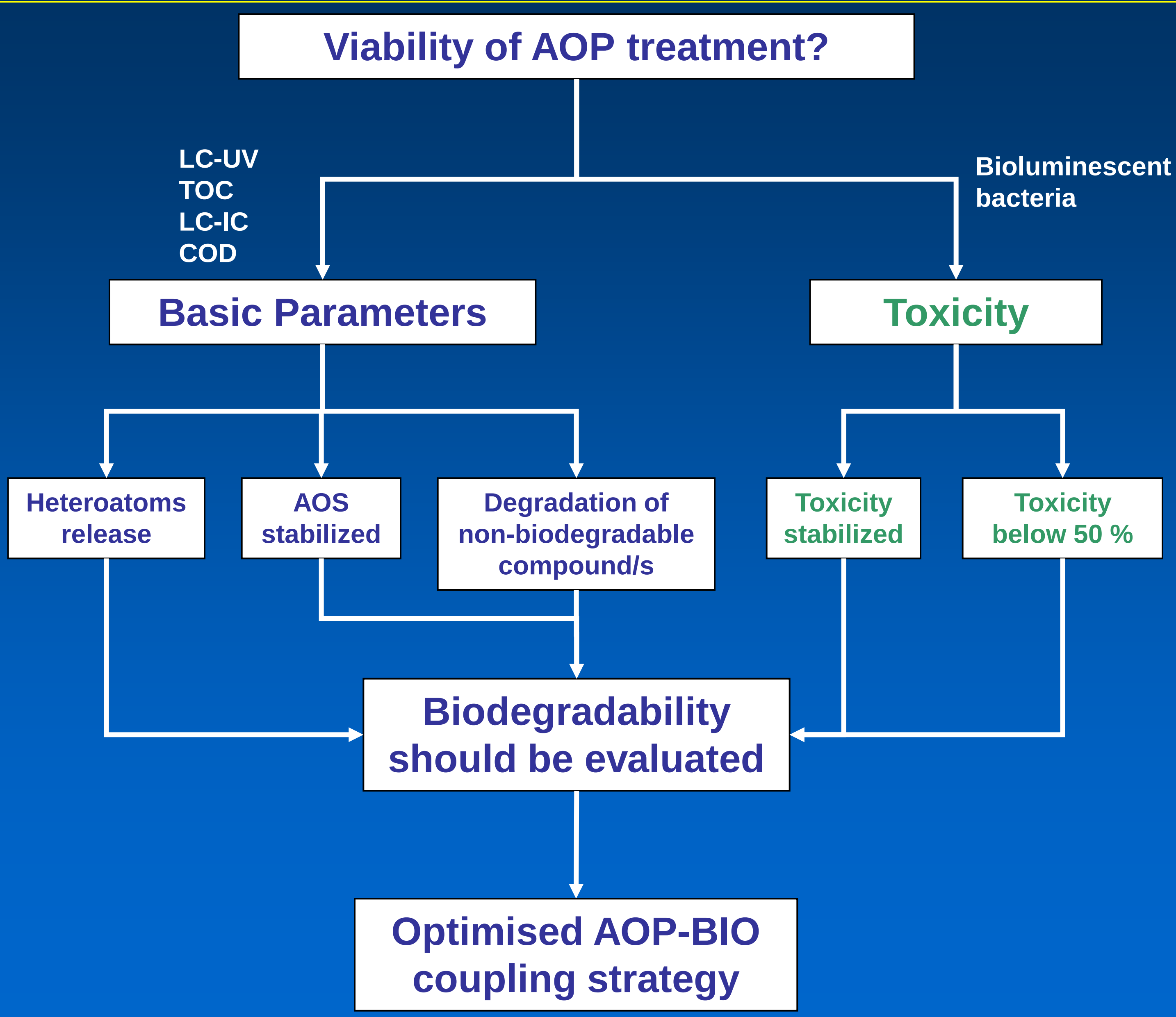
Science and technology for water purification in the coming decades. Nature, 452, 301-310, 2008.

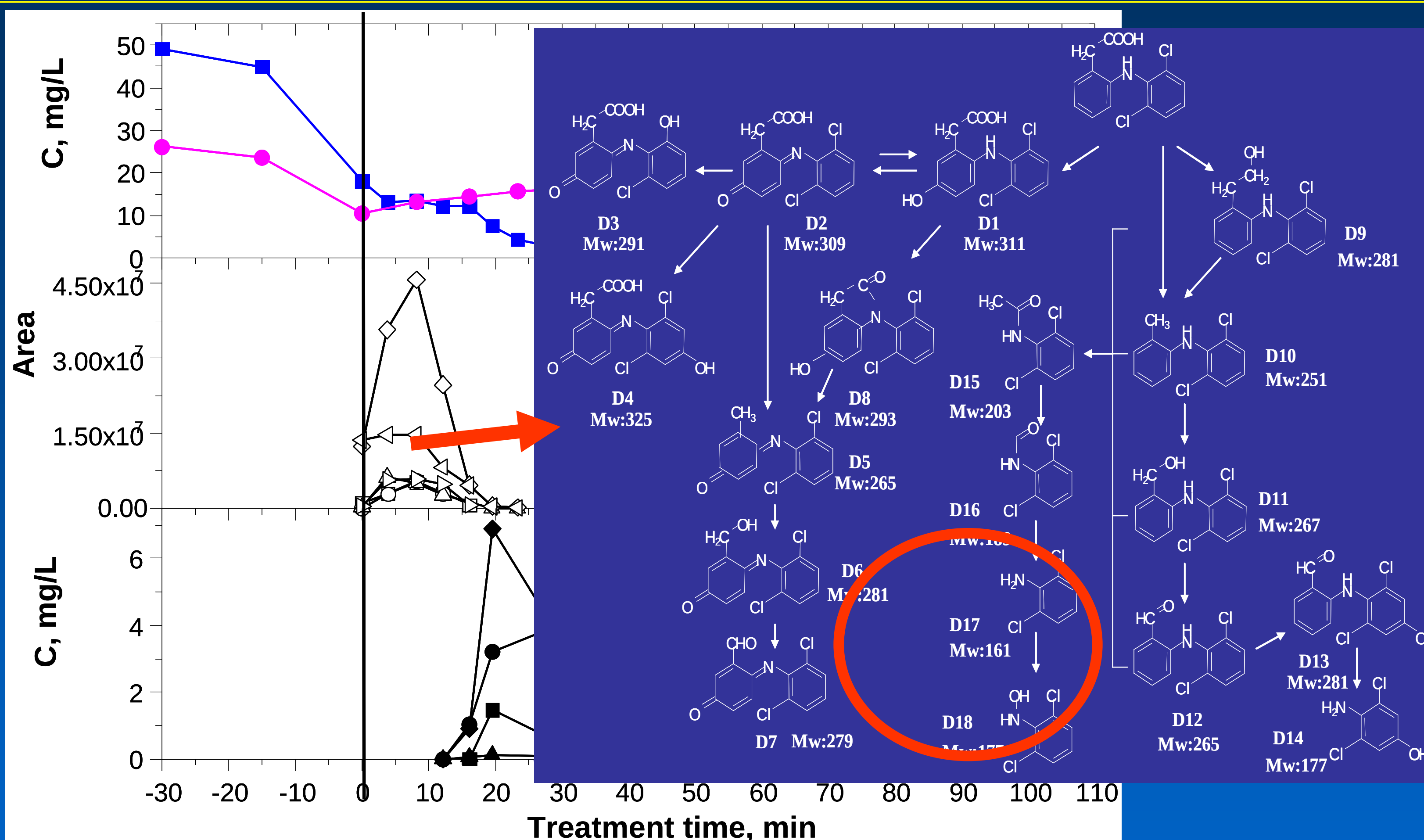
Nevertheless, **technical applications are still scarce**. Process costs may be considered the main obstacle to their commercial application

