European PhD School on Advanced Oxidation Processes

2nd Summer School on
Environmental applications of Advanced Oxidation Processes
***and* Training School** on
Advanced Treatment Technologies and Contaminants of Emerging Concern (NEREUS COST Action ES1403)

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Applications of raceway pond reactors for solar photo-Fenton: principles and uses

ADVANCED TECHNOLOGIES FOR WATER RECYCLING

José Antonio Sánchez Pérez

Principles

WWTP

Activated sludge biotreatment

AOPs

Photo-Fenton process

Wastewater

COD abatement
BOD abatement
Nutrient removal (N, P)

Treated water

Microcontaminant removal

Decontaminated water

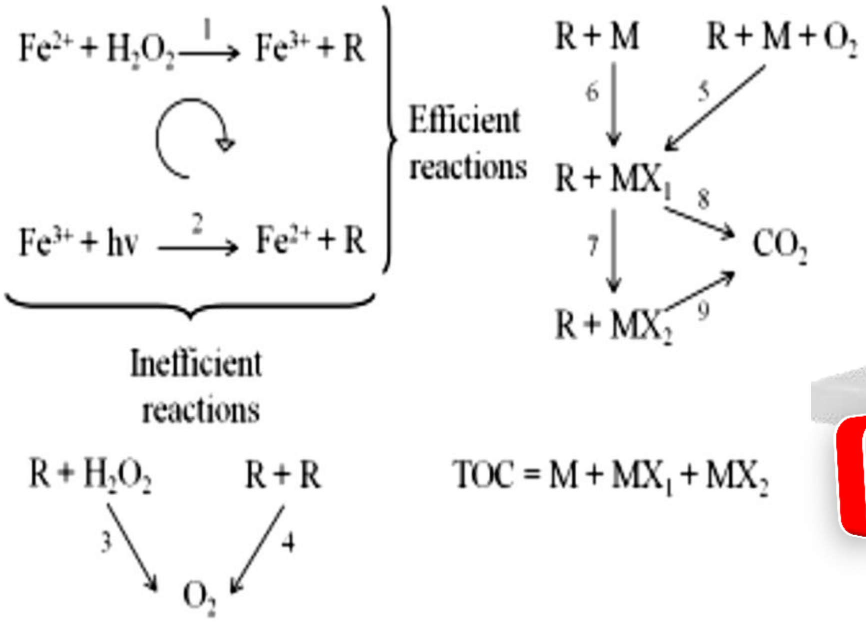
Very low concentration of persistent pollutants (tens or hundreds of µg/L)

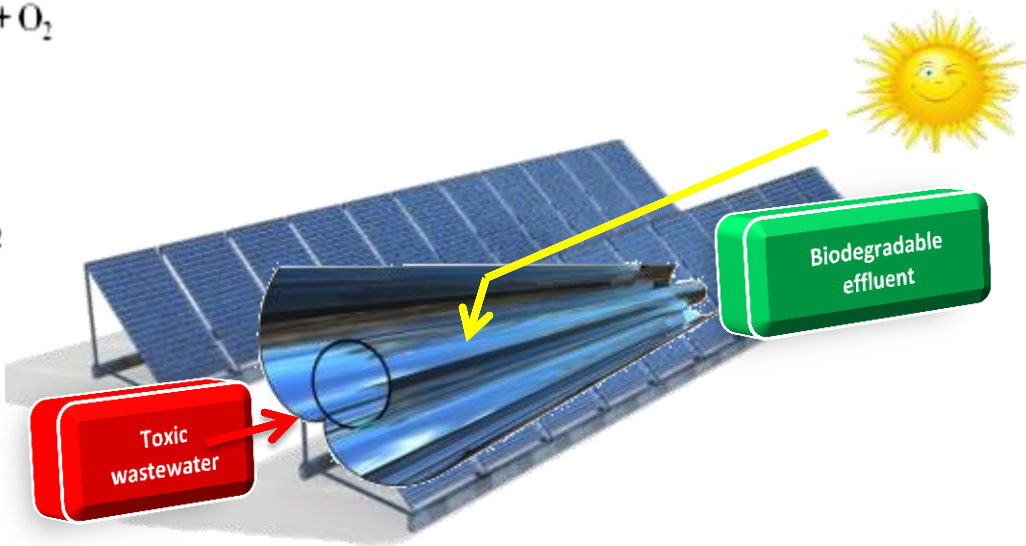
AOPs are proposed for micropollutant removal as polishing treatment

The photo-Fenton process

is especially interesting since it has been successfully applied for the removal of persistent organic contaminants using solar UV-A radiation

Photo-Fenton (UV light)		Fenton (dark)	
$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^{\bullet}$	Eq. 1	$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^{\bullet}$	Eq. 1
$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + HO^{\bullet} + H^+$	Eq. 3	$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + OOH^{\bullet} + H^+$	Eq. 2

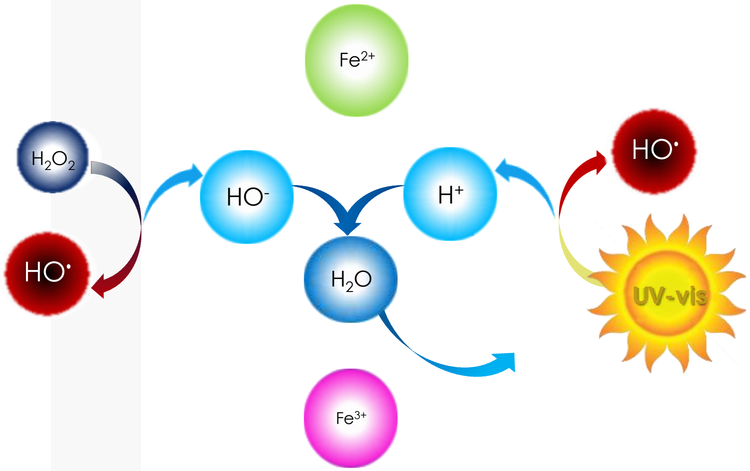




Applied Catalysis B: Environmental. 119-120: 132-138 (2012)

