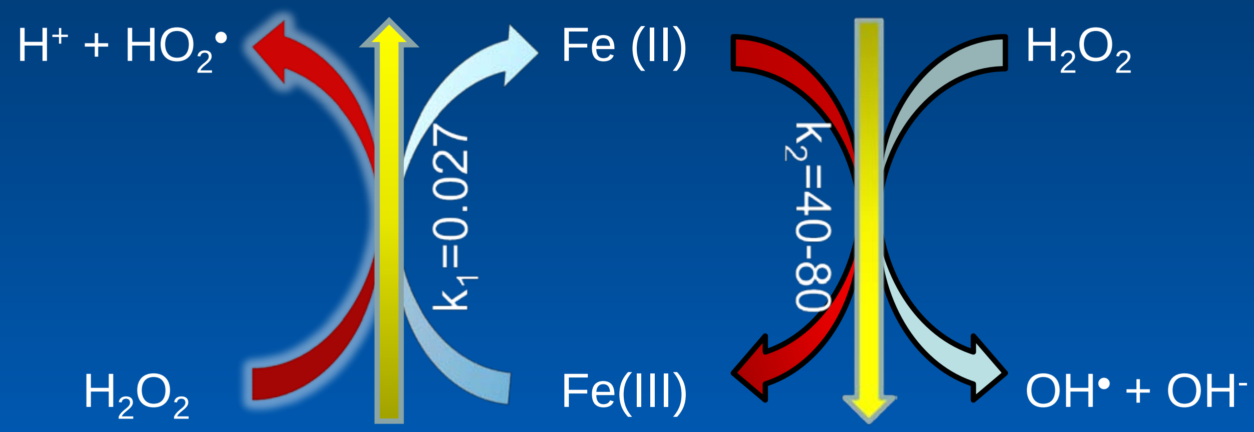
Heterogeneous photo-Fenton system for solar degradation of organic pollutants

Félicien Mazille, César Pulgarin

ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

Ecole Polytechnique Fédérale de Lausanne

Fenton chemistry



Light enhance Fenton rates
via photo-induced LMCT

$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + OH^•$

$Fe(III)L_n + h\nu \rightarrow Fe(II)L_{n-1} + L_{ox}^{•+}$

And by iron oxide bandgap illumination
In the case of heterogeneous photo-Fenton

$FeOOH + h\nu \rightarrow FeOOH(e^- + h^+)$

$FeOOH(e^-) + Fe(III) \rightarrow FeOOH + Fe(II)$

$FeOOH(e^-) + H_2O_2 \rightarrow FeOOH + OH^• + OH^-$

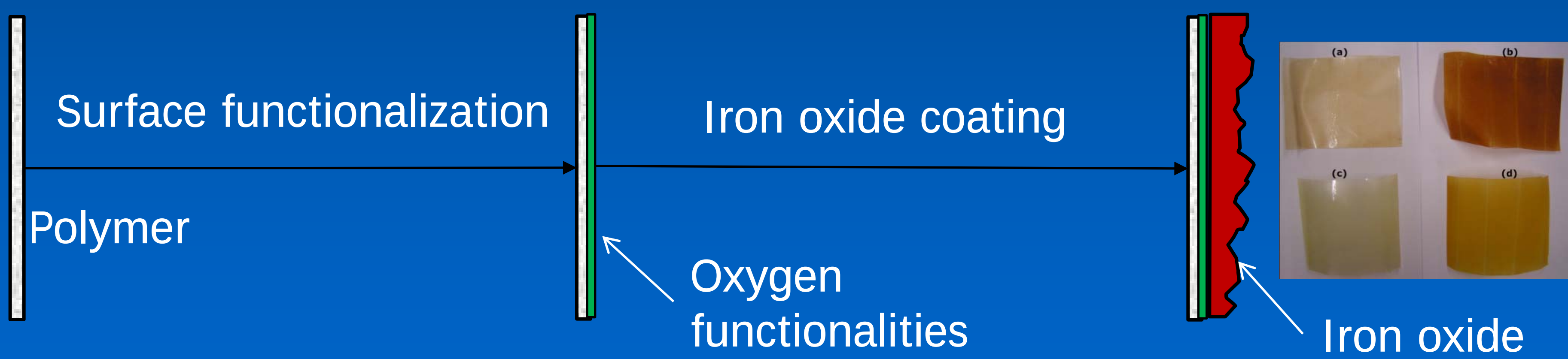
$FeOOH(h^+) + L \rightarrow FeOOH + L_{ox}^{•+}$

Why Heterogeneous photo-Fenton processes could be advantageous ?

