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European PhD School on Advanced Oxidation Processes

1st Summer School on

Environmental applications of Advanced Oxidation Processes

University of Salerno

Fisciano (Italy), June 15-19, 2015

AOPs PhD School

Erasmus+

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CIESOL-ADVANCED TECHNOLOGIES FOR WATER RECYCLING

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Microcontaminants removal by solar photo-Fenton: the role of UV radiation

ADVANCED TECHNOLOGIES FOR WATER RECYCLING

José Antonio Sánchez Pérez

Introduction

WWTP

Activated sludge biotreatment

AOPs

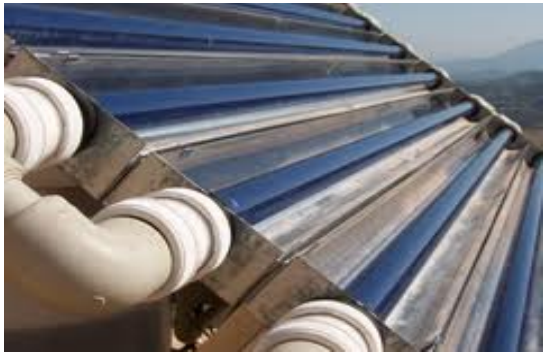


Photo-Fenton process

Wastewater → COD abatement, BOD abatement, Nutrient removal (N, P) → Treated water → Microcontaminant removal → Decontaminated water

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)

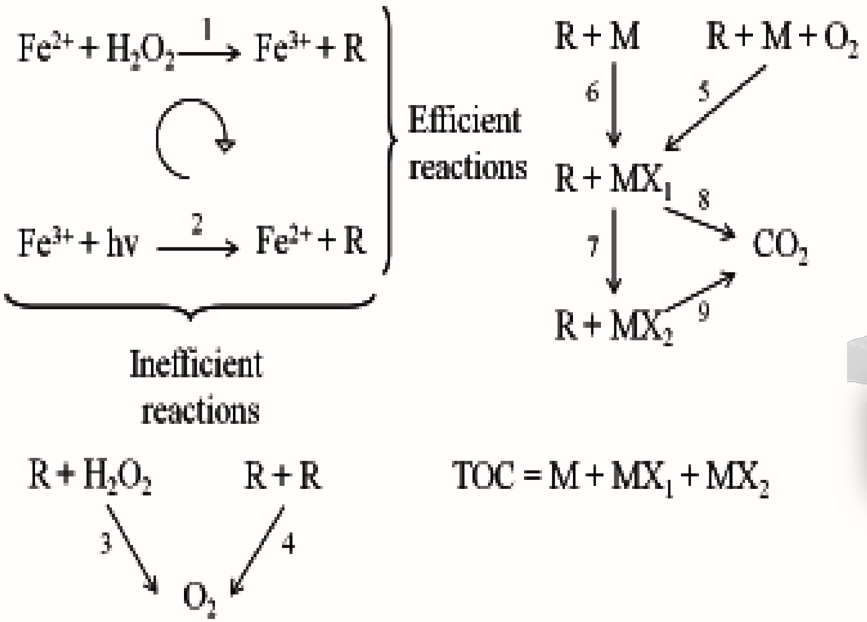
$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^\bullet$ Eq. 1

$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + HO^\bullet + H^+$ Eq. 3

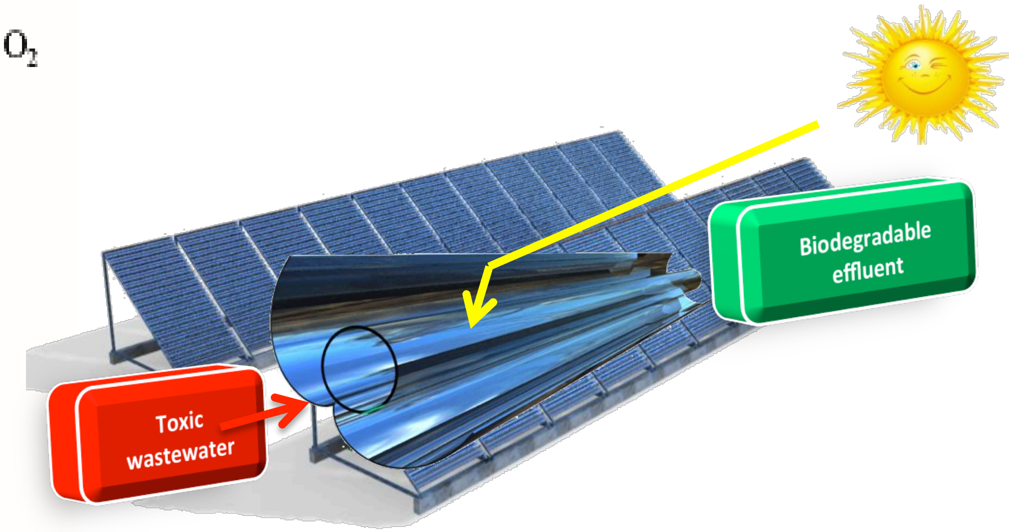
Fenton (dark)

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^\bullet$ Eq. 1

$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + OOH^\bullet + H^+$ Eq. 2

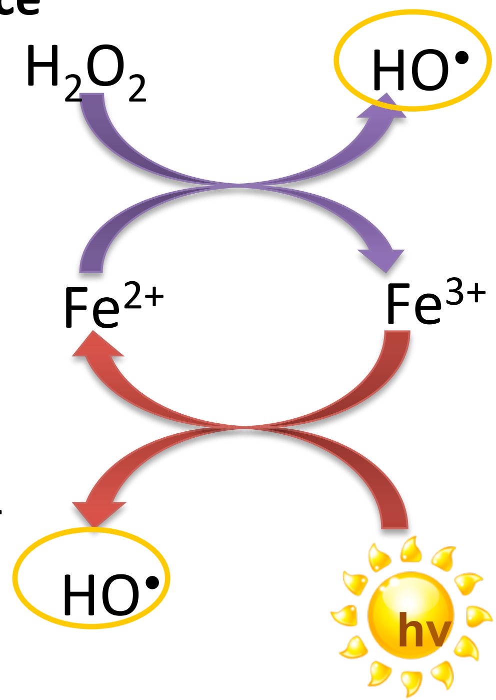


Applied Catalysis B: Environmental. 119-120: 132-138 (2012)



- ✓ Dependent on iron redox cycle
- ✓ Photoactive species at pH 2.8

Factors affecting solar photo-Fenton process performance



Inputs:

UV-A radiation
Operating pH
Catalyst concentration
Hydrogen peroxide consumption
Wastewater →

Outputs:

Solar collector surface
Reaction time
Costs

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

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)

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.