Principles:

Factors affecting solar photo-Fenton process performance



Inputs:	Outputs:
UV-A radiation	Solar collector surface
Operating pH	Reaction time
Catalyst concentration	Reactant supply
H_2O_2 consumption	Costs

Wastewater → Decontaminated water

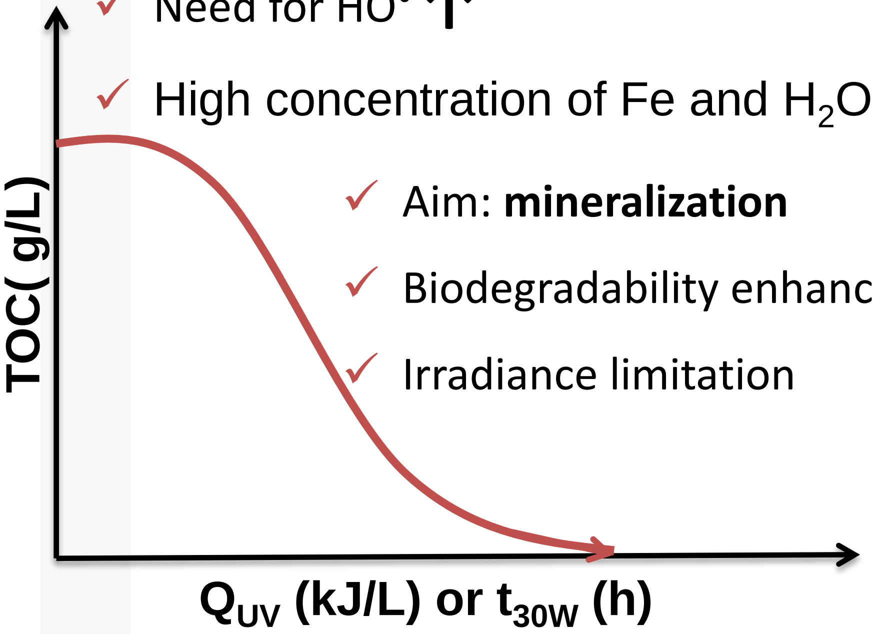
Tubular reactors provided with compound parabolic collectors CPC

- ✓ 5 cm-diameter tubular loop
- ✓ Low volume/surface ratio, ~10 L/m^2
- ✓ Tube evenly illuminated
- ✓ Efficiently direct light into the tubes

Impact of pollutant concentration

Highly polluted effluents (g/L or mg/L)

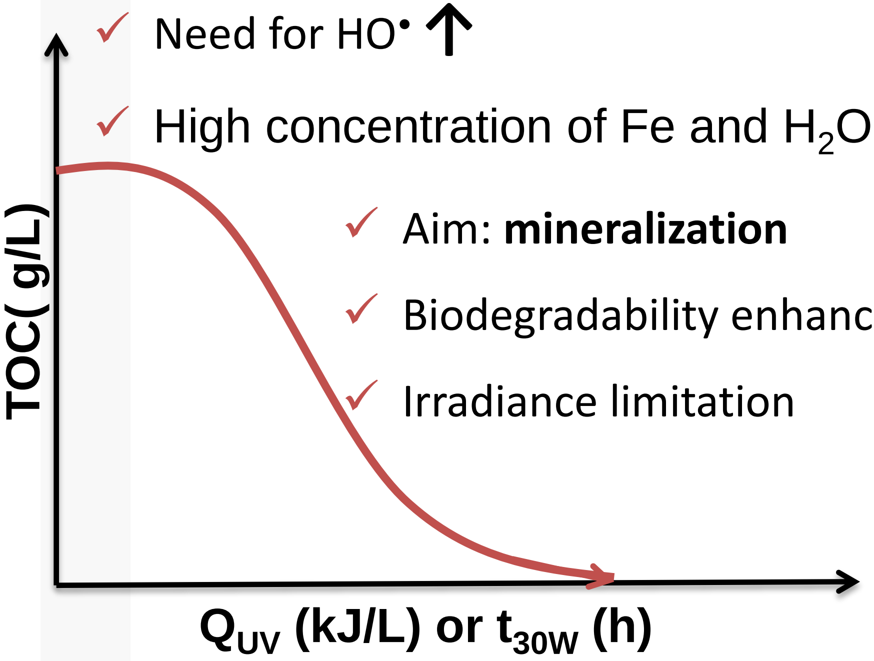
- ✓ Need for $HO^{\bullet}$ ↑
- ✓ High concentration of Fe and H_2O_2
  - ✓ Aim: **mineralization**
  - ✓ Biodegradability enhancement
  - ✓ Irradiance limitation



$$Q_{UV} = \sum Q_{UV\,n-1} + UV_{n-1}\frac{A_r}{V_T}\Delta t_n \qquad t_{30W} = t_{30W,n-1} + \Delta t_n \frac{\overline{UV}}{30}\frac{V_i}{V_T}$$

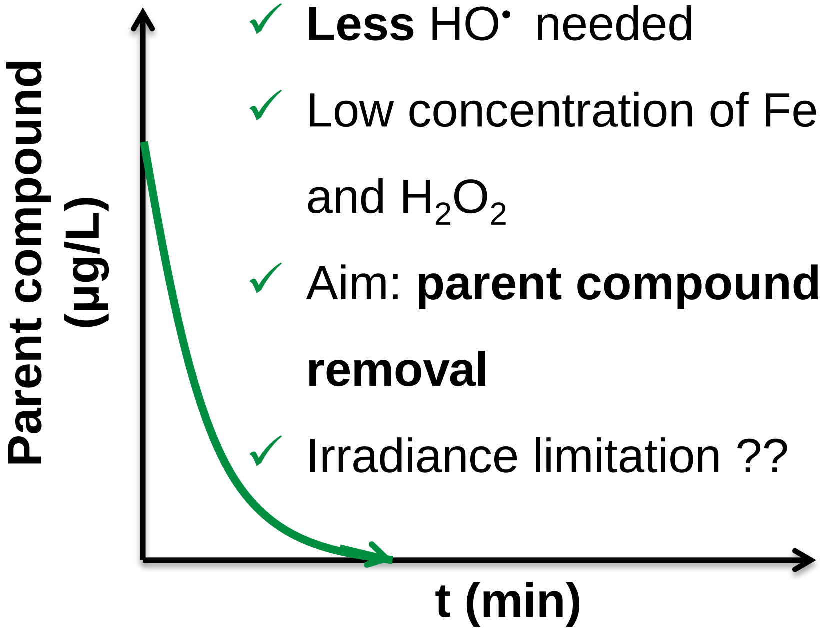
Impact of pollutant concentration

Highly polluted effluents (g/L or mg/L)