PROMISING COST-CUTTING APPROACHES

- To minimize residence time (i.e. energy) and reagent consumption in the more expensive AOP stage by applying an optimized coupling strategy.
- The use of renewable energy sources, i.e., sunlight as the irradiation source for running the AOP.
- Integration of AOPs as part of a treatment train: ***Application of AOPs as a pre-treatment stage to enhance biodegradability and reduce toxicity followed by biological post-treatment.***

Step 1	**Check if WW is potentially treatable by AOP and/ or biotreatment**	***Wastewater characterisation + check for volatility, solubility, pre-liminary kinetic study***
Step 2	**Selection of treatment strategy as a function of wastewater characteristics**	***Decision if only AOP, AOP-BIO, only BIO or discharge are the best option***
Step 3	**Develop and optimise coupling strategy**	***Only if AOP-BIO was chosen as the best option. Various AOPs can be tested.***
Step 4	**Pilot-plant studies on process kinetics**	***Process optimisation. Strategy depends on problem and AOP. Various AOPs can be tested.***
Step 5	**Theoretical up-scaling**	***Necessary for correct posterior economic assessment.***
Step 6	**Economic study**	***Takes into account investment + O&M costs + their variation depending on process scale.***
Step 7	**Choose best-performing AOP**	***= AOP that solves given problem (defined by WW characteristic + flowrate) at lowest price.***
Step 8	**Final plant design**	


Viability of AOP treatment?
LC-UV
TOC
LC-IC
COD
Bioluminescent bacteria
Basic Parameters
Toxicity
Heteroatoms release
AOS stabilized
Degradation of non-biodegradable compound/s
Toxicity stabilized
Toxicity below 50 %
Biodegradability should be evaluated
Optimised AOP-BIO coupling strategy

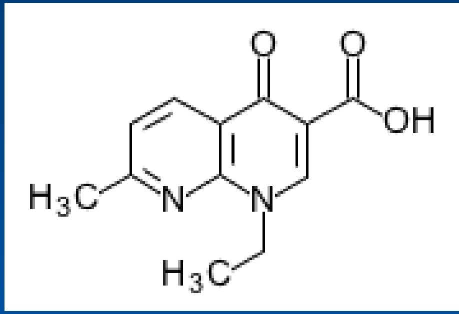


DPs → *R-COOH* → **Toxicity?**

R-COOH → $CO_2 + H_2O + XH$

R-COOH → **Biodegradability?**

Pharmaceutical Wastewater (AUSTEP)



Nalidixic acid

sample after sedimentation

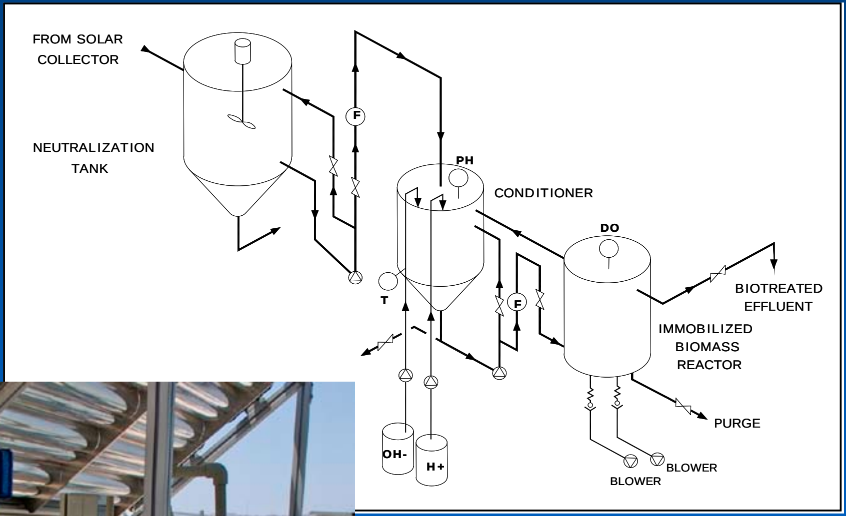
Parameter	Amount
pH	3.98
Conductivity	7 $mS.cm^{-1}$
TOC	775 $mg.L^{-1}$
COD	2660 $mg.L^{-1}$
Nalidixic acid	45 $mg.L^{-1}$
TSS	0.407 $g.L^{-1}$
Cl^-	2.8 $g.L^{-1}$
PO_4^{3-}	0.01 $g.L^{-1}$
SO_4^{2-}	0.16 $g.L^{-1}$
Na^+	2 $g.L^{-1}$
Ca^{2+}	0.02 $g.L^{-1}$