- Process operational at a broad pH range, no initial and final pH adjustment required.
- Dissolve iron concentration is minimised, a separation of catalyst avoidable.

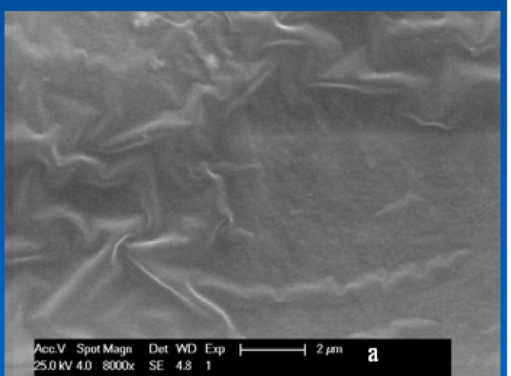
Innovative preparation strategy

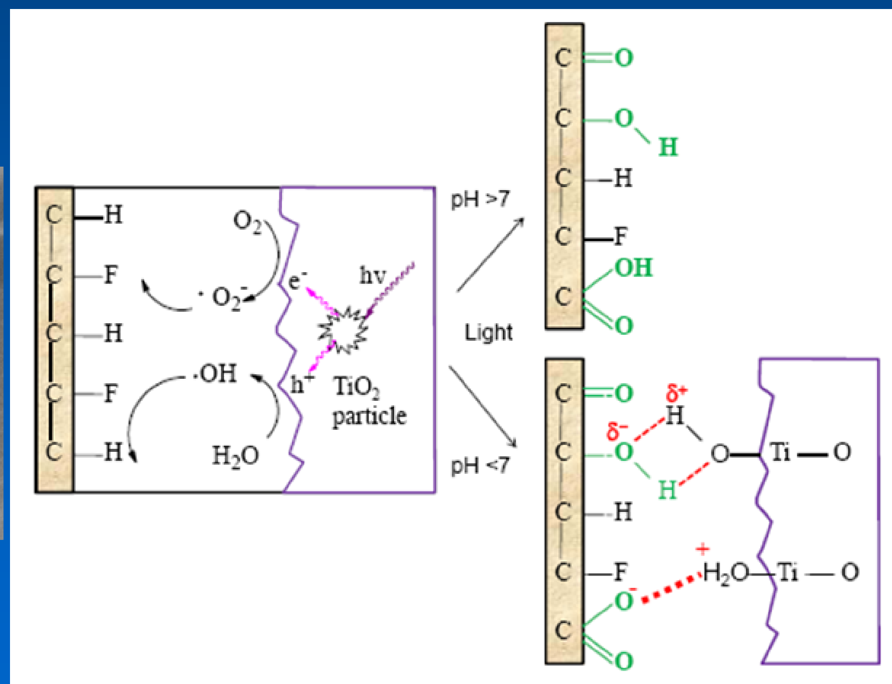
- Transparent polymer films substrate (PVF, PE, PET)
- Application of surface functionalization : TiO_2 photocatalysis
- Iron oxide coating (Forced hydrolysis $FeCl_3$)

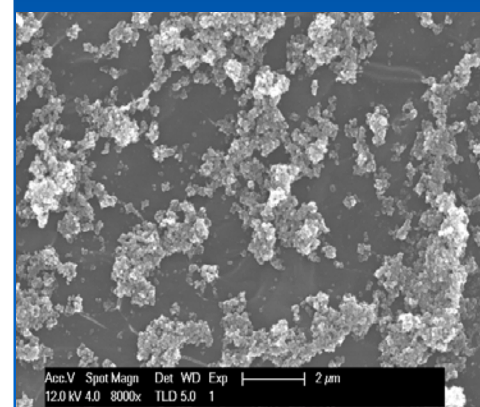


- **Characterization methods**: X-ray photoelectron spectroscopy (XPS), UV-visible spectrophotometry, scanning electron microscopy (SEM)