- ✓ Need for HO• ↑
- ✓ High concentration of Fe and H_2O_2
  - ✓ Aim: **mineralization**
  - ✓ Biodegradability enhancement
  - ✓ Irradiance limitation

Effluents containing micropollutants (µg/L)



- ✓ **Less** HO• needed
- ✓ Low concentration of Fe and H_2O_2
- ✓ Aim: **parent compound removal**
- ✓ Irradiance limitation ??

$$Q_{UV} = \sum Q_{UV\,n-1} + UV_{n-1} \frac{A_r}{V_T} \Delta t_n \qquad t_{30W} = t_{30W,n-1} + \Delta t_n \frac{\overline{UV}}{30} \frac{V_i}{V_T}$$

The reaction time for photo-Fenton process

Most of the studies on solar photo-Fenton for organic contaminant removal deal with mineralisation rate or pollutant conversion rate as a function of two equivalent parameters:

Catalysis Today 147(1): 1-59 (2009)

The reaction time for photo-Fenton process

Most of the studies on solar photo-Fenton for organic contaminant removal deal with mineralisation rate or pollutant conversion rate as a function of two equivalent parameters:

✓ The normalized exposure time calculated for standard conditions of solar UV irradiance of 30 W m^{-2}, t_{30W}, min

$$t_{30W} = t_{30W,n-1} + \Delta t_n \frac{\overline{UV}}{30} \frac{V_i}{V_T}$$

where Δt_n is the experimental time for each sample, UV is the average solar ultraviolet radiation measured during Δt_n, and t_{30W} is the “normalized illumination time”

t_{30W} refers to a constant solar UV power of 30 W m^{-2} (typical solar UV power on a perfectly sunny day around noon), V_T is the total water volume loaded in the plant and V_i is the irradiated volume

Catalysis Today 147(1): 1-59 (2009)

- ✓ The accumulated solar UV energy received per unit volume of treated water, Q_{UV}, kJ L^{-1}

$$Q_{UV} = \sum Q_{UV\,n-1} + UV_{n-1} \frac{A_r}{V_T} \Delta t_n$$

where Δt_n is the experimental time interval for sample n, UVA_{n-1} is the average of solar at exposure time interval t_n-t_{n-1}, A_r is the illuminated area of the reactor (m^2) and V_T is the total volume of treated water (L)

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These parameters are used for the evaluation of organic matter degradation in water for different solar reactors (regardless of the concept design used e.g. for stirred tanks or tubular reactors)

Q_{UV} and t_{30W} are expressions of treatment time taking into account irradiance reaching the reactor surface.

Q_{UV} and t_{30W} are useful in case of reaction rate is limited by light availability

Photon absorption

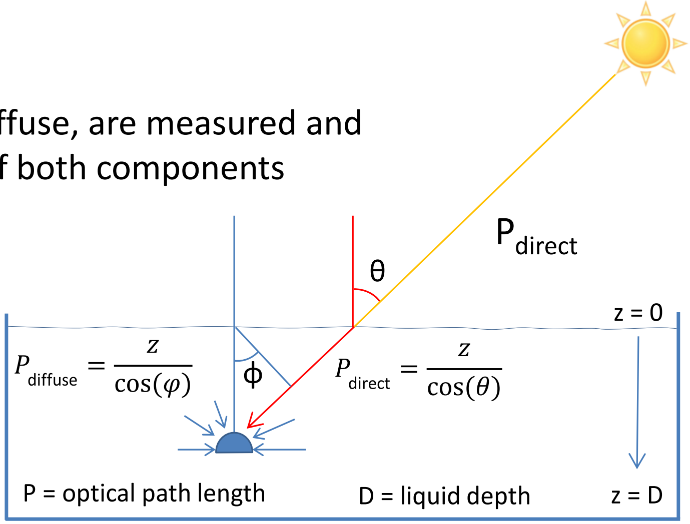
Volumetric rate of photon absorption, VRPA, combines the effects of Fe concentration, irradiance, optical properties of the absorbing species and liquid depth

$$VRPA_{Direct} = \frac{log_e 10}{D} \int_{Z=0}^{z=D} k_A\, [Fe^{3+}]\, UV_{direct}\, 10^{-k_A [Fe] z / cos\theta}\, dz$$

$$VRPA_{Diffuse} = \frac{log_e 10}{D} \int_{Z=0}^{z=D} \frac{1}{\pi} \int_{\emptyset=-\pi/2}^{\emptyset=\pi/2} k_A\, [Fe^{3+}]\, UV_{diffuse}\, 10^{-k_A [Fe] z / cos\emptyset}\, d\emptyset\, dz$$

Specific absorption coefficient: k_A (mM^{-1} m^{-1}) = 36.84 + 0.51 T (° C) r^2= 0.998

The solar UV fractions, direct and diffuse, are measured and total VRPA is obtained by addition of both components



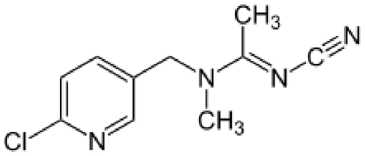
Applied Catalysis B: Environmental. 166–167: 295–301 (2015)

Applied Catalysis B: Environmental 178: 210–217 (2015)