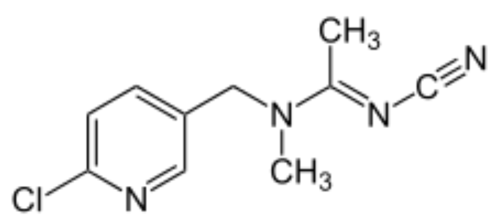
Objectives

Understanding the relationship between Fe concentration and UV-light in the photo-Fenton process when removing micropollutants

Reactor design

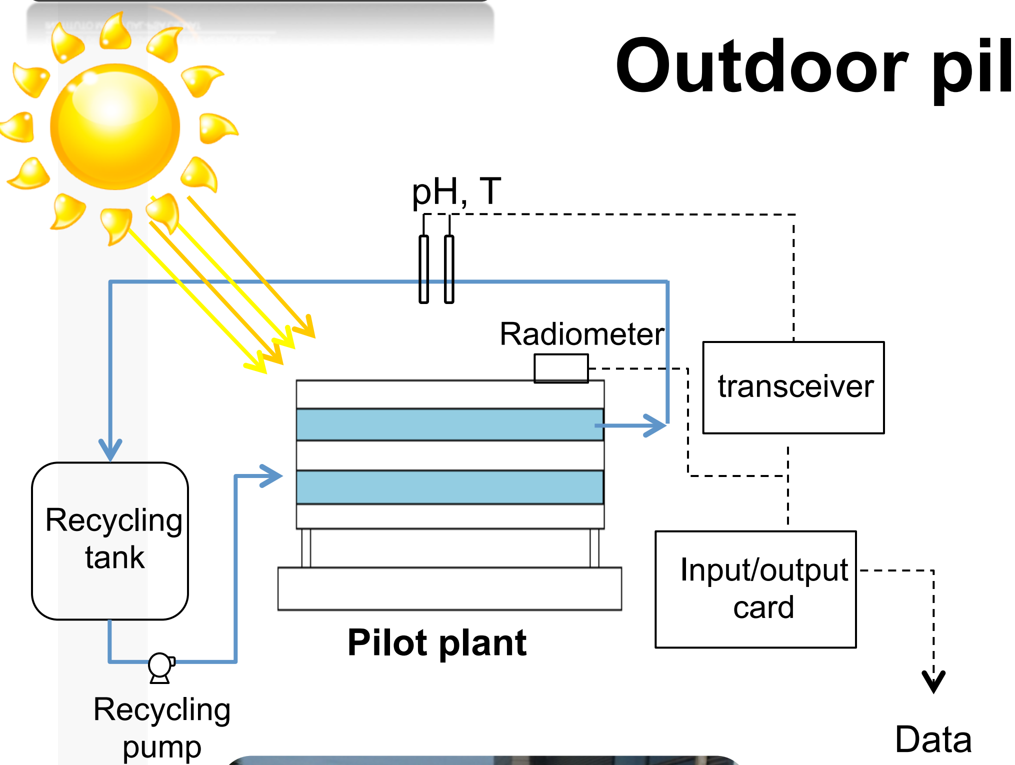
Process operation

To this end, the removal of the neonicotinoid fungicide Acetamiprid, ACTM, at 100 μg/L under several experimental conditions is going to be presented



Results

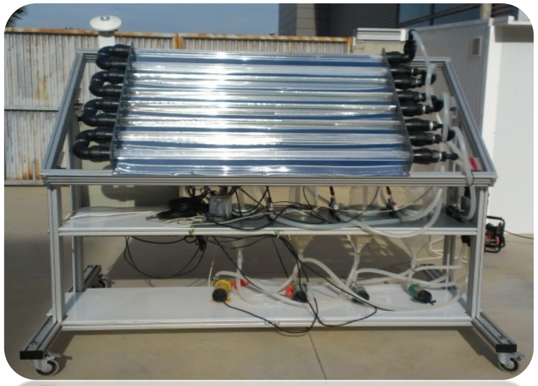
Outdoor pilot-plant



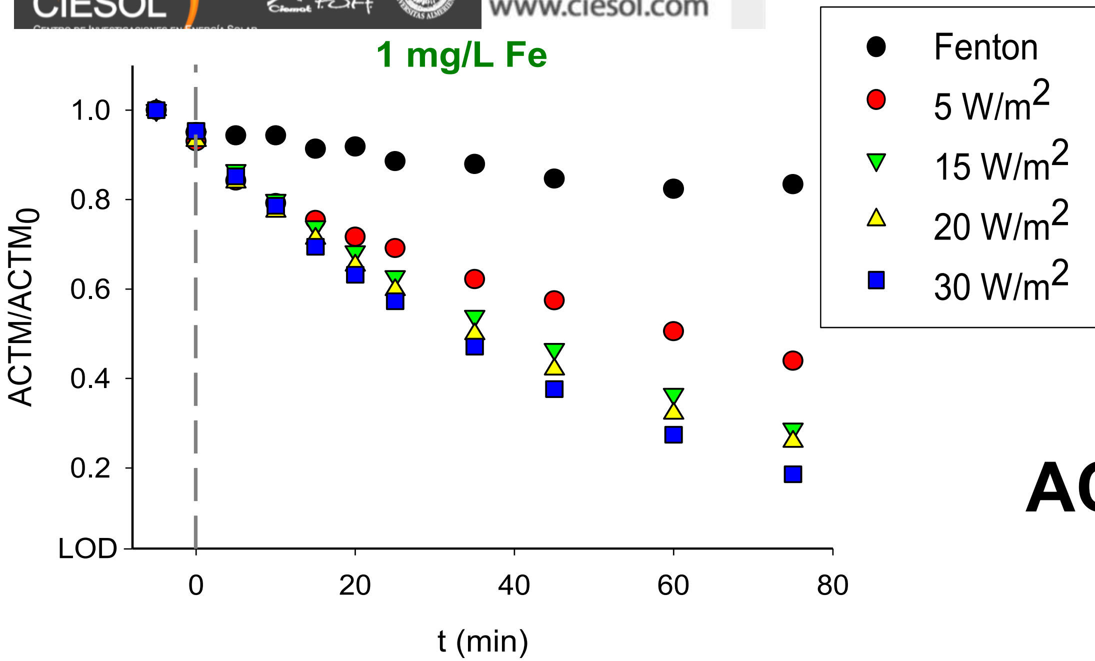
Model pollutant	**ACTM (100 µg/L)**
Initial conditions	50 mg/L H_2O_2 **(excess)** pH 2.8
Water matrix	**Simulated WWTP effluent**