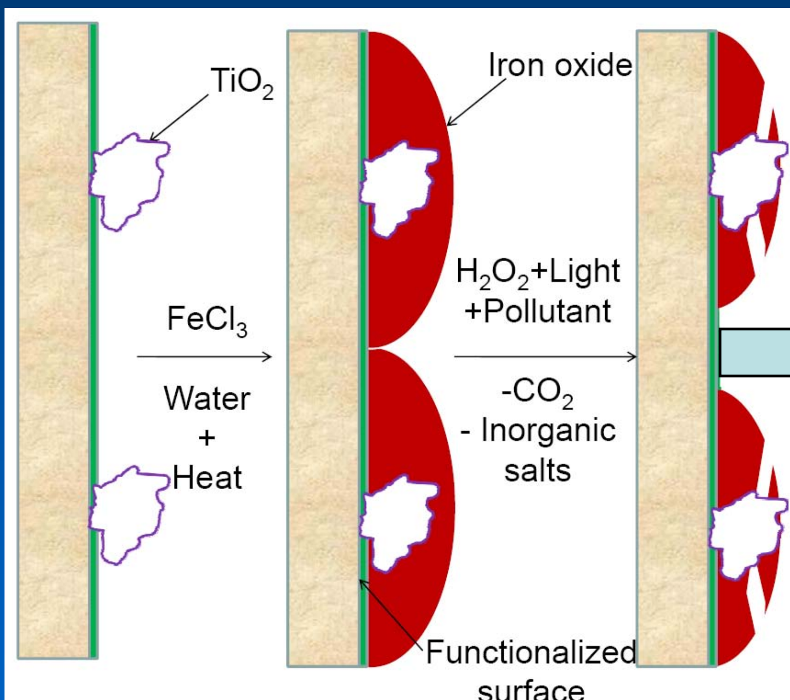
TiO_2 photocatalytic surface functionalization-deposition method (PSFD)