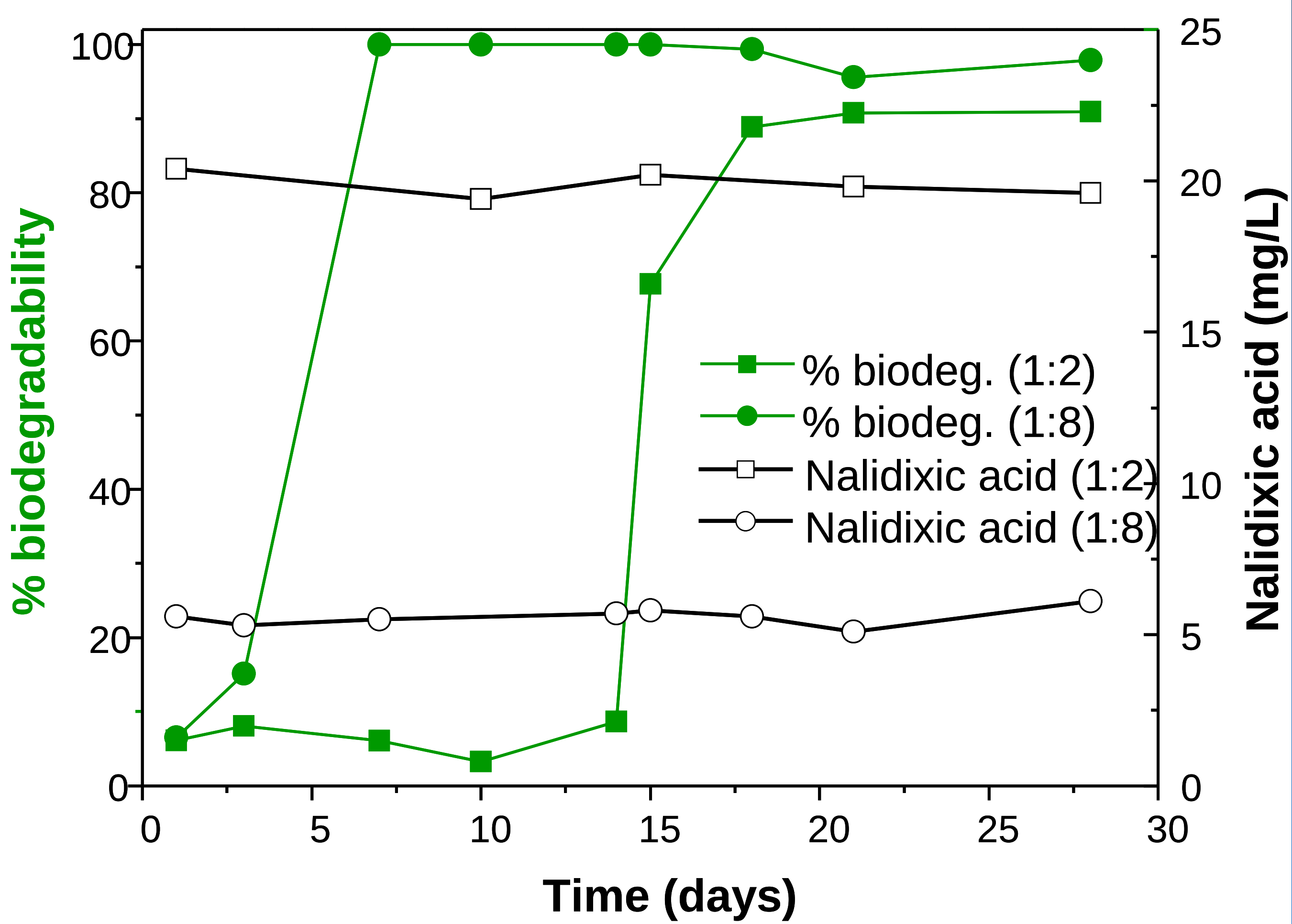
CPC (compound parabolic collector) reactor

- Photo Fenton process
- Modules mounted on a fixed platform tilted 37º (local latitude)
- Total reactor I volume 450 L: irradiated volume (108 L) + piping and tank. Total illuminated area : 9m^2
- Total reactor II volume 40 L: irradiated volume (22 L) + piping and tank. Total illuminated area : 3m^2

IBR (immobilised biomass reactor)

The IBR consists of a 170 L flat bottom tank filled up with 90-95 L polypropylene 15 mm Pall Rings supports colonized by activated sludge coming from a conventional aerobic wastewater treatment plant.





Coupling Process?

APPROACH 1 (AOP + Biotreatment)

APPROACH 2 (Biotreatment + AOP)

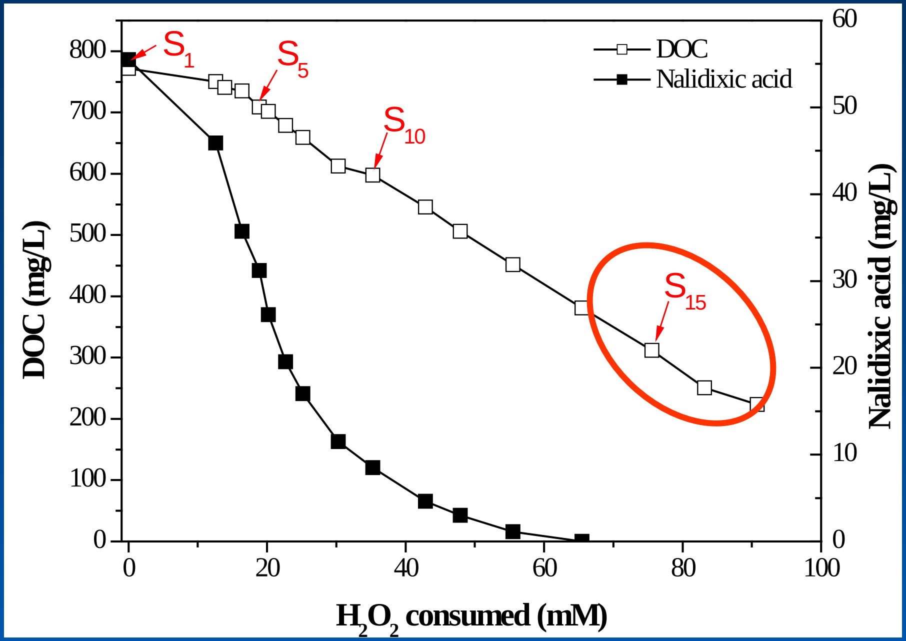
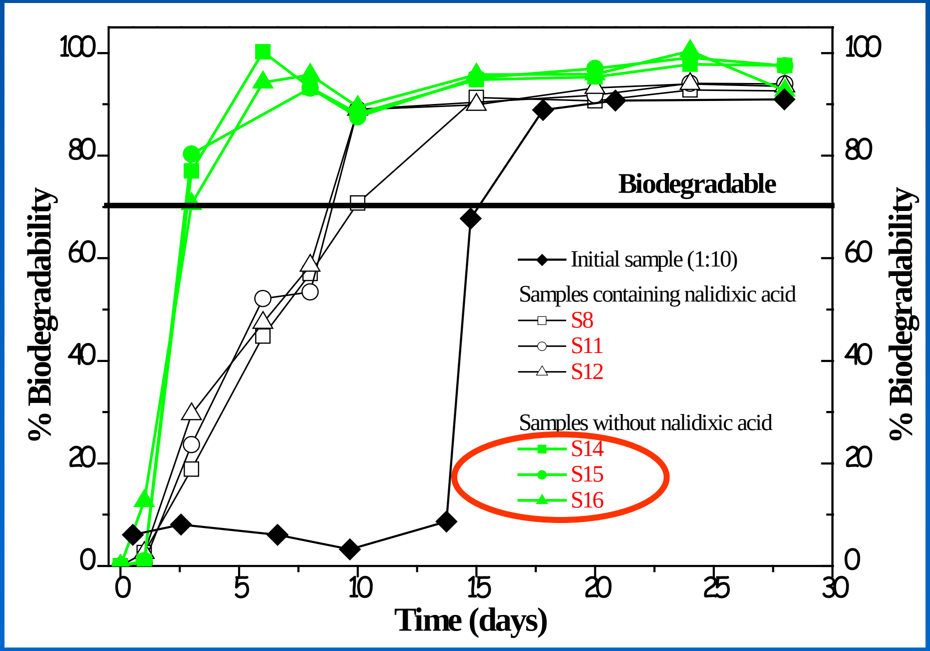