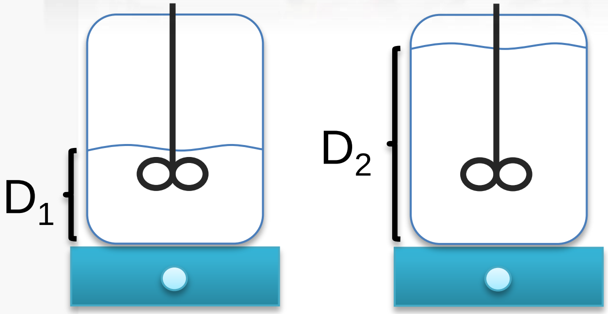
Principles:

Effect of irradiance and liquid depth on micropollutant removal by solar photo-Fenton

Effect of irradiance and liquid depth on micropollutant removal by solar photo-Fenton



Tube diameter: 5 cm

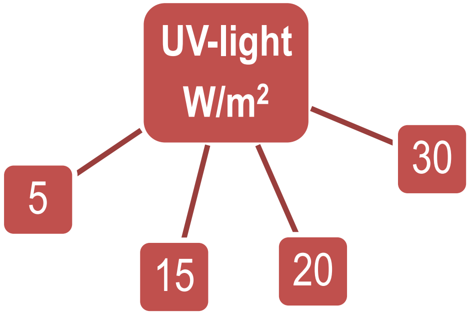


D_1=5 cm D_2=10 cm

Model pollutant	Acetamiprid, ACTM (100 µg/L)
Initial conditions	50 mg/L H_2O_2 (excess)
Water matrix	Simulated WWTP effluent, pH 2.8

Acetamiprid: neonicotinoid included in the watch list of EU Commission Decision 495/2015 on CECs

5 mg Fe / L



UV-light W/m²

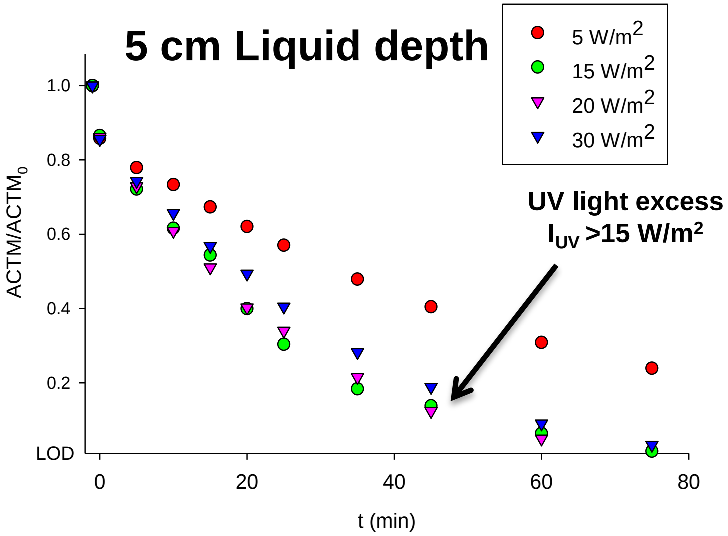
5

15

20

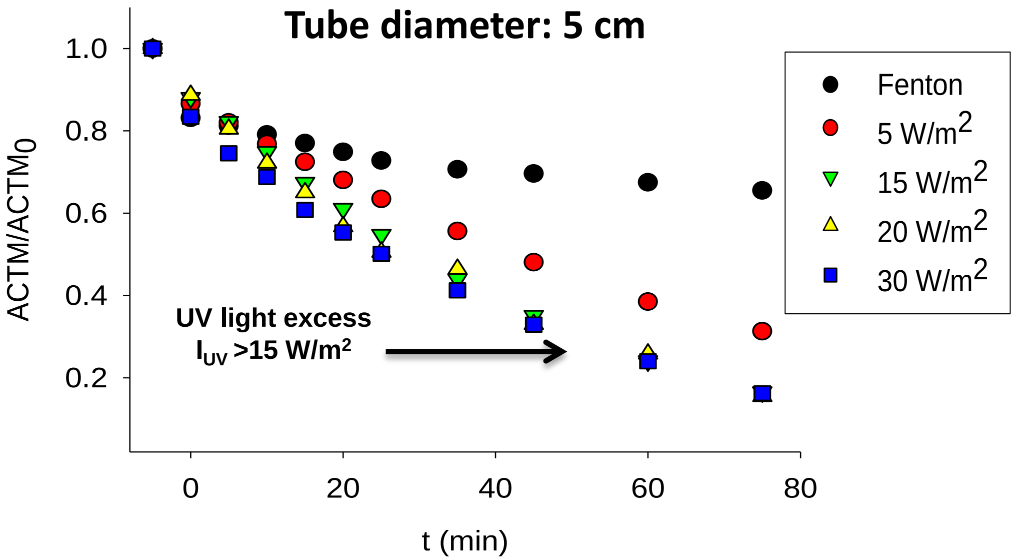
30

Science of the Total Environment 478: 123–132 (2014)



5 cm Liquid depth

UV light excess
I_{UV} >15 W/m²



Tube diameter: 5 cm

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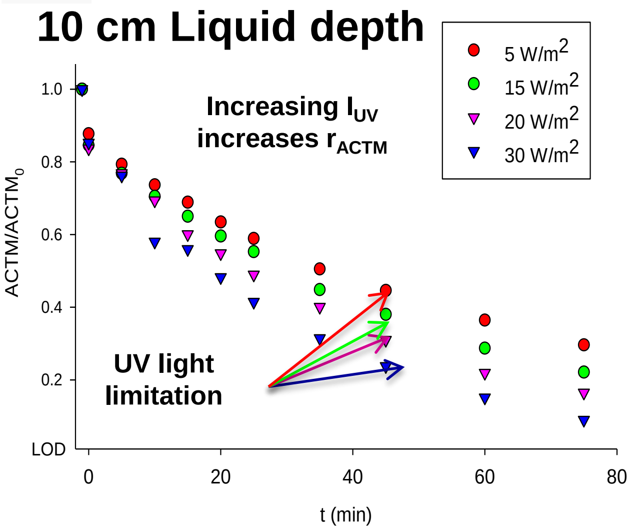


10 cm Liquid depth

Increasing I_{UV} increases r_{ACTM}

UV light limitation

Increasing light path length:

- ✓ better use of the photons reaching the system
- ✓ increase the treated volume per surface unit

Science of the Total Environment 478: 123–132 (2014)

As there is photon excess

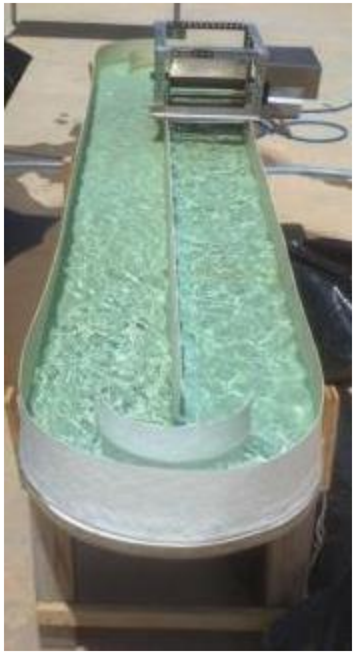
Reactor path length can be enlarged

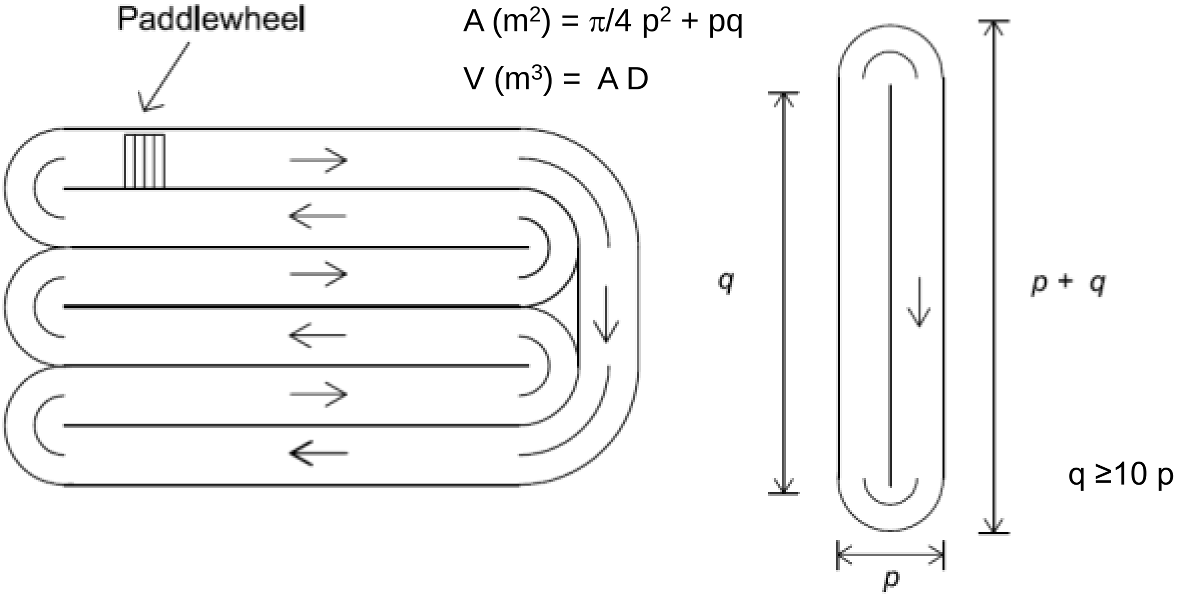
(new reactor configurations)

New strategy: to use a reactor with variable light path

Principles:
Raceway Pond Reactors

Raceway Pond Reactors (RPRs)





$A\ (m^2) = \pi/4\ p^2 + pq$

$V\ (m^3) = A\ D$

$q \geq 10\ p$

Extensively applied for microalgal mass culture

Production costs in RPR are markedly lower than in tubular photobioreactors for microalgal applications

In Raceway Pond Reactors (RPR) liquid depth can be easily varied

5 cm liquid depth

15 cm liquid depth

Low cost materials, mainly plastic liners. Construction cost ~ **10 €/m²**

Saving in costs is expected for micropollutant removal

Journal of Hazardous Materials 279: 322-329 (2014)

Uses:

Operation of raceway pond reactors at acidic pH

Modelling of acetamiprid removal at acidic pH

The model should take into account:

- ✓ Temperature
- ✓ Irradiance & depth ➔ rate of photon absorption
- ✓ Photolimitation
- ✓ Photosaturation

Modelling of acetamiprid removal at acidic pH

Reaction	Rate equation
$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + R$	$r_1 = k_1 [H_2O_2] [Fe^{2+}]$
$Fe^{3+} + UV \rightarrow Fe^{3+*}$	$r_2 = VRPA$
$Fe^{3+*} \rightarrow Fe^{3+} + Q$	$r_3 = k_3 [Fe^{3+*}]$
$Fe^{3+*} + H_2O \rightarrow Fe^{2+} + R$	$r_4 = k_4 [Fe^{3+*}]$
$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + R$	$r_5 = k_5 [H_2O_2] [Fe^{3+}]$
$OM + R \rightarrow MX$	$r_6 = k_6 [OM] [R]$
$H_2O_2 + R \rightarrow H_2O + O_2$	$r_7 = k_7 [H_2O_2] [R]$
$A + R \rightarrow MX$	$r_8 = k_8 [A] [R]$

The model should take into account:
Temperature
Irradiance & depth ➔ rate of photon absorption
Photolimitation
Photosaturation

Q - heat released

R - radicals (HO•, mainly)

OM - organic matter

MX - oxidized organic matter

A - target micropollutant

- ✓ A fraction of absorbed radiation can be converted into heat
- ✓ Saturation of Fe^{3+} photoreduction, explained by the excess of photon absorption being split between heat release and electron transfer which forms Fe^{2+} and hydroxyl radicals