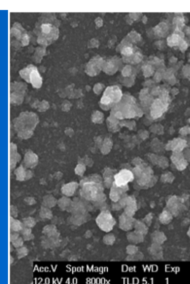


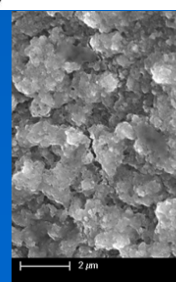




Iron oxide coating and activation



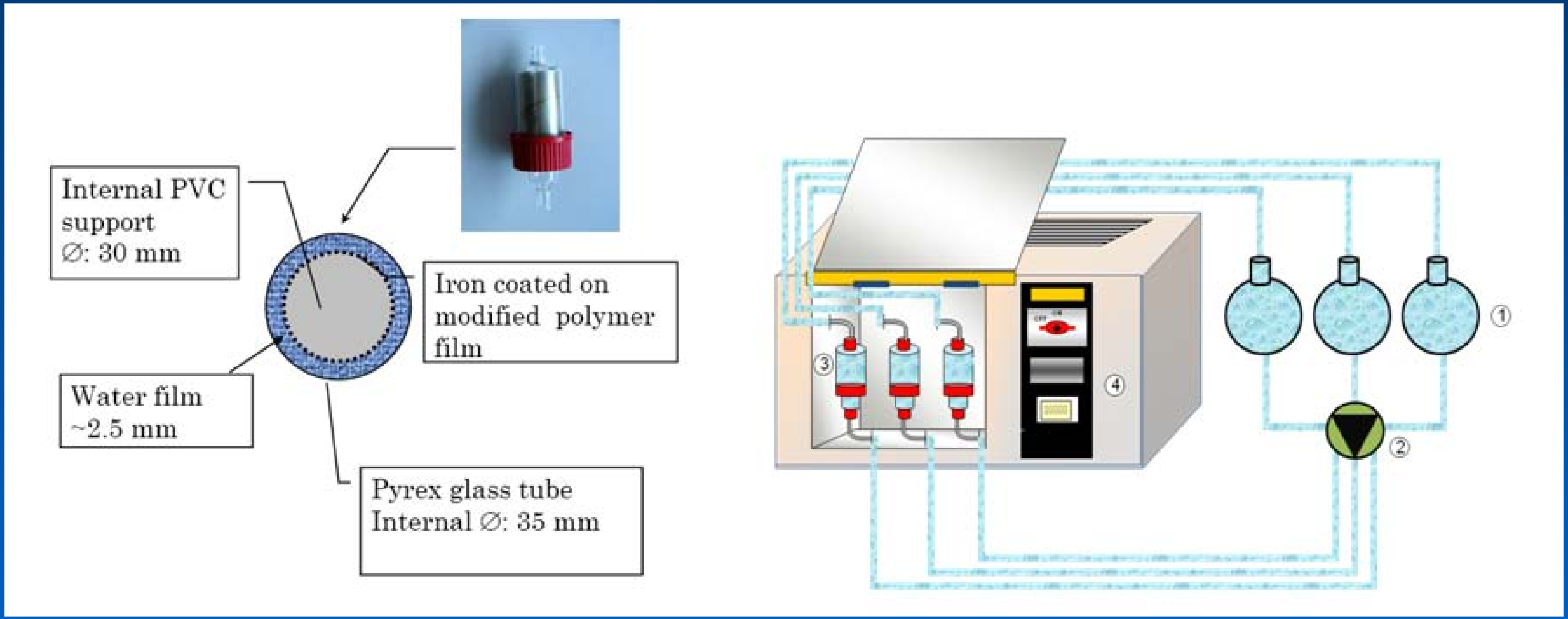




Iron and Titanium oxide **c**oated functionalized **p**olymer films (**ICP**) showing synergistic activity

Mazille et al. Applied catalysis B (2009)

Laboratory scale Set up



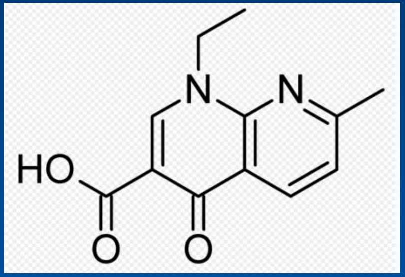
V_{total} = 110ml; $V_{irradiated}$ = 25mL

$A_{photocatalyst}$ = 75cm^2

Natural pH

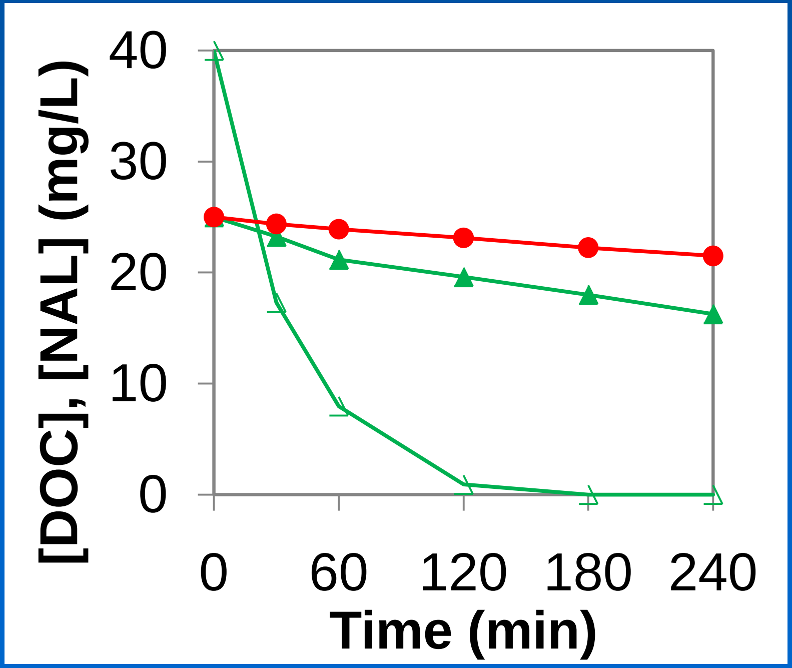
Solar simulation

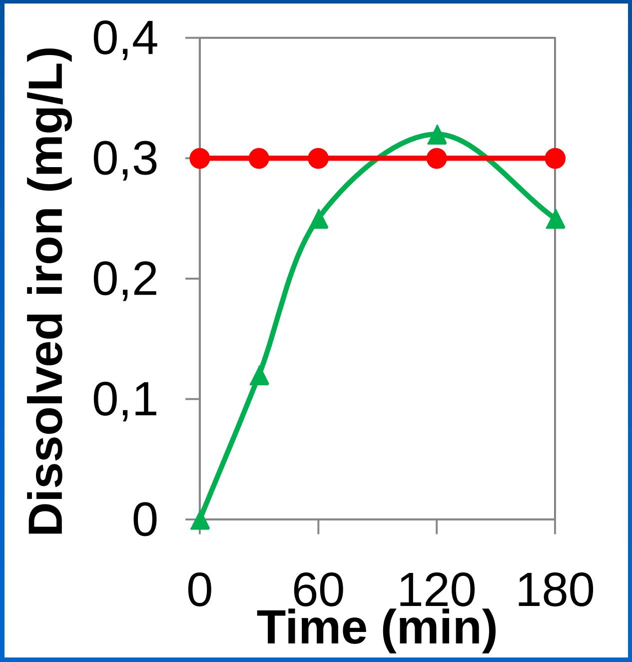
Nalidixic acid degradation Laboratory scale