Photo-Fenton

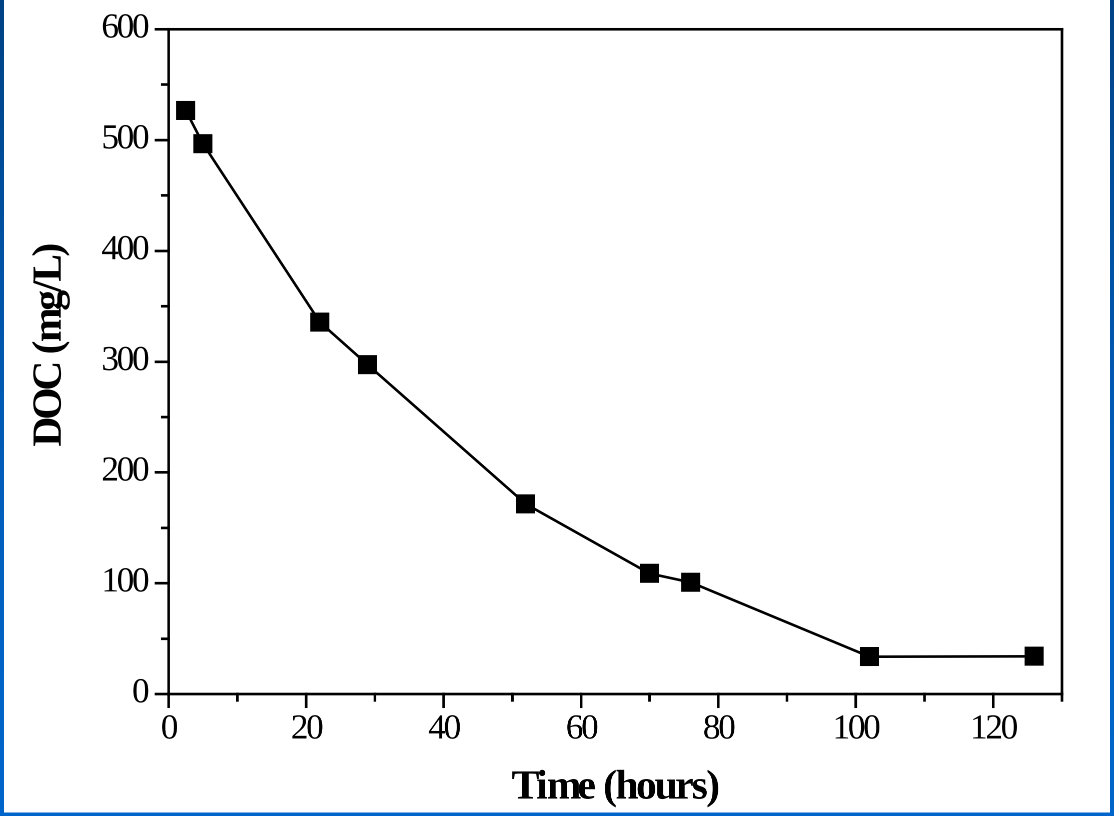
APPROACH 1 (AOP + Biotreatment)

Zahn-Wellens



APPROACH 1 (AOP + Biotreatment)

Biotreatment



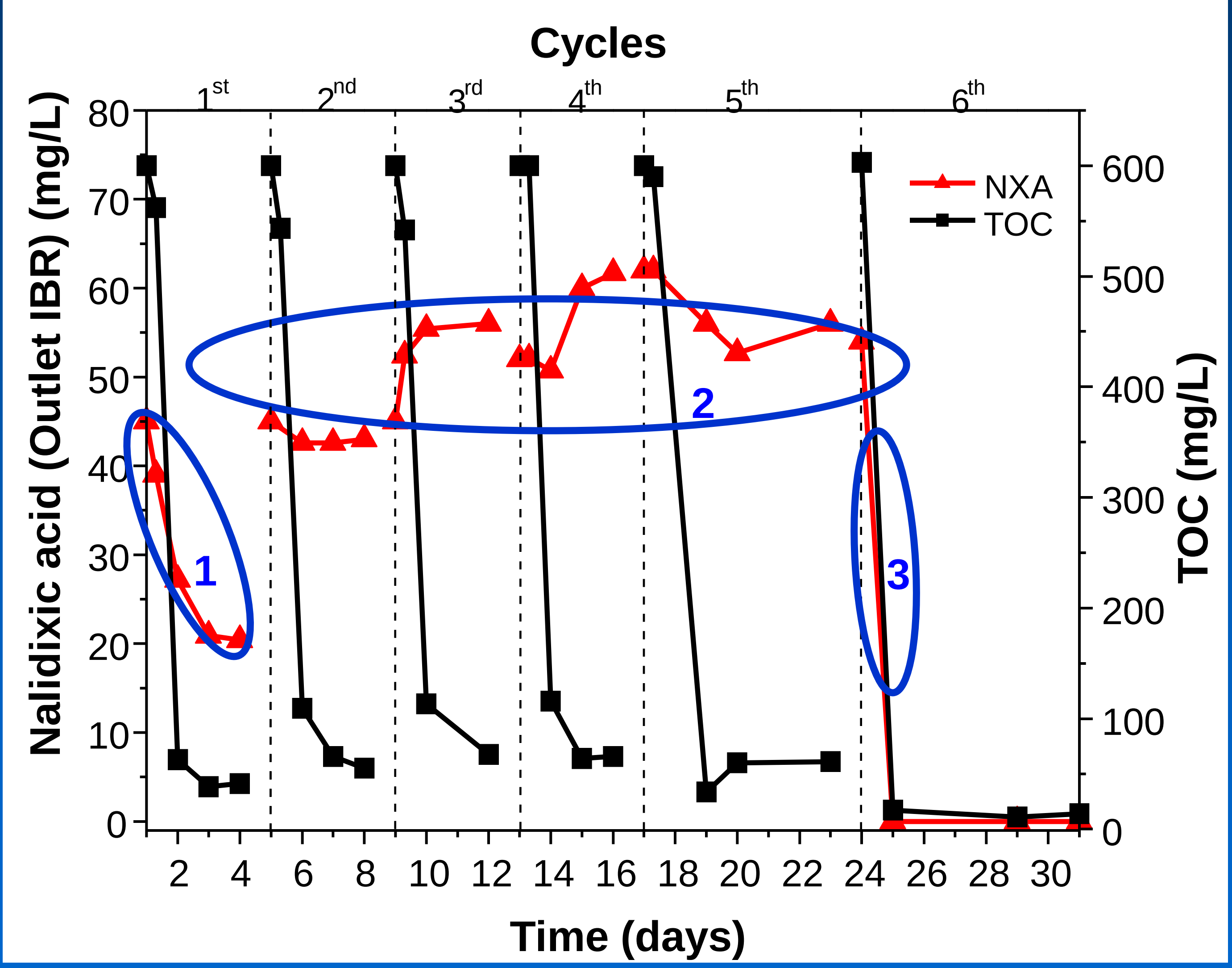
APPROACH 2 (Biotreatment + AOP)

Biotreatment

$C_{0, NXA}$= 45 mg/L (cycles 1-5th)