Model state mass balances
$\frac{d[Fe^{2+}]}{dt} = -r_1 + r_4 + r_5$
$\frac{d[Fe^{3+}]}{dt} = -r_2 + r_1 + r_3 - r_5$
$\frac{d[Fe^{3+*}]}{dt} = r_2 - r_4 - r_3$
$\frac{d[H_2O_2]}{dt} = -r_1 - r_5 - r_7$
$\frac{d[R]}{dt} = r_1 + r_4 + r_5 - r_6 - r_7 - r_8$
$\frac{d[A]}{dt} = -r_8$
$\frac{d[OM]}{dt} = -0.0005$

The dynamic model was obtained by imposing mass balances for each of the model states, assuming the hypothesis of batch operation and perfect mixing

Mixing time << reaction time

Chemical Engineering Journal 310 (2017) 464–472

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Mixing time << reaction time

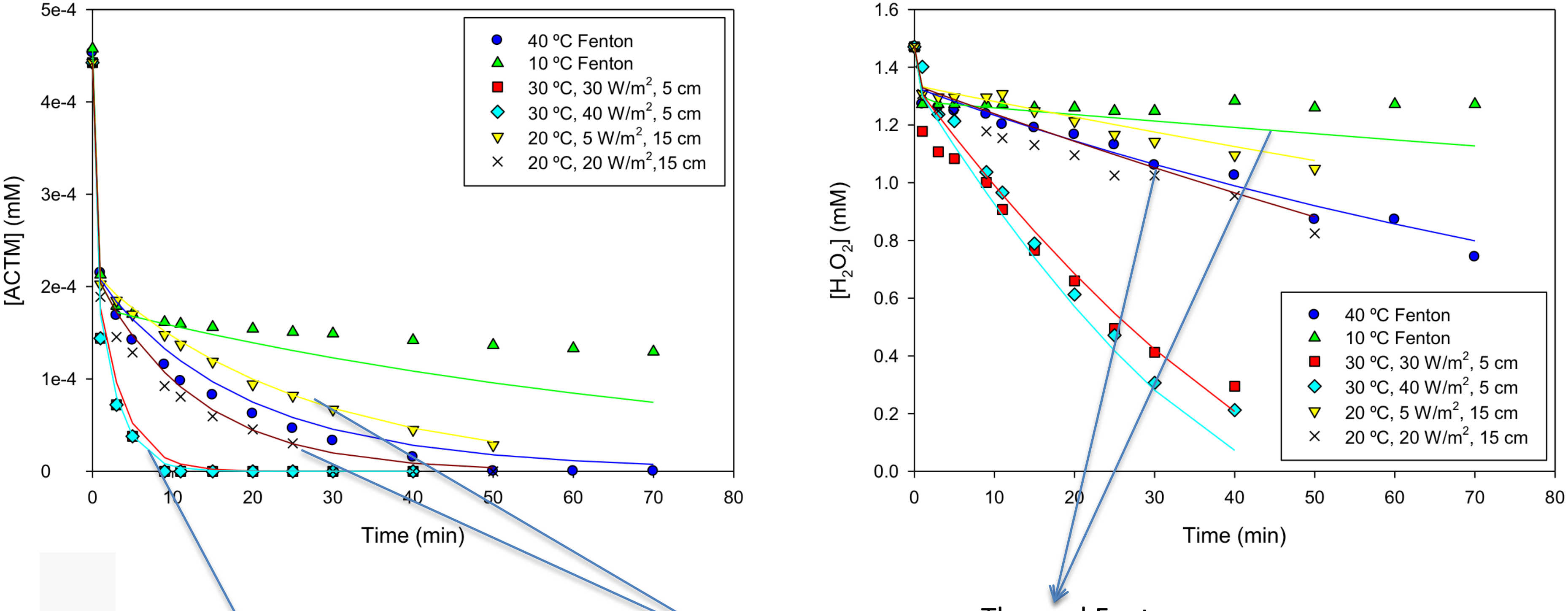
The kinetic parameters were obtained by the built-in functions of the MATLAB® optimization toolbox

Kinetic constants	
$k_1 = 5.93\ 10^6 e^{-(\frac{34200}{RT})}$, r^2=0.94	($mM^{-1}min^{-1}$)
$k_3 = 16.8$	(min^{-1})
$k_4 = 4.98$	(min^{-1})
$k_5 = 3.28\ 10^5 e^{-(\frac{42000}{RT})}$, r^2=0.98	($mM^{-1}min^{-1}$)
$k_6 = 1.83$	($mM^{-1}min^{-1}$)
$k_7 = 1.67$	($mM^{-1}min^{-1}$)
$k_8 = 35.8$	($mM^{-1}min^{-1}$)

Chemical Engineering Journal 310 (2017) 464–472

Time-courses of ACTM and H_2O_2 of lab-scale experiments with Fe^{2+} 0.095 mM

The model properly fits the data and takes into account the variation in T and VRPA



Thermal Fenton:
Temperature increases from 10 ° C to 40 ° C

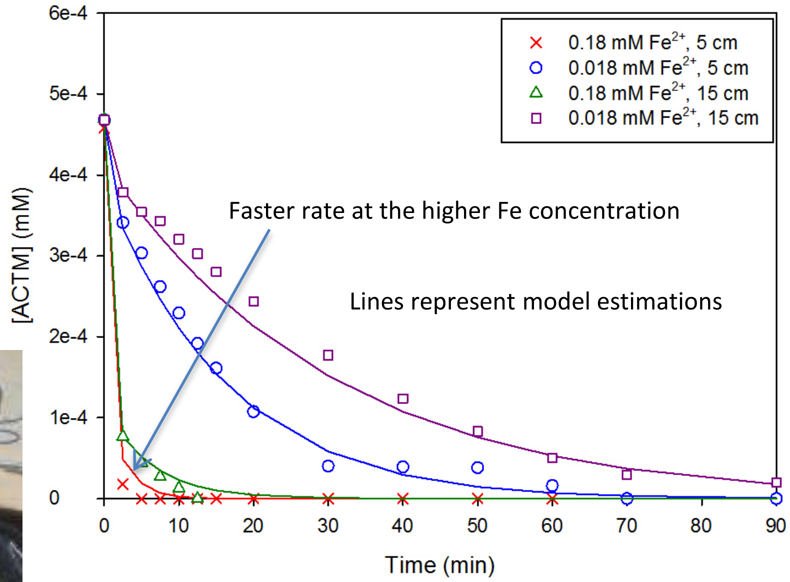
Photosaturation:
Irradiance from 100 to 127 µE/m²s
VRPA from 866 to 1080 µE/m³s