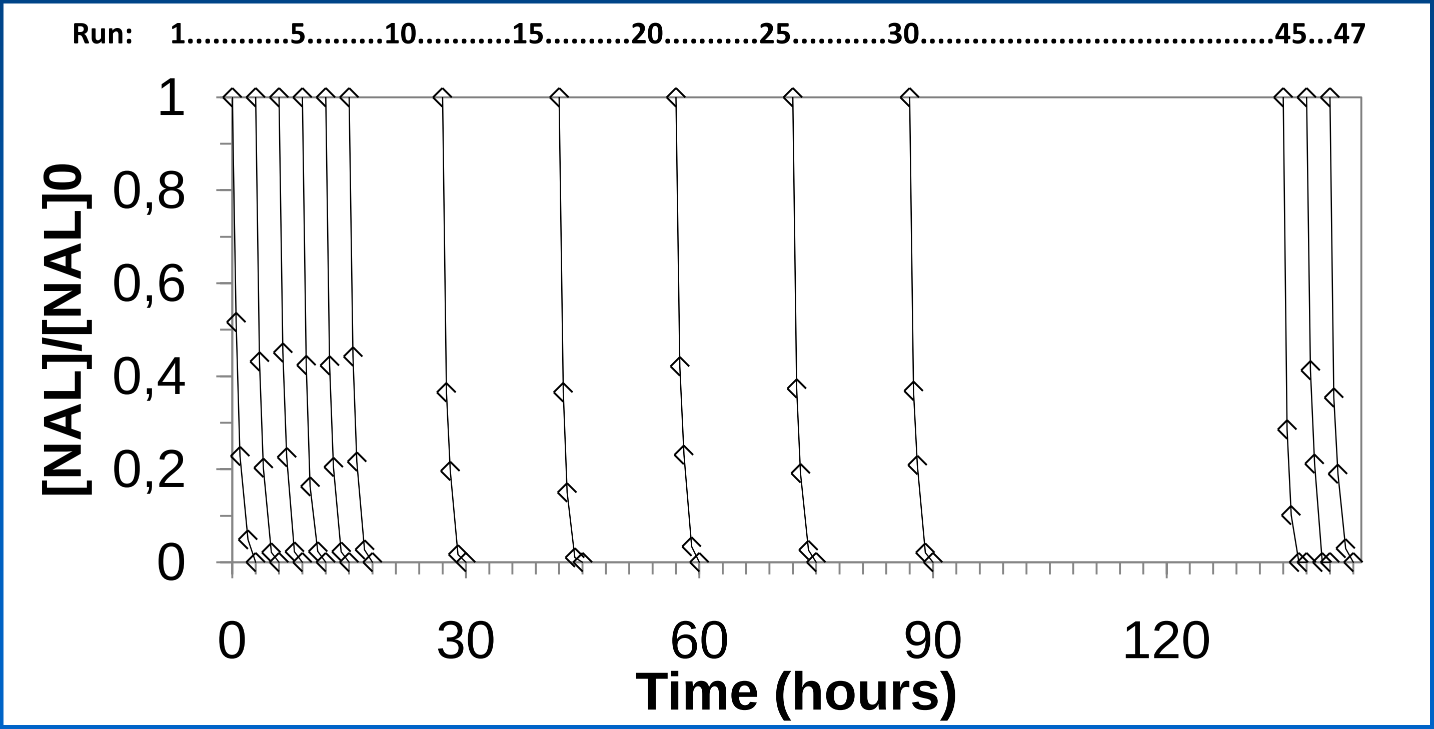
Nalidixic acid (NAL)

- **initial "natural" pH 6**
- H_2O_2 approx. 100mg/l
- Average over 5 runs exp. error ≈ 3%
- Homogeneous contribution