Fe (mg/L): 1, 5, 20

UV-light W/m²: 5, 15, 20, 30



Reactor capacity: 7 L
Tube diameter: 5 cm

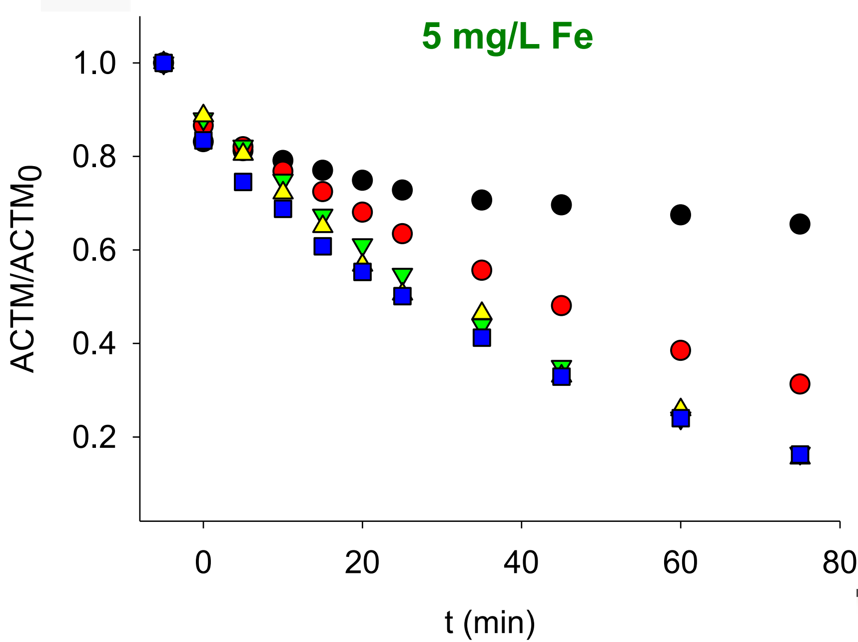


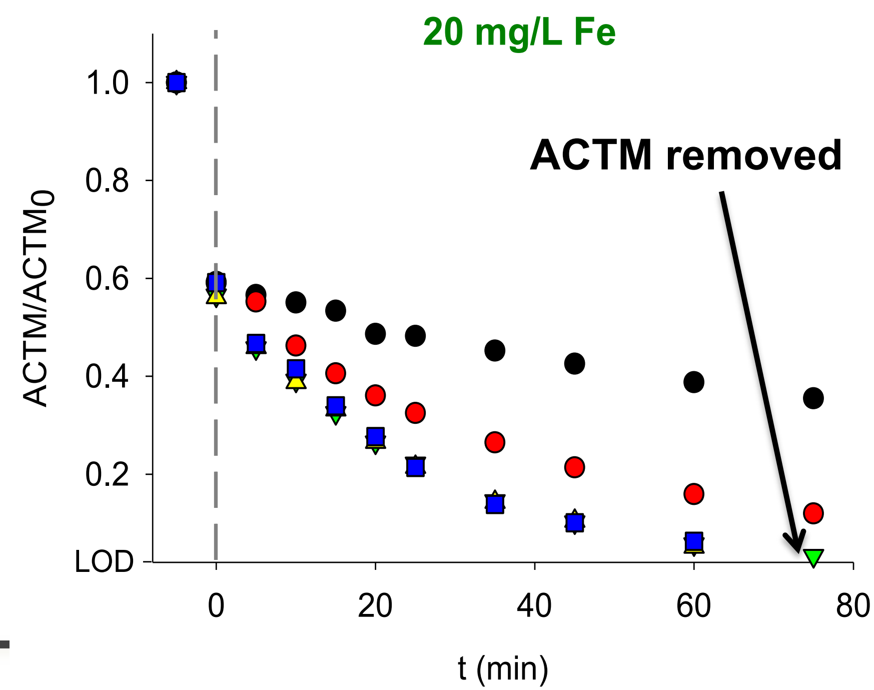
Irradiance excess I_{UV} >15 W/m^2

r_{ACTM} **does not increase** with I_{UV}

r_{ACTM} **increases** with Fe

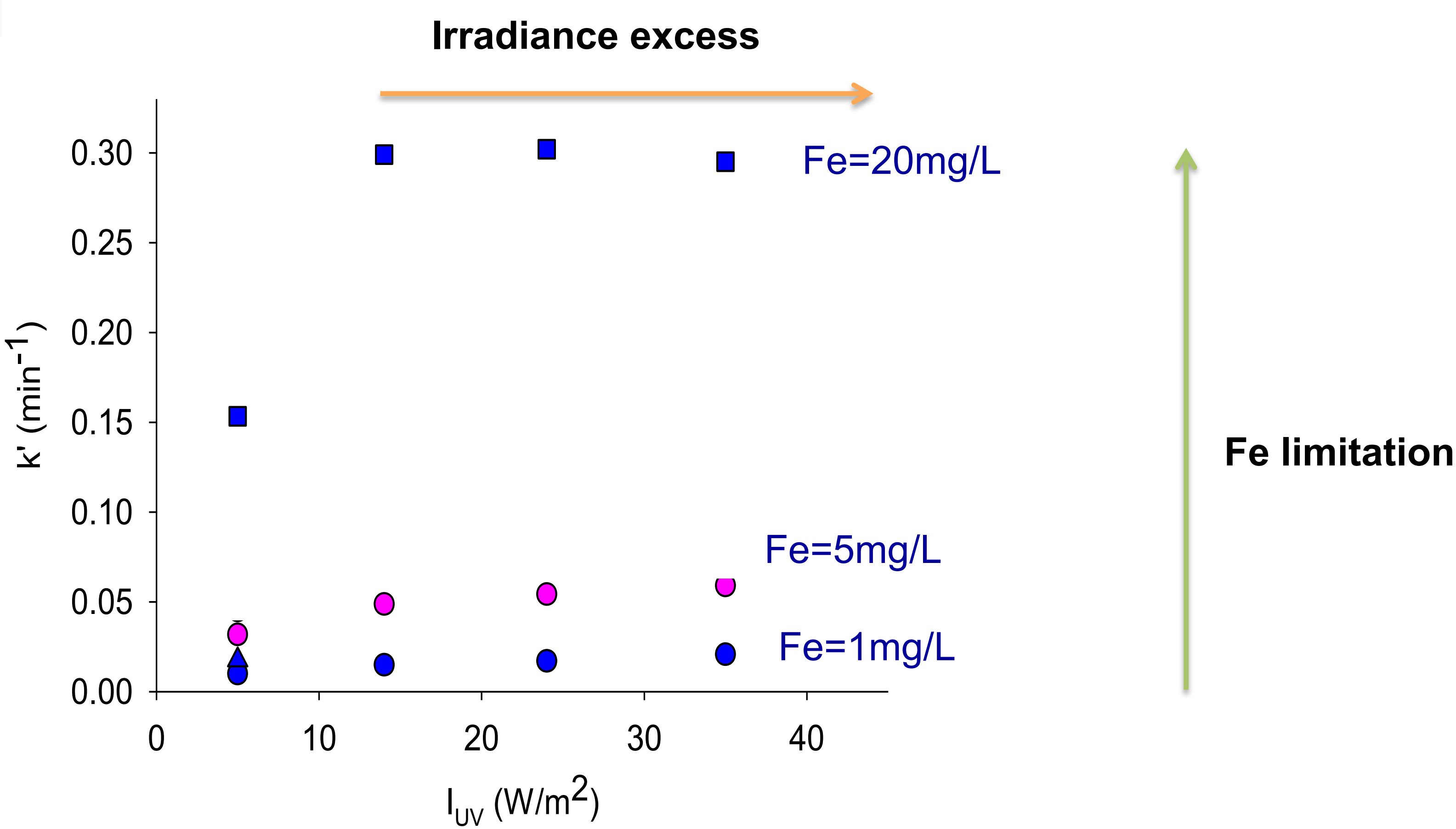
ACTM degradation





Kinetic analysis

Pseudo-first order rate constants for ACTM degradation



José Antonio Sánchez Pérez

Consequences

As Fe limits the process

Fe dosage as function of I_{UV} (automatization)