Photolimitation:
Irradiance from 17 to 54 µE/m²s VRPA
from 88 to 283 µE/m³s

Model validation with outdoor experiments carried out in a 360-L RPR

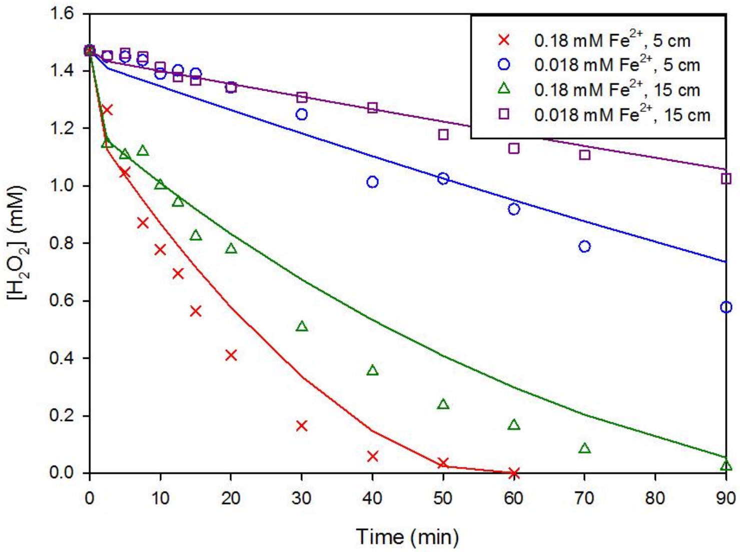
Fe^{2+} 0.018 and 0.18 mM (1 and 10 mg/L) H_2O_2 1.47 mM (50 mg/L)

Irradiance ≈ 27 – 29 W/m^2 Temperature ≈ 21 – 27 ° C



Faster rate at the higher Fe concentration

Lines represent model estimations



Proper fit using rate constants obtained at lab scale

Reaction time for 90% ACTM removal

0.018 mM Fe^{2+}: 5 cm ➔ 34 min 15 cm ➔ 64 min
0.18 mM Fe^{2+}: 5 cm ➔ 3 min 15 cm ➔ 6 min

Uses:

Operation of raceway pond reactors at neutral pH

Solar photo-Fenton at neutral pH

- ✓ Need to keep iron dissolved
- ✓ Use of Fe complexing agents
- ✓ EDDS: stable soluble complex with Fe^{3+}
  (S,S)-ethylenediamine-N,N`-disuccinic acid
- ✓ Biodegradable and non toxic
- ✓ 1:2 as the best Fe^{3+}/EDDS molar ratio

Fe^{3+}/EDDS complex at 0.2/0.4 mM (10 mg/L Fe)

Simulated secondary effluent at pH 6.5 – 7

Irradiance ≈ 34 – 36 W/m^2 Temperature ≈ 28 – 29 ° C

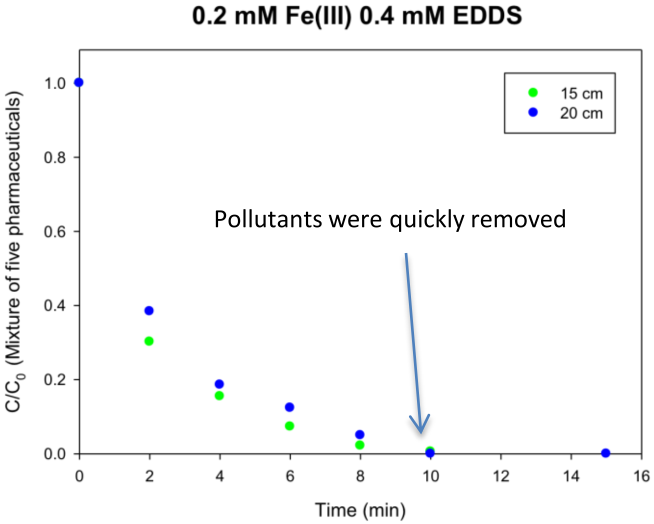
H_2O_2 1.47 mM (50 mg/L)

A mixture of five pharmaceuticals:
Ofloxacin, Sulfamethoxazole, Ibuprofen, Carbamazepine, Flumequine, 100 µg/L each (500 µg/L in total)

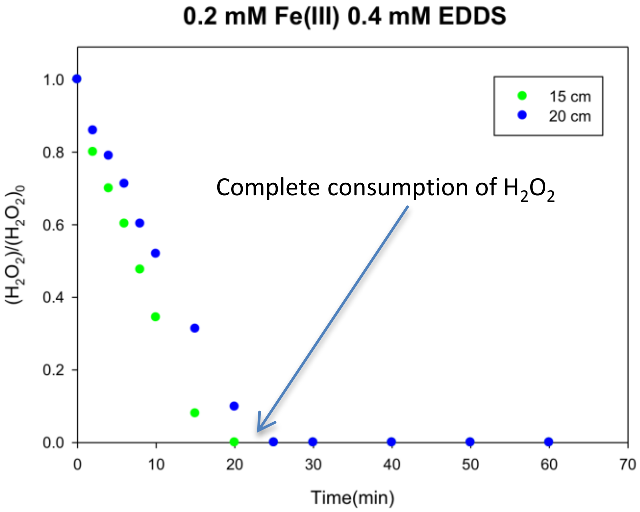
Outdoor experiments carried out in 80-L and 120-L raceway pond reactors