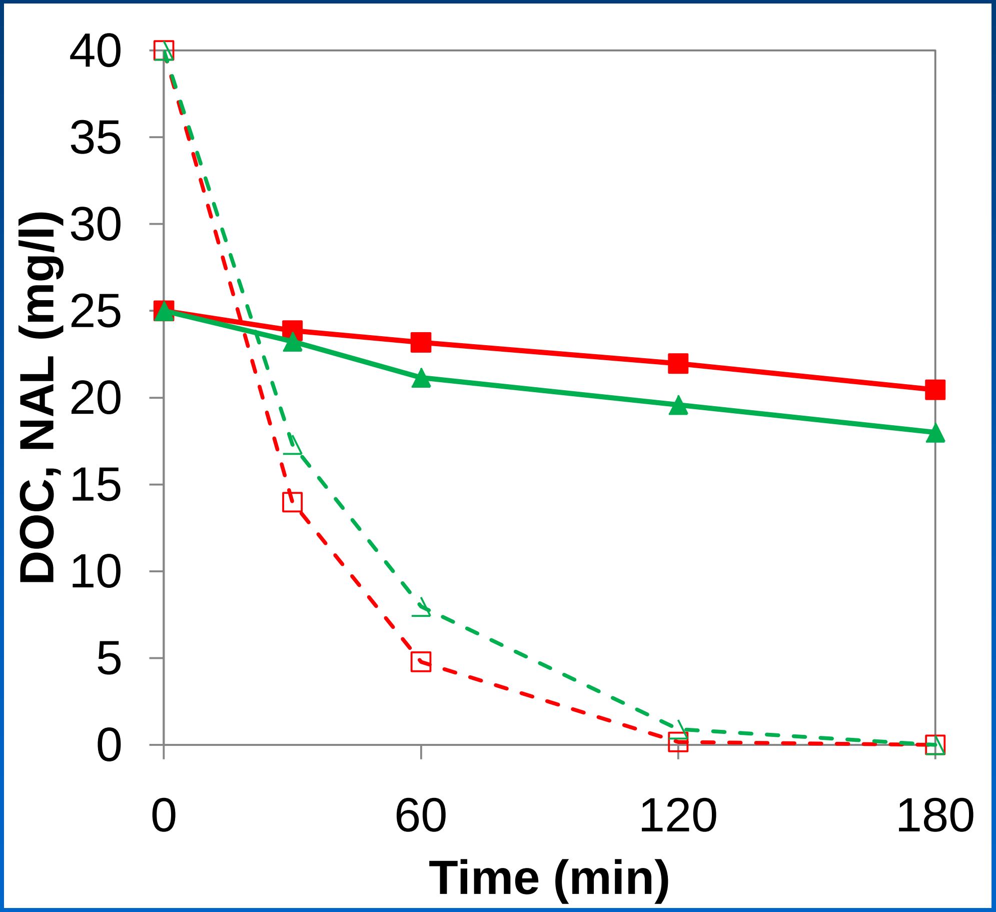




Nalidixic acid degradation : long-term stability

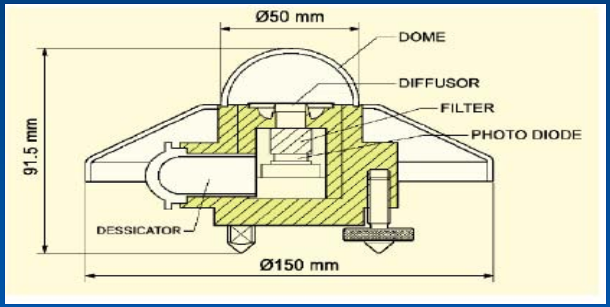


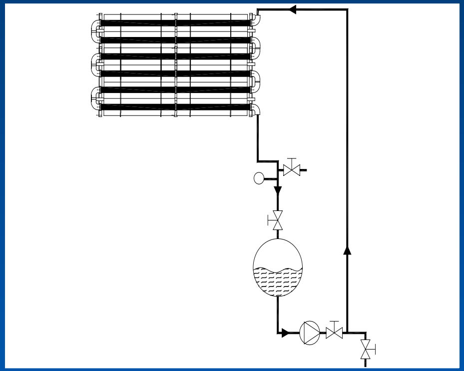
Nalidixic acid degradation: salt content

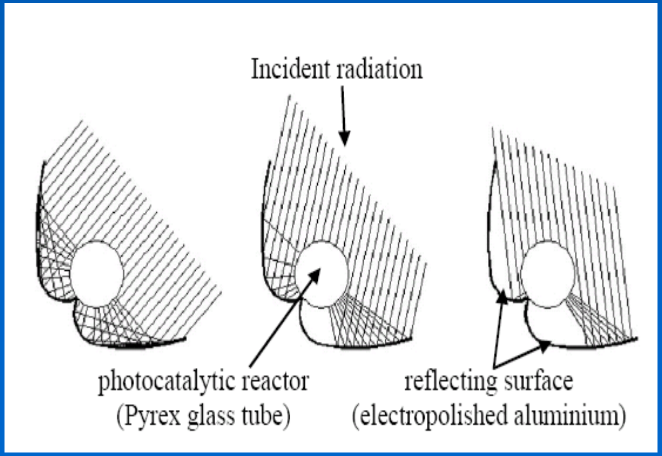


- 25 ml photoreactor, total volume 110 mL
- Nalidixic acid (NAL) 40 mg/L, initial pH 6
- Presence and absence of NaCl 5g/L
- Solar simulator
- H_2O_2 approx. 100mg/l
- Average over 5 runs Exp. error ≈ 3%