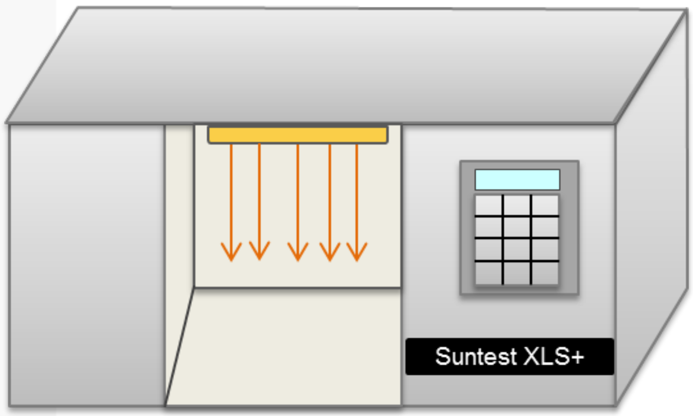
Science of the Total Environment 478: 123–132 (2014)

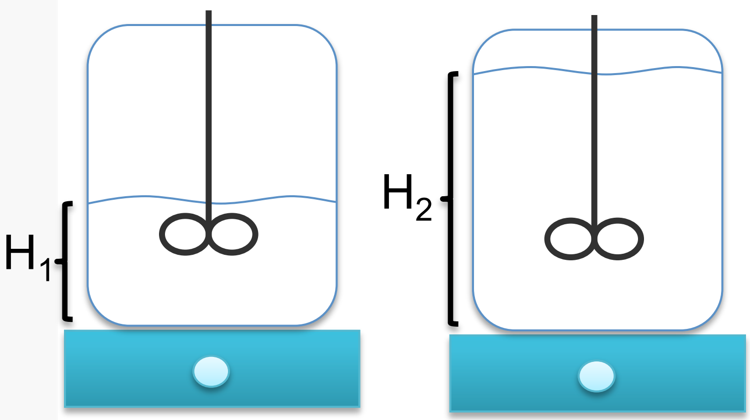
As there is photon excess

Reactor path length can be enlarged (new reactor configurations)

Real time can be used for process analysis instead of normalised time

Effect of reactor path length





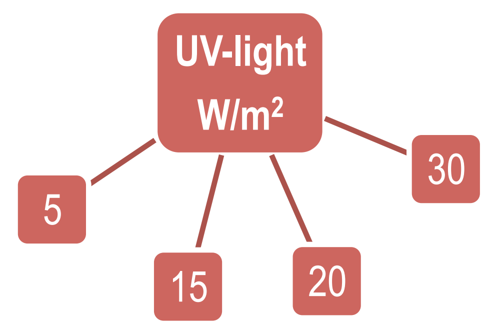
H_1=5 cm

H_2=10 cm

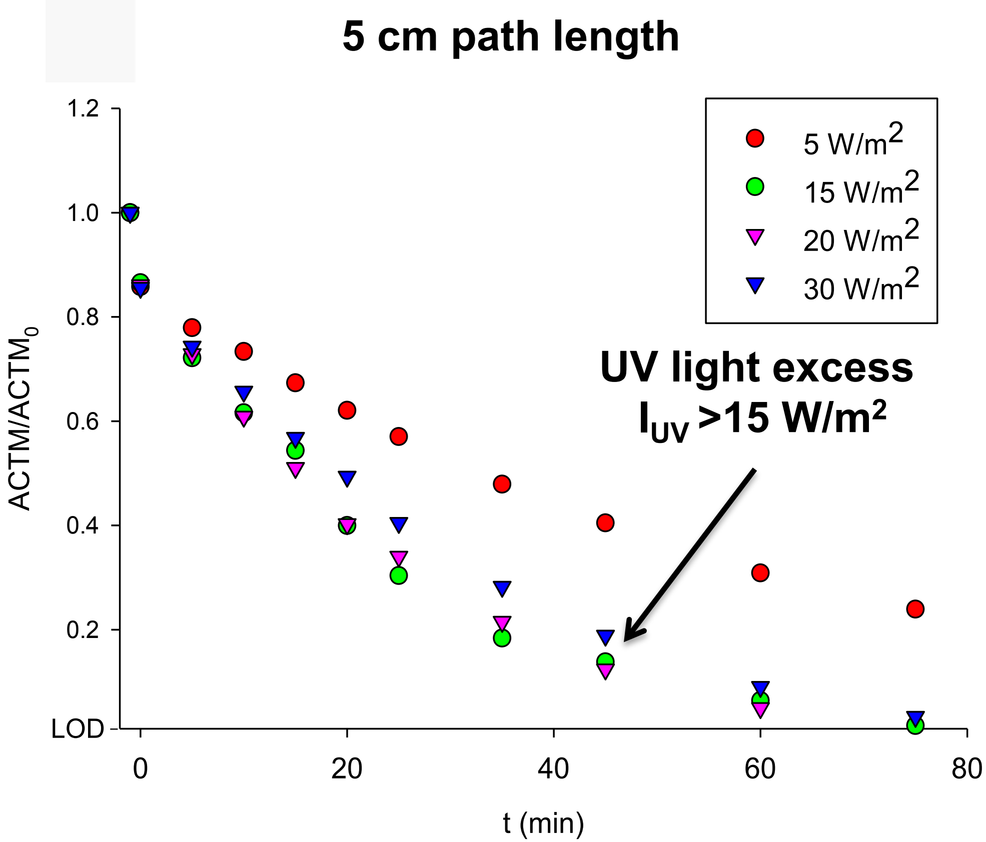
Assays in solar box

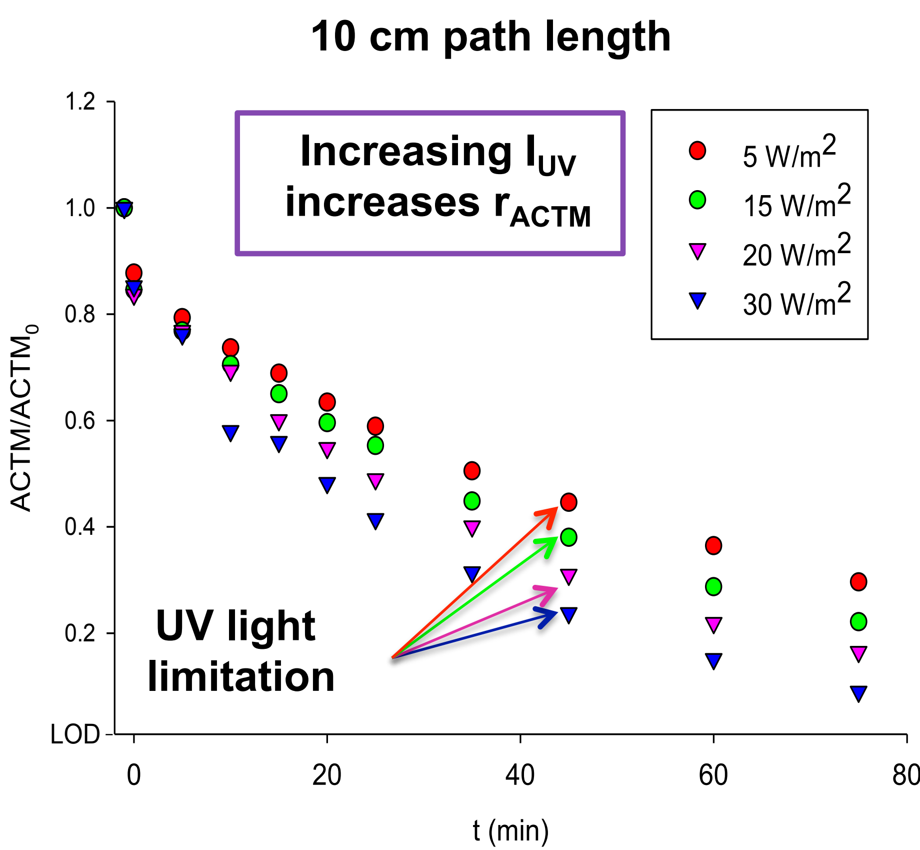
Model pollutant mixture	**ACTM (100 µg/L)**
Initial conditions	50 mg/L H_2O_2 **(excess)** pH 2.8
Water matrix	**Simulated WWTP effluent**