80-L = 15 cm Liquid depth

120-L = 20 cm Liquid depth



Pollutants were quickly removed

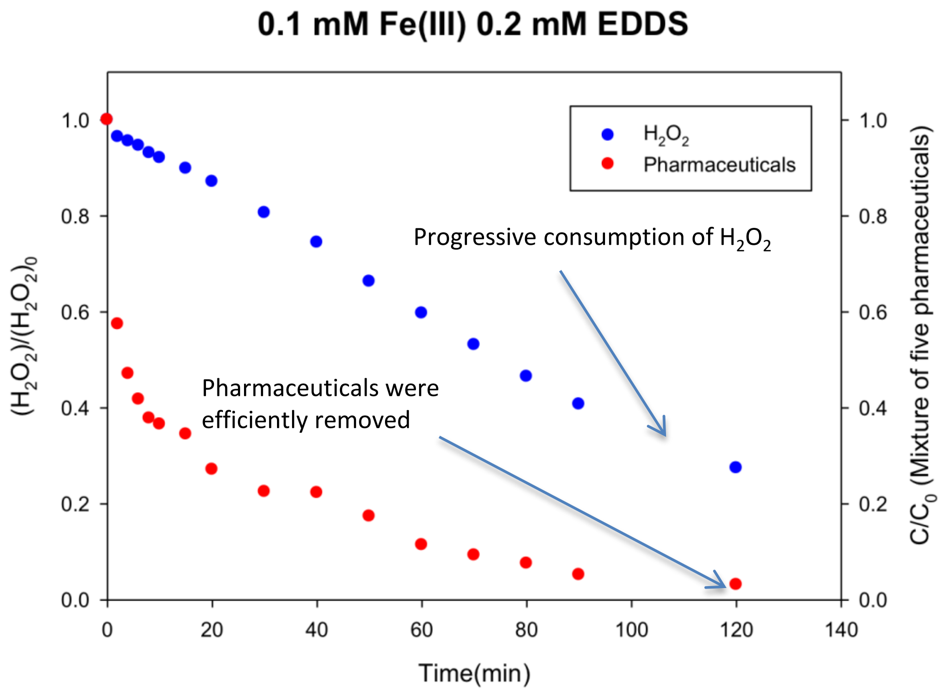


Complete consumption of H_2O_2

There were no significant differences between both liquid depths

Treatment of a real WWTP secondary effluent spiked with 500 µg/L of five pharmaceuticals

120-L = 20 cm Liquid depth



Fe^{3+}/EDDS complex at 0.1/0.2 mM (5.5 mg/L Fe)

H_2O_2 1.47 mM (50 mg/L)

Irradiance ≈ 20 W/m^2

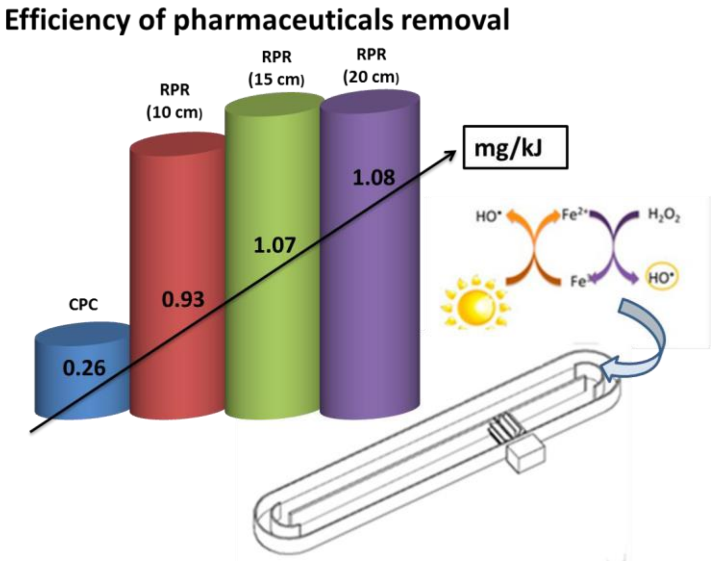
Temperature ≈ 20 ° C

pH ≈ 7

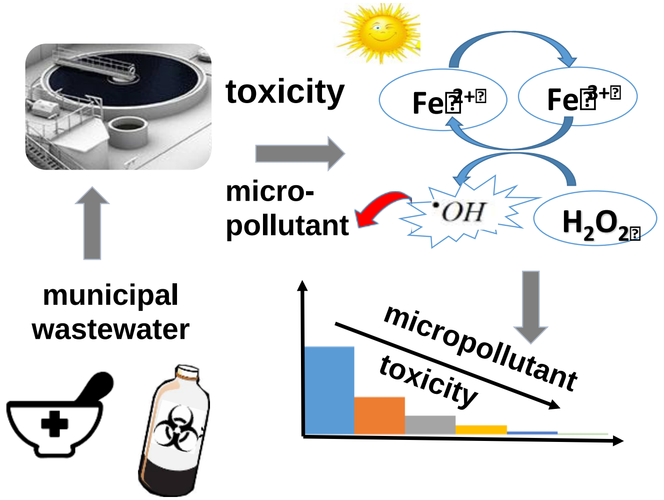
A mixture of five pharmaceuticals:
Ofloxacin, Sulfamethoxazole, Ibuprofen, Carbamazepine, Flumequine, 100 µg/L each (500 µg/L total)

The operation of RPRs at neutral pH by using the Fe^{3+}:EDDS complex gave rise to:

- ✓ High efficiency in toxicity removal by solar photo-Fenton at neutral pH with Fe^{3+}:EDDS
- ✓ Higher micropollutant removal efficiency for RPRs than CPCs



Catalysis Today 287:10-14 (2017)



Journal of Chemical Technology & Biotechnology. DOI: 10.1002/jctb.5212 (2017)

Concluding remarks

- ✓ It is necessary to consider whether photon flux is rate limiting or there is photon excess
- ✓ To make better use of photons under irradiance excess conditions, Fe concentration can be increased or reactor light path length can be enlarged
- ✓ RPRs allow light path length to be changed as a function of solar irradiance
- ✓ The photoreactor can be operated at up to 20 cm liquid depth (200 L/m^2)
- ✓ The presented results demonstrate the operational viability of the solar photo-Fenton process in RPRs for the removal of micropollutants

11-07-2017

Research group: Water Treatment

Solar Energy Research Center (CIESOL)

Joint Center Universidad de Almería – Plataforma Solar de Almería

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See you in Almería!!