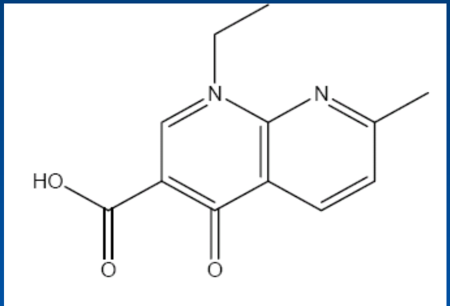
Pilot scale photo-reactor







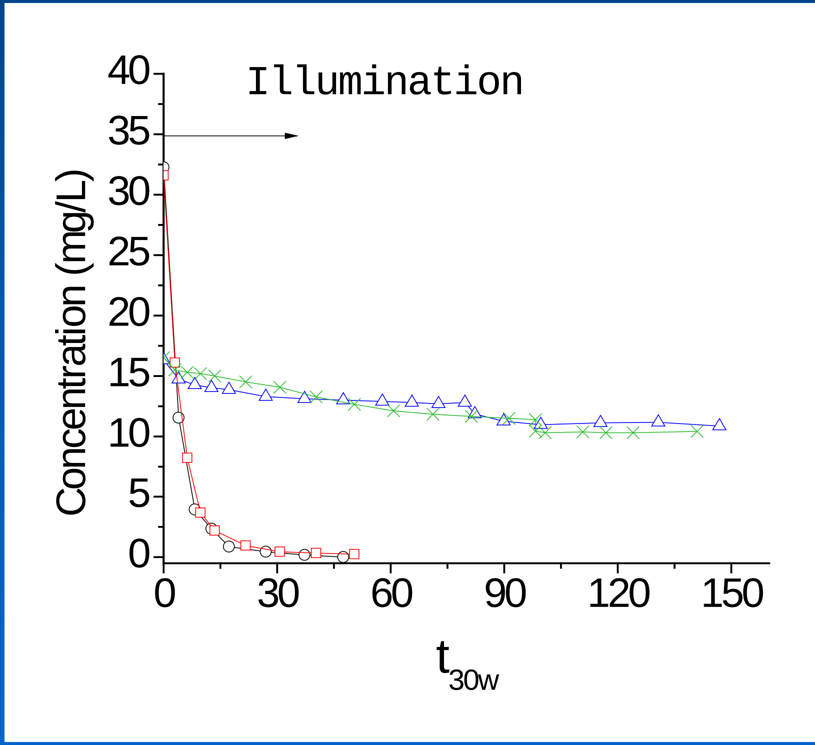
Nalidixic acid degradation: scale up



$[H_2O_2]$ = 100 mg/L

Reaction pH :7

Dissolved iron concentration <0.2 mg/L

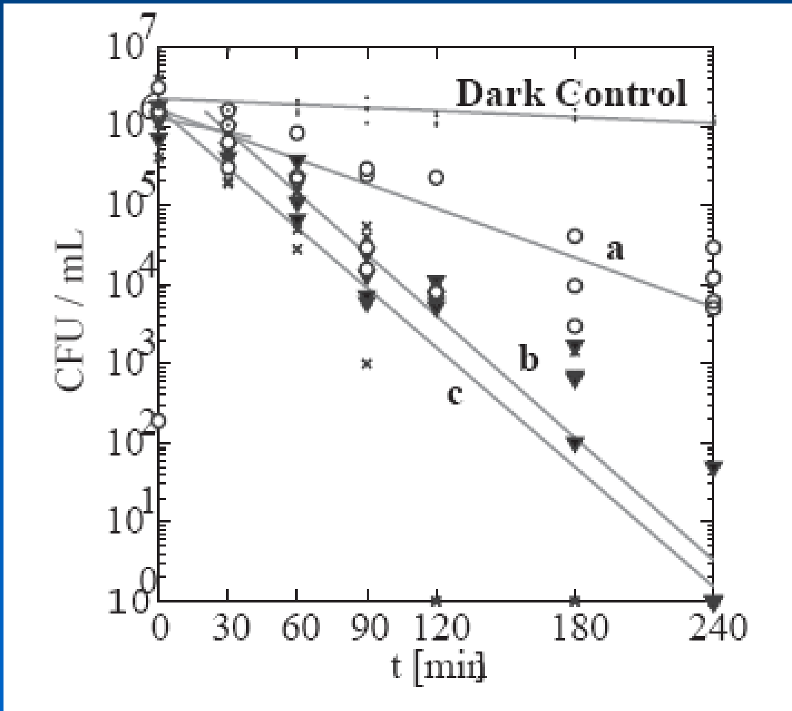


Conclusions

- A innovative way to prepare supported photocatalysts on polymer films was proposed (TiO_2 PSFD+ $FeCl_3$ hydrolysis)
- Photocalyst films were efficient to degrade nalidixic acid at controlled neutral pH and low iron leaching was observed
- The presence of salt was not detrimental for the process
- The materials showed good long term stability (>150 hour)
- The application of the new material to pilot scale solar photo-reactor was successful.

Perspectives
E.Coli inactivation in PET bottle reactors

	Photocatalyst	H_2O_2 (mM)	k_{obs} (min^{-1})
a	Light only	-	0.024 ±0.004
b	Fe^{3+} (0.6 mg/L)	0.3	0.053 ±0.008
c	$PET_b^{TiO2\text{-}PC}$-Fe-oxide	0.3	0.060 ±0.004



- **initial "natural" pH 6**
- *E. Coli* K12, 10^6 CFU/mL

Peer review articles

M. Lapertot, S. Ebrahimi, I. Oller, M. I. Maldonado, W. Gernjak, S. Malato, C. Pulgarin.
"Evaluating Microtox as a tool for biodegradability assessment of partially treated solutions of pesticides using Fe^{+3} and TiO_2 solar photoassisted processes"
Ecotoxicology and Environmental Safety, 69 (2008), 546-556

R. Mosteo, D. Gumy , C. Pulgarin
"Coupled Photo-Fenton - biological system: Effect of the Fenton parameters such as residual H2O2,Fe $^{2+}$ and pH on the efficiency of biological process"
Water Science and Technology**,** 58 (2008) 1679-1685.

F. Mazille, T. Schoettl, C. Pulgarin,
"Synergistic effect of TiO2 and iron oxide supported on fluorocarbon films. Part 1: Effect of preparation parameters on photocatalytic degradation of organic pollutant at neutral pH"