5 Fe (mg/L)



ACTM degradation





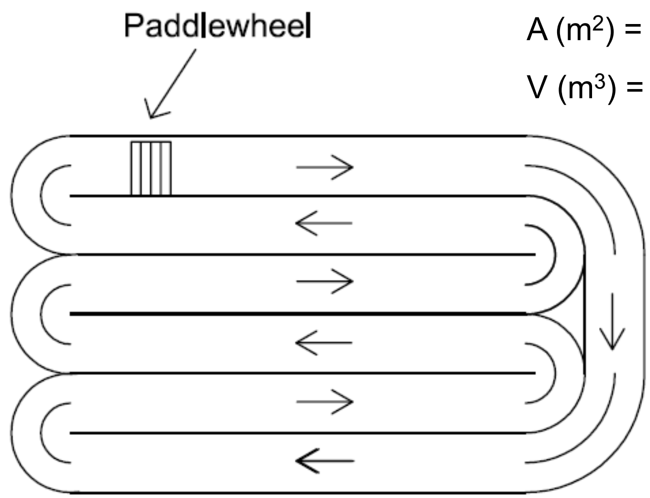
New strategy: to use a reactor with variable light path

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

Towards new photoreactor configuration

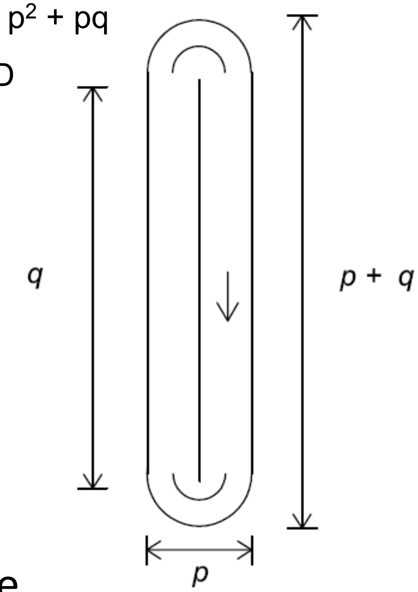
In Raceway Pond Reactors (RPR) liquid depth can be easily varied

Microalgal cultures in RPR and TPBR. Almería.



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

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



Applied for microalgal mass culture

$q \geq 10\,p$

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

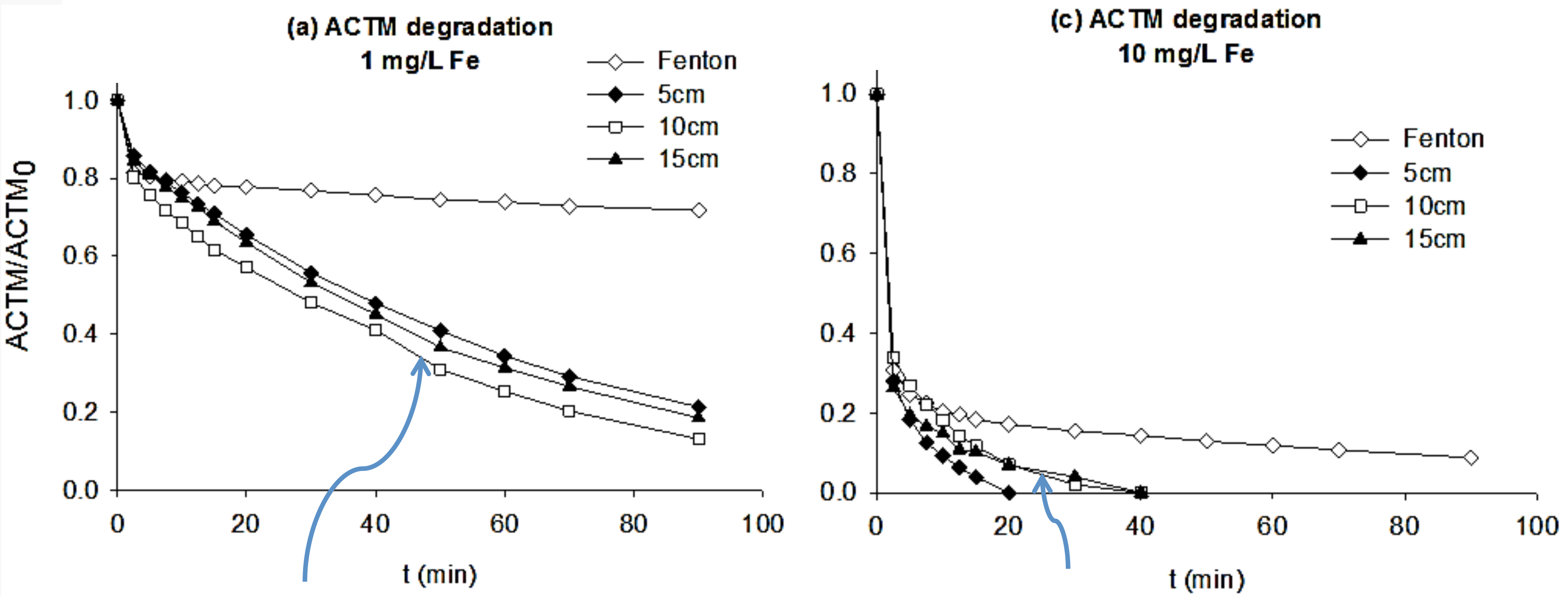
Production costs in RPR are markedly lower than in tubular photobioreactors for microalgal applications

Study the applicability of raceway pond reactors (RPRs) to the removal of micropollutants using solar photo-Fenton

RPR

- ❑ Acetamiprid (ACTM), 100 µg/L, in simulated secondary effluent
- ❑ A 360 L-fiberglass-RPR pilot plant was used
- ❑ The effect of iron concentration (1, 5.5 and 10 mg/L) and liquid depth (5, 10 and 15 cm) at pH 2.8
- ❑ Light propagation inside the reactor, 10-30 W_{UV}/m^2