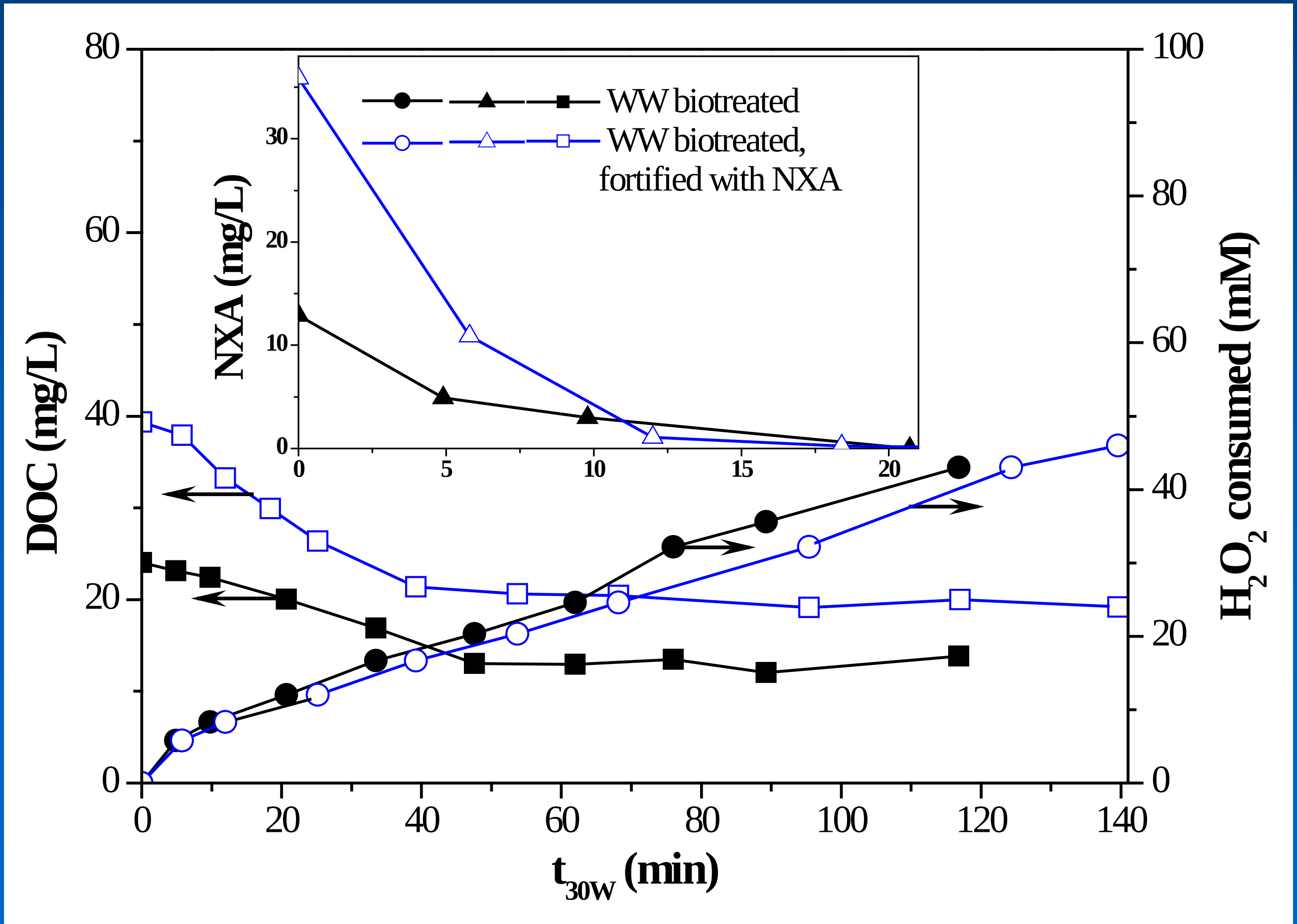
$C_{0, NXA}$= 0 mg/L (cycle 6th)

1. Adsorption of NXA
2. Saturation of NXA
3. No desorption of NXA



APPROACH 2 (Biotreatment + AOP)

Photo-Fenton



Coupling Process?

APPROACH 1 (AOP + Biotreatment)

APPROACH 2 (Biotreatment + AOP)