Applied Catalysis B : Environmental 89 (2009) 635-644.

F. Mazille, A. Lopez, C. Pulgarin
"Synergistic effect of TiO2 and iron oxide supported on fluorocarbon films. Part 2: Long term stability and influence of reaction parameters on photoactivated degradation of pollutants"
Applied Catalysis B : Environmental 90 (2009) 321-329.

A. Moncayo-Lasso, J. Sanabria, C. Pulgarin, N. Benítez
"Simultaneous *E. coli* Inactivation and NOM Degradation in River Water via Photo-Fenton Process at Natural pH in Solar CPC Reactor. A New Way for Enhancing Solar Disinfection of Natural Water"
Chemosphere 77 (2009) 296-300.

Peer review articles

F. Mazille, T. Schoettl, A. Lopez, C. Pulgarin.
“Physico-chemical properties and photo-reactivity relationship for *para-substituted* phenols in photo-assisted Fenton system”
Journal of photochemistry and photobiology A: Chemical (2010) In press.

F. Mazille, T. Schoettl, N. Klamerth, S. Malato, C. Pulgarin.
“Field solar degradation of pesticides and emerging water contaminants mediated by polymer films containing titanium and iron oxide with synergistic heterogeneous photocatalytic activity at neutral pH.”
Submitted in Water Research

F. Mazille, A. Moncayo, D. Spuhler, A. Serra, J. Peral, N.L Benítez, C. Pulgarin.
“Comparative evaluation of polymer surface functionalization techniques before iron oxide deposition. Activity of the iron oxide-coated polymer films in the photo-assisted degradation of organic pollutants and inactivation of bacteria.”
Submitted in Journal of photochemistry and photobiology A: Chemical

L. F. Gonzalez-Bahamon, F. Mazille, N. Benitez, C. Pulgarin.
“Transparent iron coated polymers prepared by “green chemistry” for the photo-assisted degradation of organic pollutants”
In preparation

Acknowledgment

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Questions?

Synergistic action