Effect of liquid depth and iron concentration on pesticide removal



Degradation rate is the same for the three liquid depths

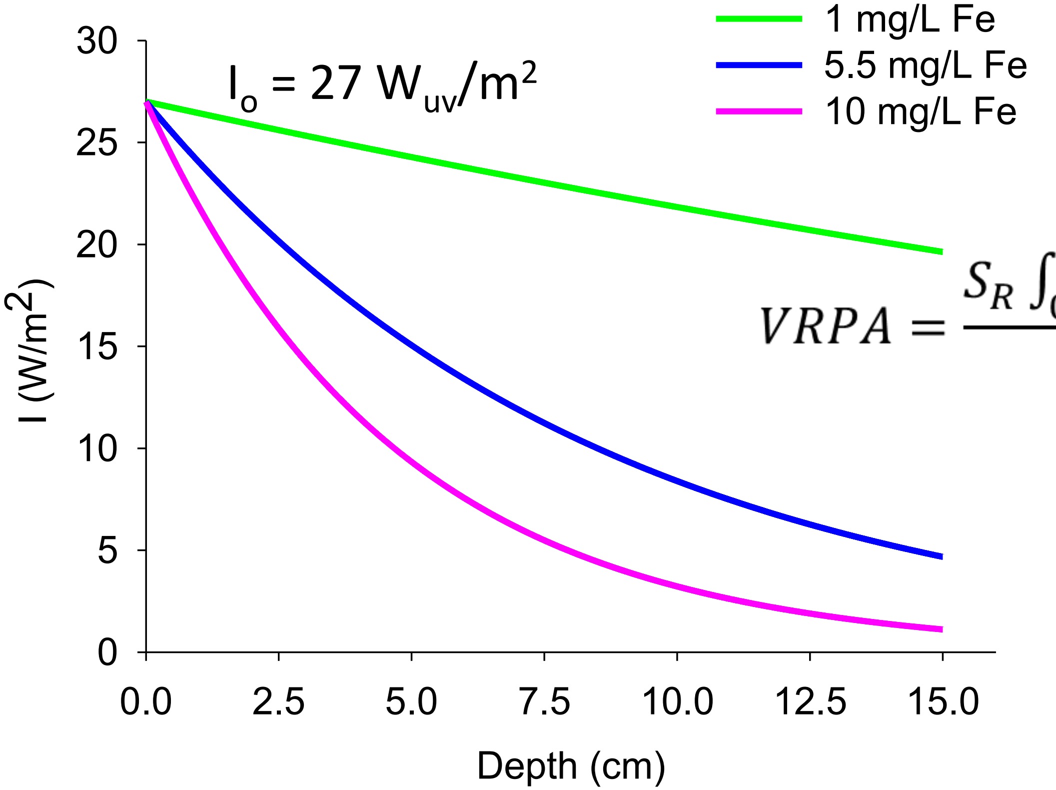
UV ~17 W_{UV}/m^2

slower degradation rates for 10 -15 cm liquid depth

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

Effect of irradiance on pollutant removal

Volumetric rate of photon absorption, VRPA, W_{uv}/m^3



VRPA combines the effects of Fe concentration, irradiance and liquid depth

$$VRPA = \frac{S_R \int_0^D k_A \cdot [Fe] \cdot I_0 \cdot 10^{-kA \cdot [Fe] \cdot x / cos\theta} dx}{V_R}$$

$$\kappa_A = \frac{\int_{\lambda_{min}}^{\lambda_{max}} k_\lambda I_\lambda d\lambda}{\int_{\lambda_{min}}^{\lambda_{max}} I_\lambda d\lambda}$$

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

Effect of irradiance on pollutant removal

Outdoor experiments, February-May 2014

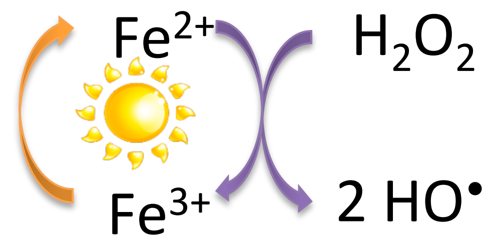
Exp.	Fe, mg/L	D, cm	Io, W/m^2	VRPA, W/m^3	k_{H2O2}, min^{-1}	k_{ACTM}, min^{-1}
1	10.00	5.00	17.10	92	0.046	0.528
2	10.00	15.00	10.50	27	0.018	0.217

9	5.50	5.00	30.84	118	0.040	0.289
10	5.50	15.00	26.73	59	0.033	0.247

17	1.00	5.00	29.26	26	0.010	0.060
18	1.00	15.00	27.37	21	0.004	0.036

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

Photo-Fenton Redox cycle



$$-\frac{d[H_2O_2]}{dt} = k \cdot [H_2O_2]$$

k = f(Fe, VRPA)

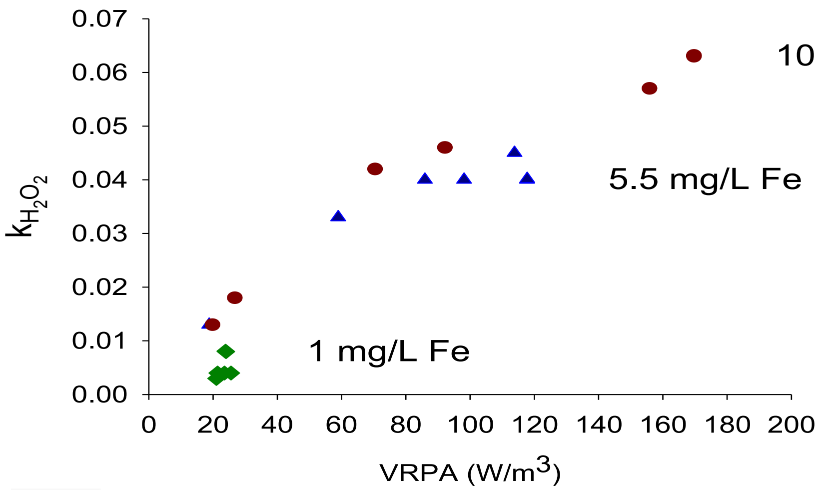
ACTM + n $HO^{\bullet}$ → TPs

$$-\frac{d[ACTM]}{dt} = k_{ACTM} \cdot [ACTM]$$

k_{ACTM} = f($HO^{\bullet}$)