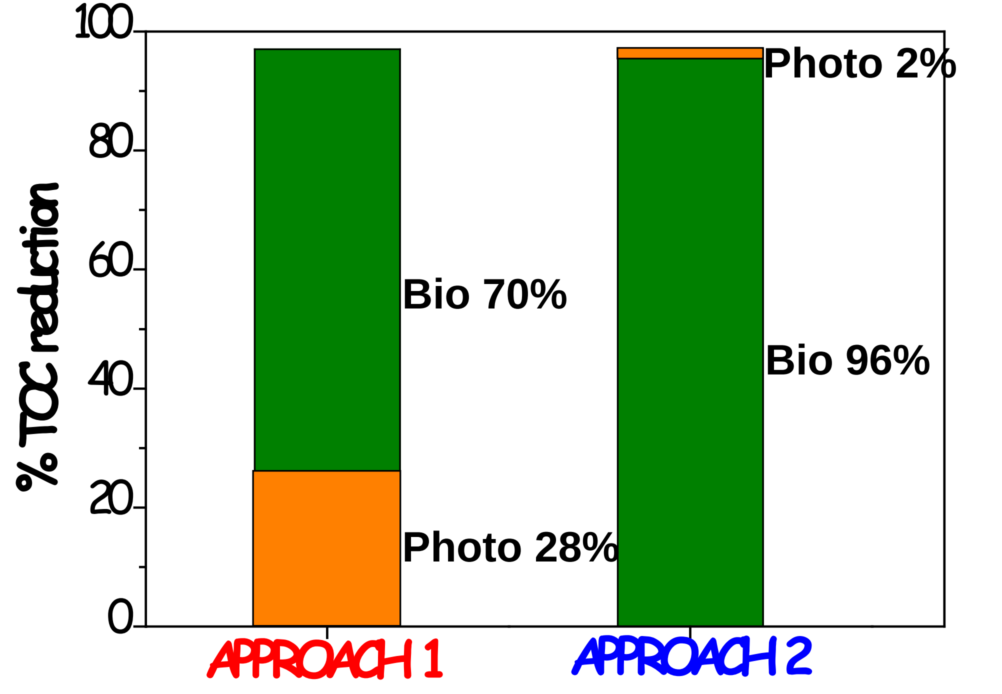
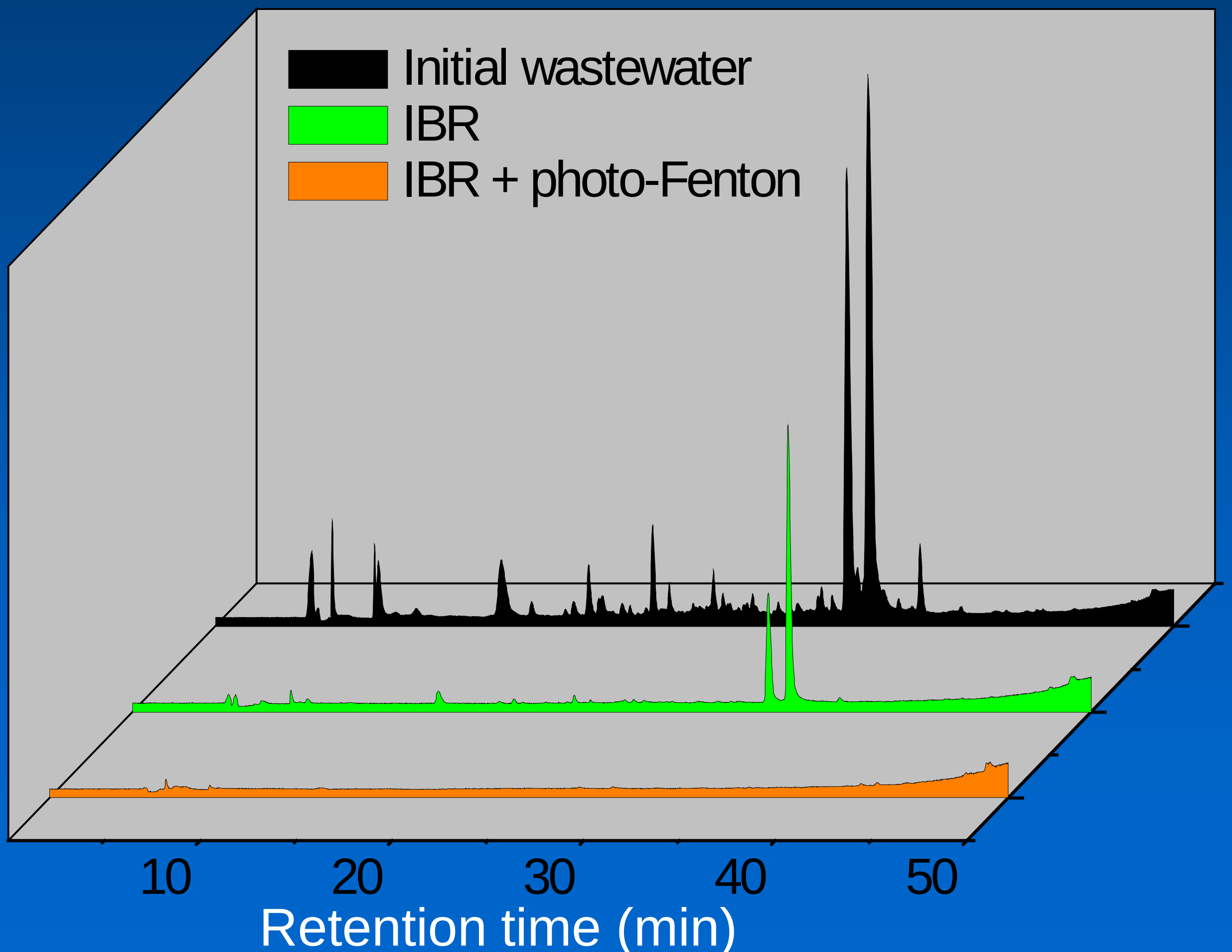


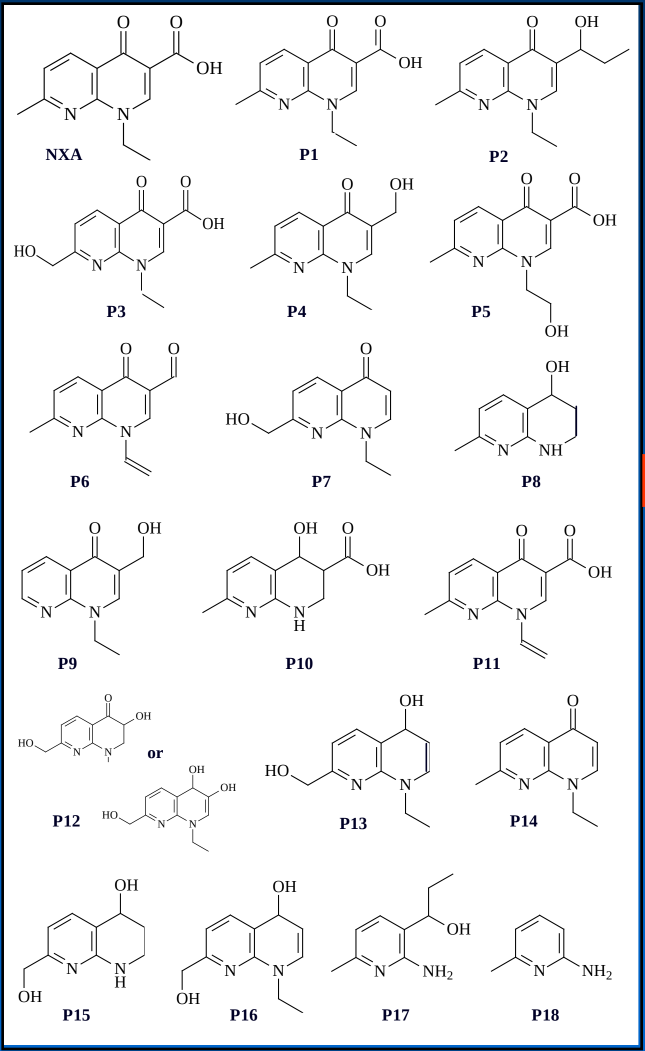
	Photo-Fenton		Biotreat.
	t_{30w} (elimination nal. acid) (minutes)	H_2O_2 consumed (mM)	treatment time (days)
APPROACH1	350	65	6
APPROACH2	21	12	4

APPROACH 2 (Biotreatment + AOP)

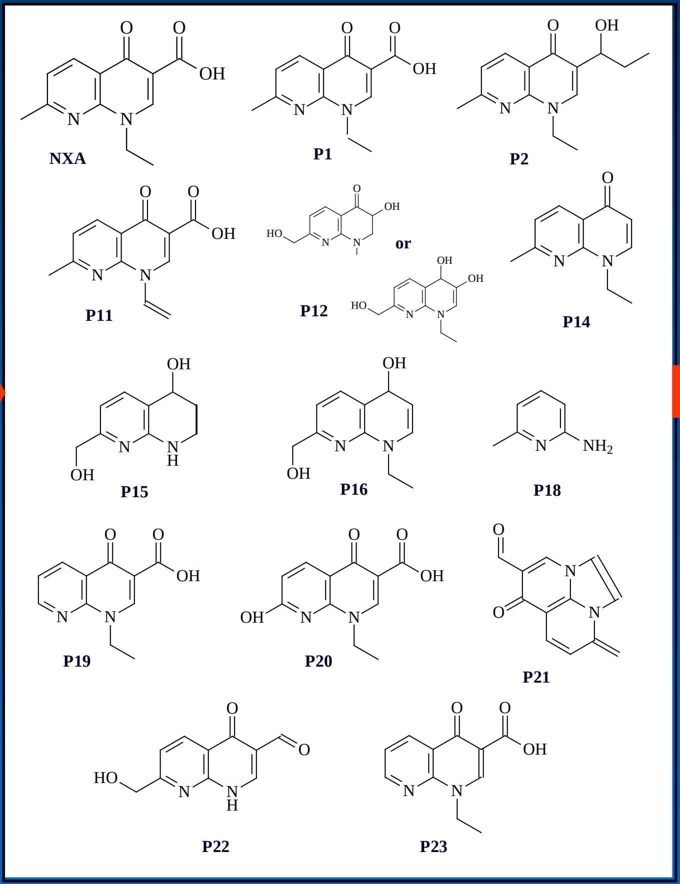
LC-TOF-MS chromatograms



APPROACH 2
(Biotreatment + AOP)