Effect of irradiance on pesticide removal

$k_{H_2O_2}$ vs VRPA



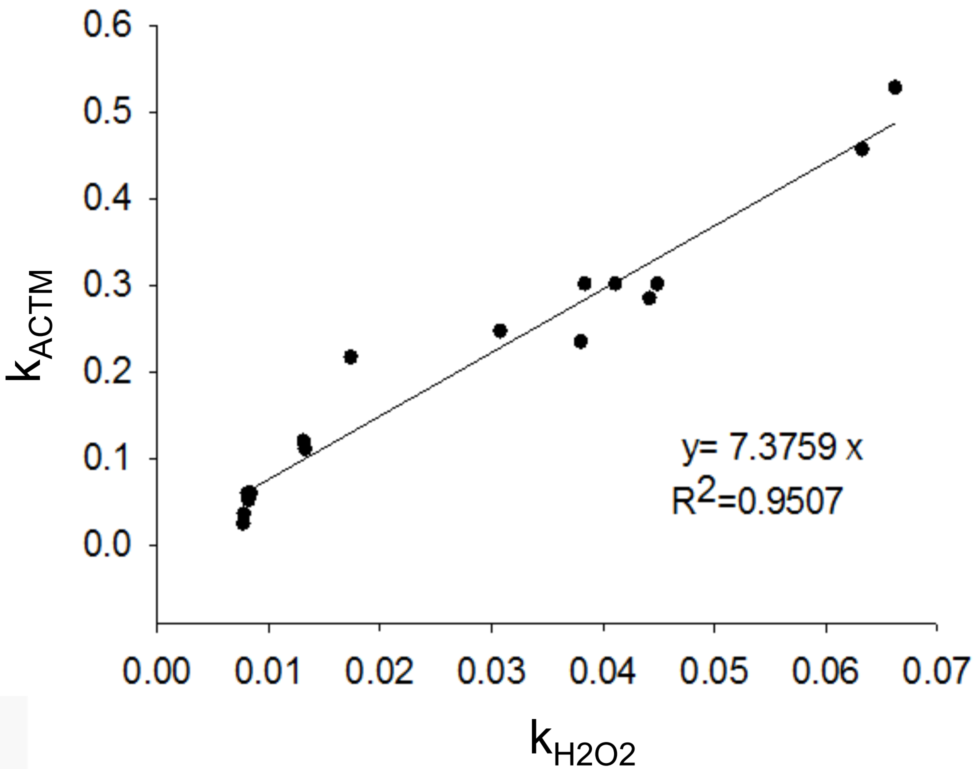
Hyperbolic relationship fits the light saturation effect

$$k_{H_2O_2} = \frac{k_m \ VRPA}{k_S + \ VRPA}$$

Fe, mg/L	k_m, m³/W min	k_s, W/m³
10	0.140	189
5.5	0.083	100
1.0	0.014	18

Effect of irradiance on pesticide removal

Apparent kinetic constant for ACTM degradation, k_{ACTM}



$$-\frac{d[ACTM]}{dt} = k_{ACTM} \cdot [ACTM]$$

k_{ACTM} = f(HO•)

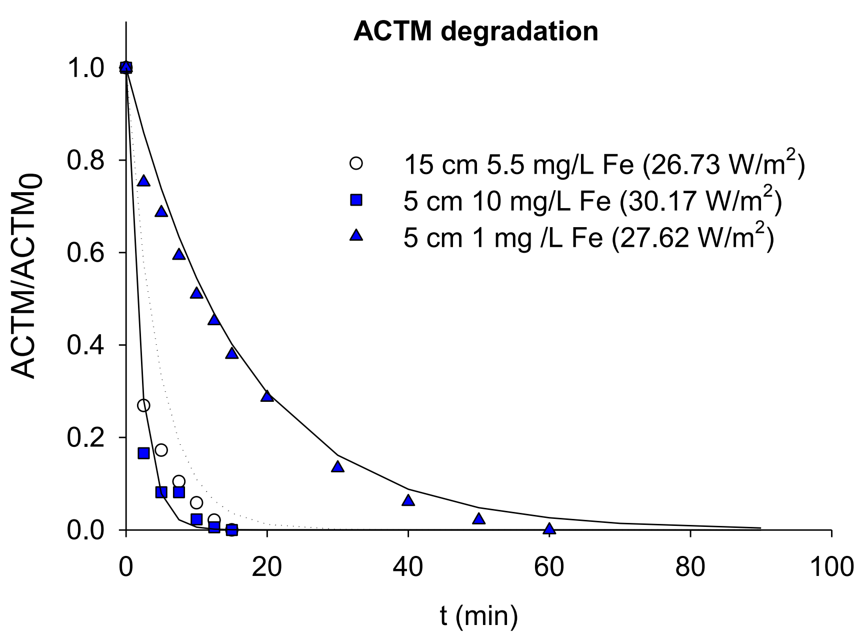
ACTM + n HO• → TPs

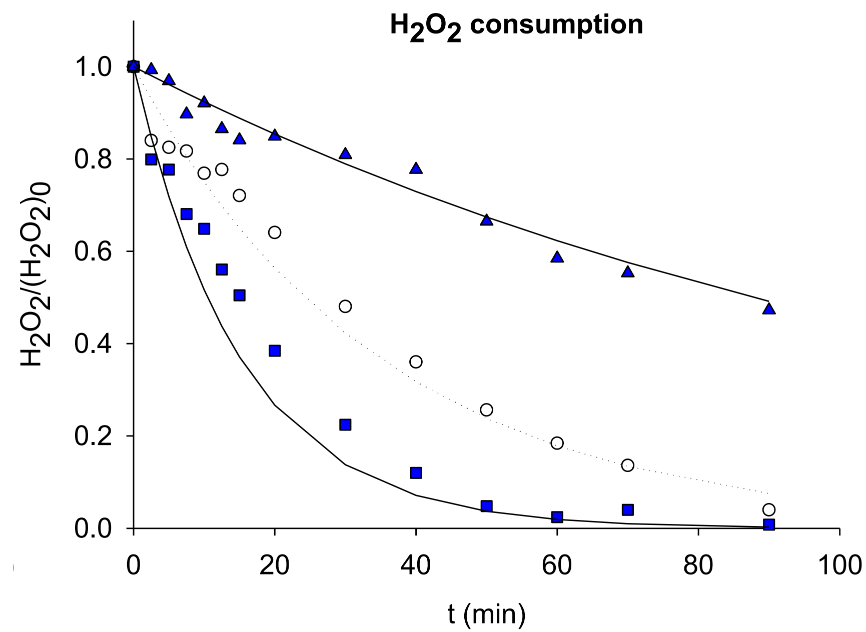
There was a linear relationship between k_{ACTM} and k_{H2O2}