Wastewater

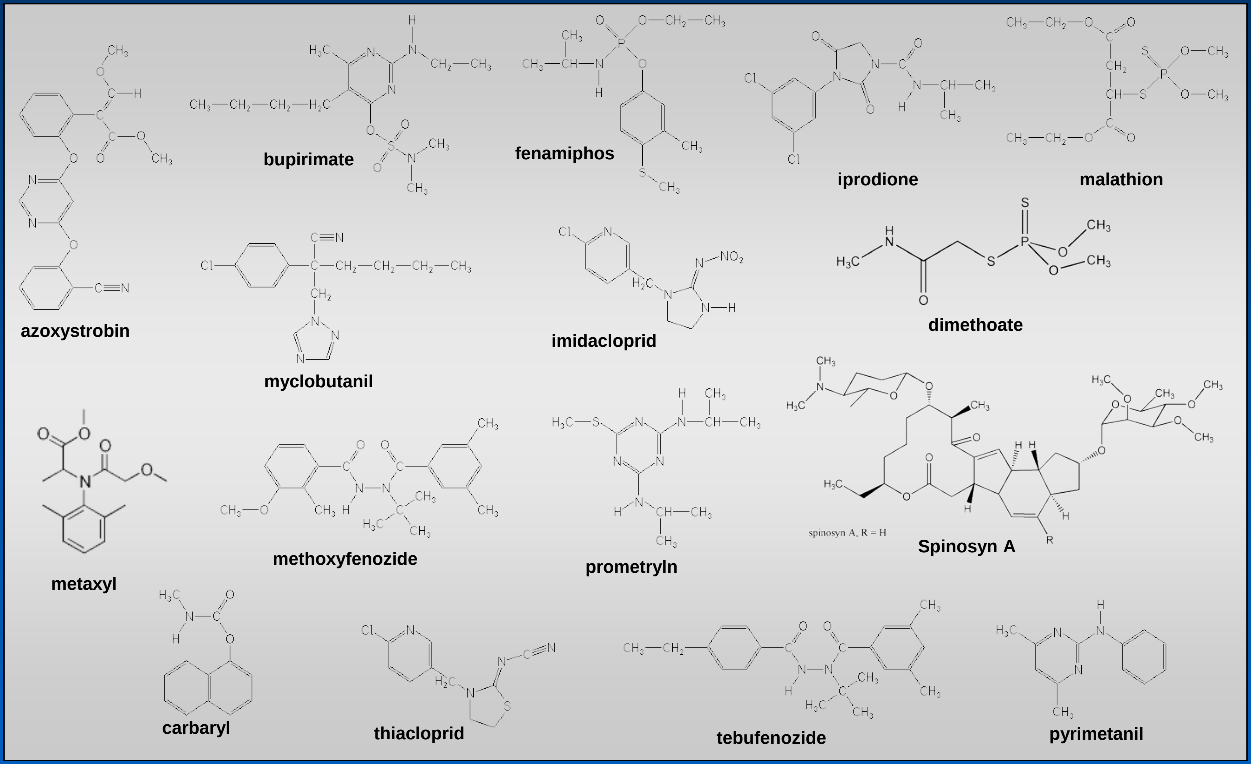


After Biotreatment

NO INTERMED. IDENTIFIED

After Photo-Fenton

Pesticide Wastewater (ALBAIDA)



ALBAIDA selectively collects the empty plastic pesticide containers used in the greenhouses of the area Almería, Granada and Jaén (Spain) for recycling (around 2 million containers per year, corresponding to 30000 Ha of greenhouses).

These containers are shredded and washed, producing water contaminated with pesticides which has usually been treated by solar photo-Fenton since the start-up of the plant in 2004.

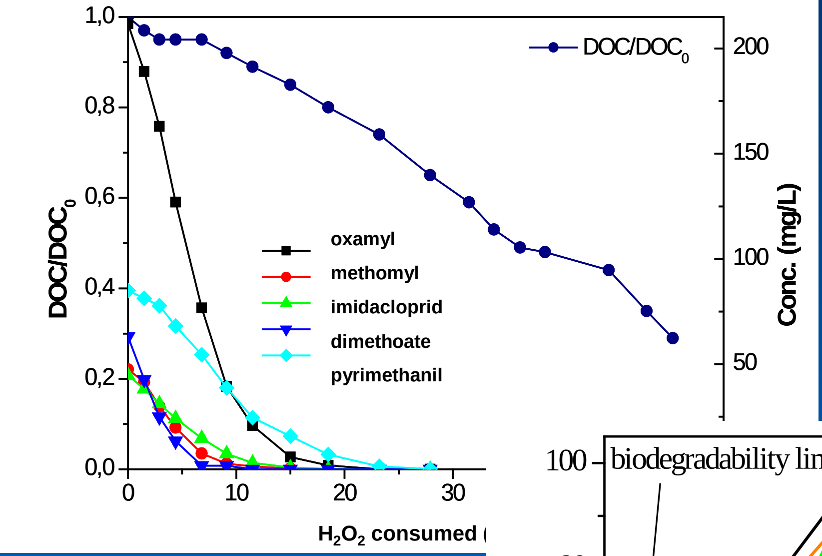
The goal is to increase the treatment capacity through a proper combination of photo-Fenton and biotreatment. With this procedure, it will also be possible to recycle the water inside the plant.

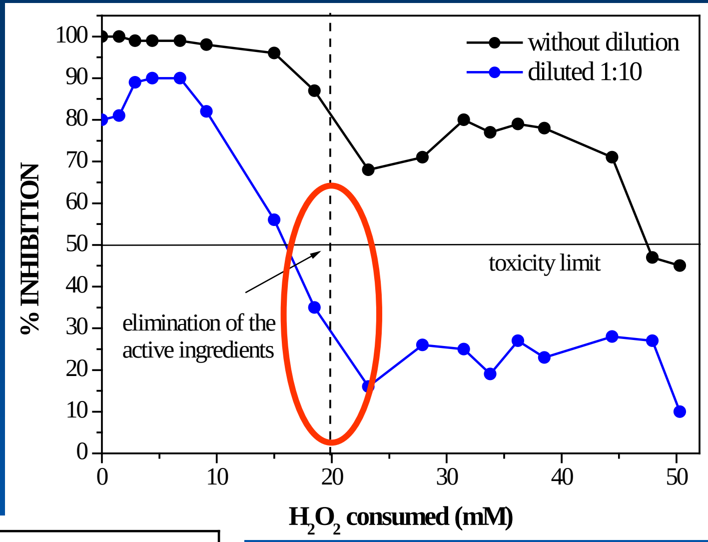
The first studies performed were focused on the decontamination of wastewater containing a selected mixture of five commercial pesticides:

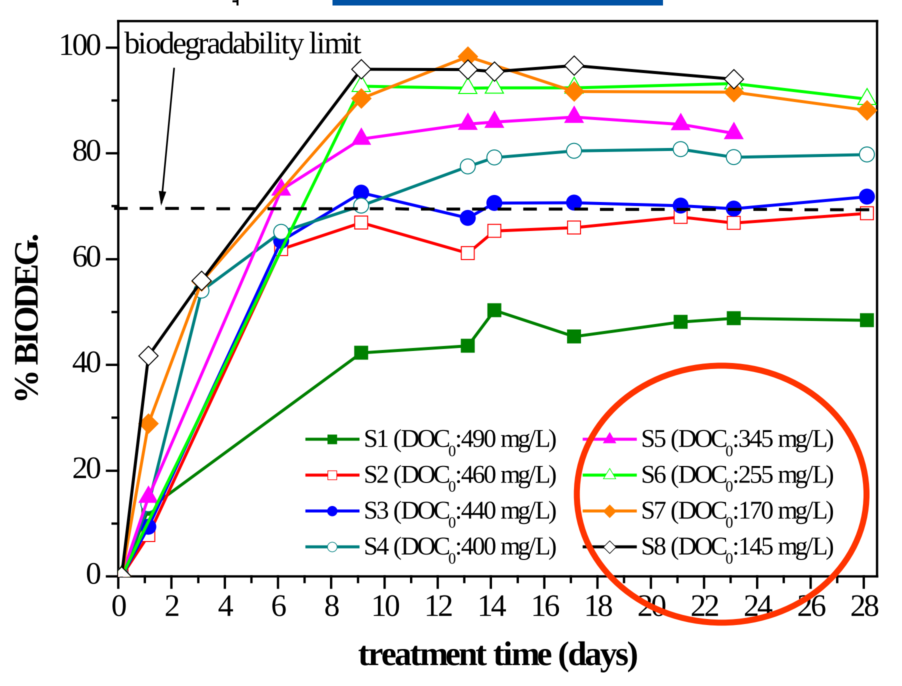
- Vydate® (10% w/v oxamyl, 47.7 g DOC/L).
- Metomur® (20% w/v methomyl, 360 g DOC/L).
- Couraze® (20% w/v imidacloprid, 395 g DOC/L).
- Ditimur-40® (40% w/v dimethoate, 500 g DOC/L).
- Scala® (40% w/v pyrimethanil, 285 g DOC/L).

This model wastewater was used for plant start up and commissioning.

Model Wastewater (5 pesticides), DOC_0: 500 mg/L (100 mg/L each), 20 mg/L Fe^{2+}



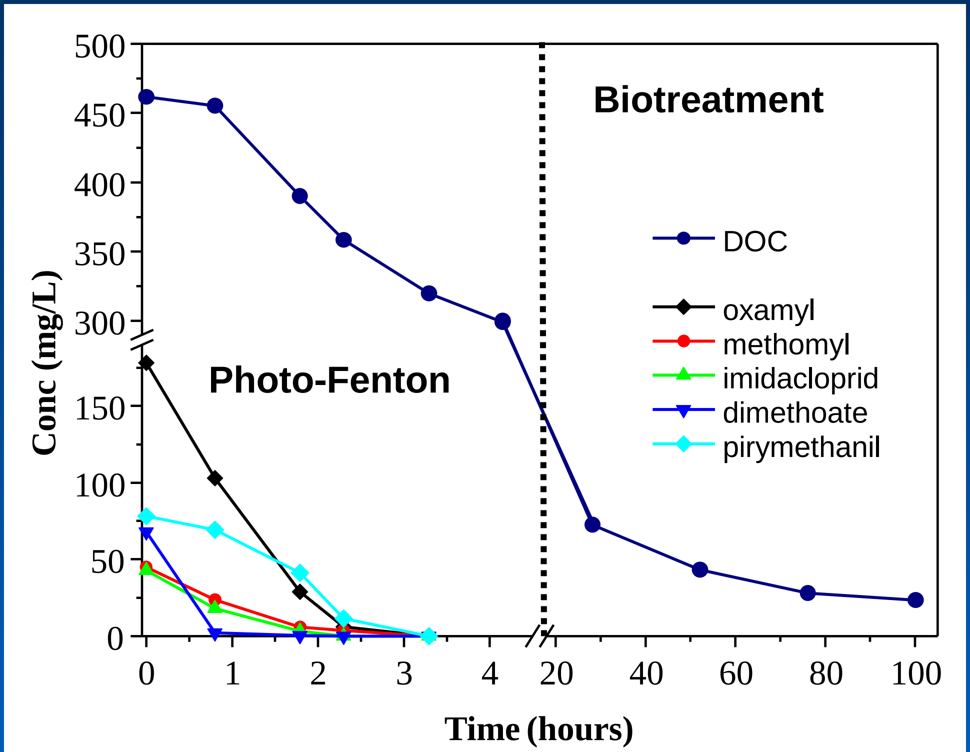




Non biodegradable

Highly toxic

APPROACH 2 (Biotreatment + AOP) not possible



APPROACH 1 (AOP + Biotreatment)

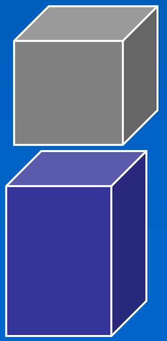
Model Wastewater (5 pesticides), DOC_0: 500 mg/L (100 mg/L each), 20 mg/L Fe^{2+}

Combined system:

DOC_0 : 480 mg/L

Photo-Fenton (42 %)

IBR (58 %)



Real wastewater, see

Decontamination of industrial wastewater containing pesticides by combining solar photo–Fenton and biological treatment at industrial-scale at ALBAIDA RESIDUOS S.L.

POSTER

CONCLUSIONS

- **Cleaning up water polluted by persistent organic may requires drastic and perhaps somewhat costly solutions.**
- **Coupled technologies (AOP/Bio) can be applied in industrial plants with difficult access to the municipal sanitation and sewage system.**
- **Use of AOPs as a pre-treatment of biorecalcitrant streams, could permit the disposal in a conventional MWTP.**
- **Each wastewater should be studied on a case by case basis**

Decontamination industrial pharmaceutical wastewater by combining solar photo-Fenton and biological treatment. *Wat Res*. **43**, 661–668, 2009.
Solar photo–Fenton as finishing step for biological treatment of a real pharmaceutical wastewater. *Env. Sci. Technol.*, **43**, 1185-1191, 2009.
Scale-up strategy for a combined solar photo-Fenton/biological system for remediation of pesticide-contaminated water. *Catalysis Today,* in press, 2010.
Decontamination of industrial wastewater containing pesticides by combining large scale homogeneous solar photocatalysis and biological treatment. *Chemical Engineering Journal*, submitted 2010.

Acknowledgment

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