Effect of irradiance on pesticide removal

Fe, I_o, D → VRPA   Fe, VRPA → k_{H2O2} → k_{ACTM}

Acceptable model fit with experimental results



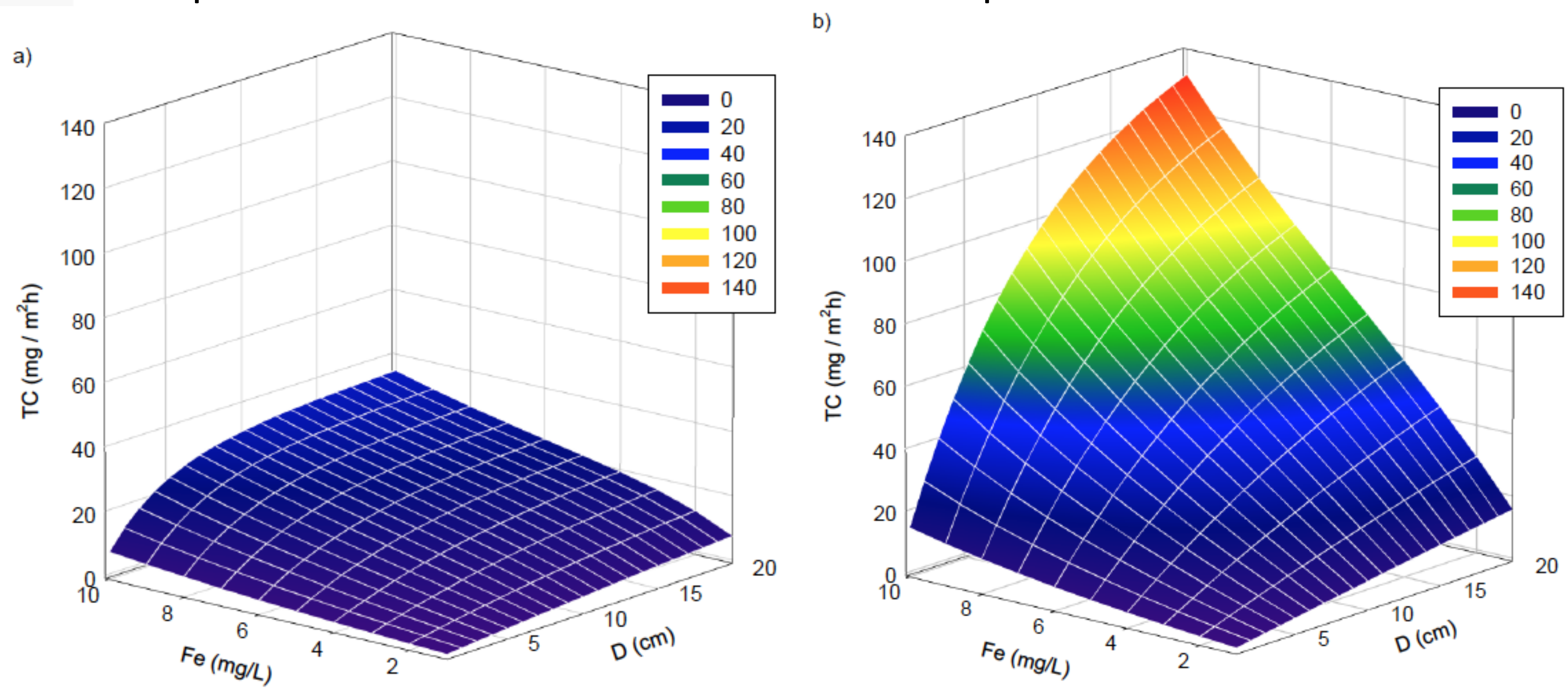


Lines represent model estimation

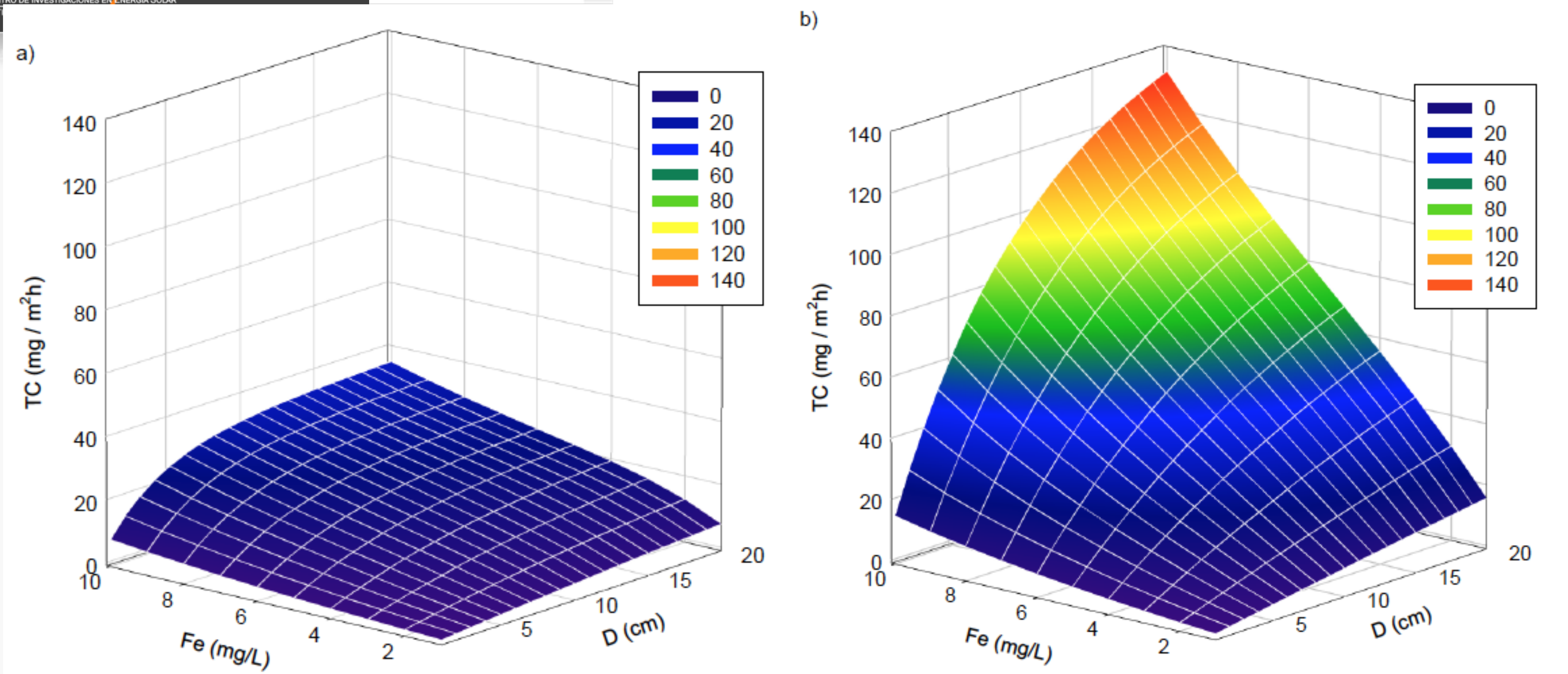
Treatment capacity, mg/h·m^2

Treatment capacity expresses the mass of oxidised pollutant per unit of time and surface of reactor exposed to radiation

Reactor performance as a function of the mass of pollutant removed



Capacity increases with liquid depth and iron concentration: a) 10 W/m^2, b) 30 W/m^2



Treatment capacity as a function of iron concentration and liquid depth: a) 10 W/m², b) 30 W/m²

Low irradiances: 5 mg/L Fe could be used with a low volume of water per surface unit, ≈100 L/m²

High irradiances: greater depths and higher iron concentrations, increasing the volume of water per surface unit up to 200 L/m².

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

Conclusions

CONCLUSIONS

From the study on the effect of UV-light on the photo-Fenton process we can see that:

- ✓ 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)
- ✓ Treatment capacity ($mg/h{\cdot}m^2$) takes into account the liquid depth and expresses the reactor performance as a function of the mass of pollutant removed
- ✓ RPRs can reach high treatment capacities (35-132 $mg/h{\cdot}m^2$) which are dependent on the yearly season and irradiance variation

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Thank you for listening !