# *Wastewater disinfection and organic microcontaminant removal by solar photo-Fenton*

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*CIESOL, joint Center UAL-PSA.*

# SOLAR ENERGY RESEARCH CENTER (CIESOL)

It is a joint research center between the University of Almeria (UAL) and the Plataforma Solar de Almeria (PSA) and has been operating since January 2006

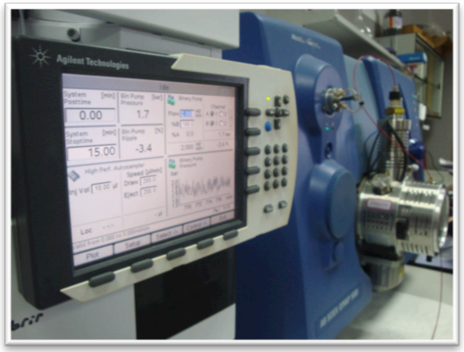


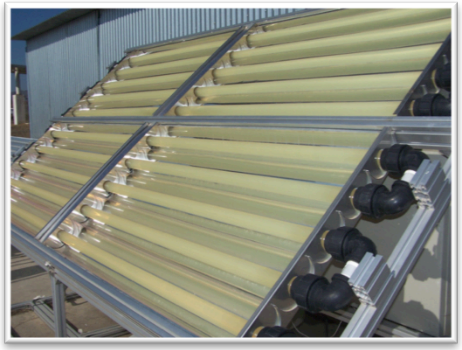
Solar energy used for heating and cooling, and photovoltaic electricity to guarantee the building's self-sufficiency.

# SOLAR ENERGY RESEARCH CENTER (CIESOL)

6 Research Groups are currently working at CIESOL on:

- ✓ Organometallics and photochemistry
- ✓ Water treatment
- ✓ Environmental chemistry
- ✓ Photosynthesis
- ✓ Desalination
- ✓ Process modelling
- ✓ Automatic control of solar processes
- ✓ Building comfort assessment
- ✓ Solar cooling
- ✓ Solar resources assessment



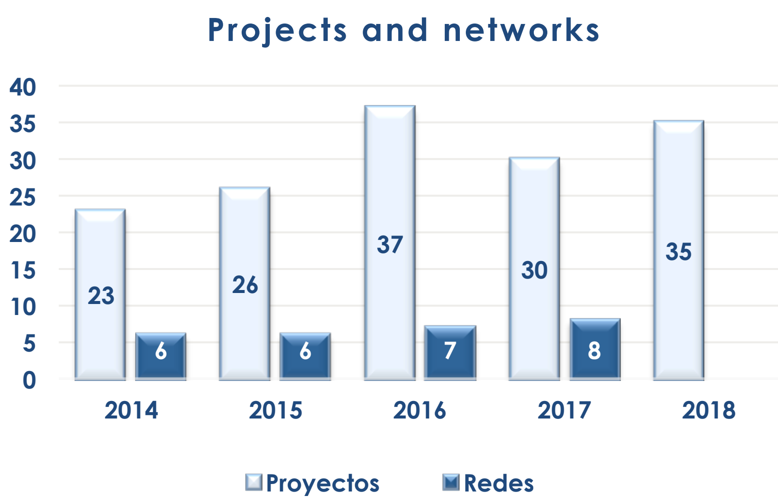


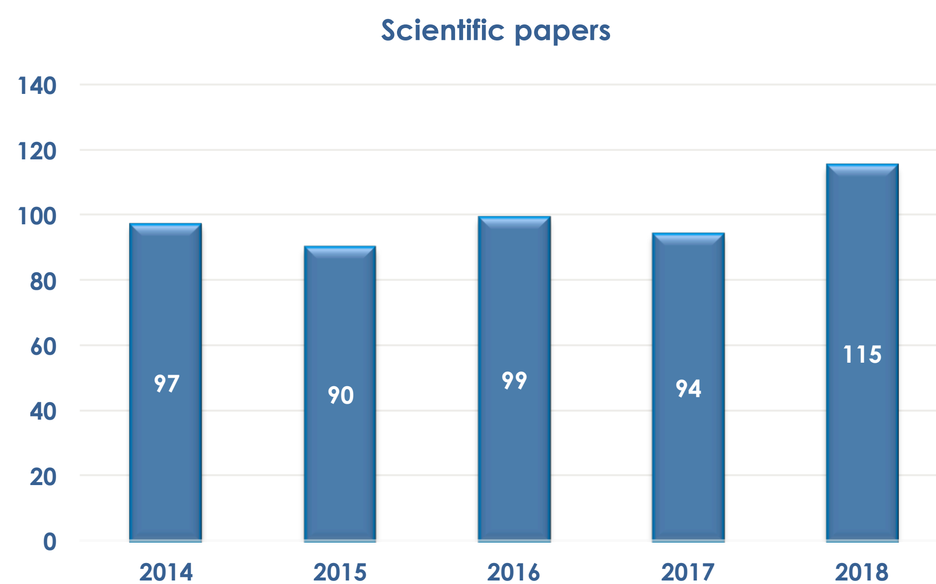
Measurements of liquid and gas composition by advanced equipment:

- ✓ AB SCIEX QTRAP 5500 LC/MS/MS TripleTOF 5600+ System
- ✓ BRUKER 320MS MS triple quadrupole coupled to BRUKER 450GC

# SOLAR ENERGY RESEARCH CENTER (CIESOL)

Around 60 researchers work at CIESOL with an annual average budget of 1,500,000 €



World Health Organization

Half of the world population will be living in water stressed areas in 2025

This trend will require better use of wastewater as an important source of irrigation water all over the world


Conventional WWTPs are not efficient in pathogenic bacteria inactivation and removal of contaminants of emerging concern

**New tertiary treatments are needed !!**

# ADVANCED OXIDATION PROCESSES

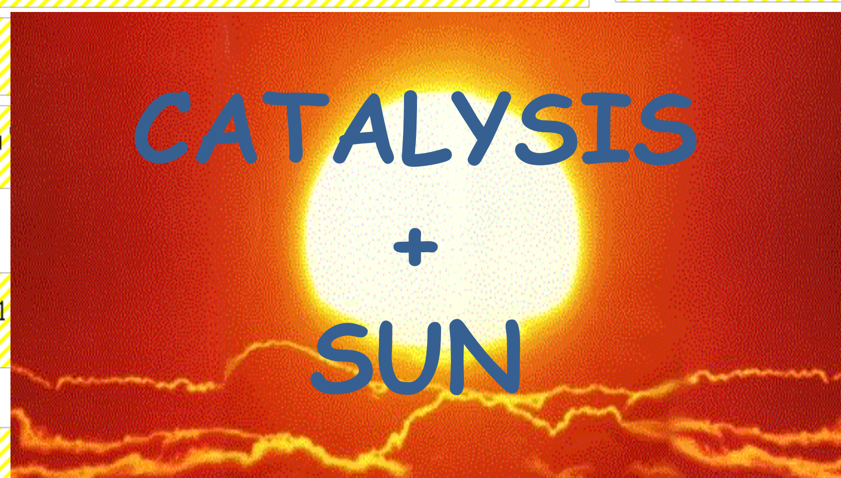
Near ambient temperature and pressure water treatment, which involve the generation of hydroxyl radicals in enough quantity for an effective water purification

- **$H_2O_2/Fe^{2+}$ (Fenton):** $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet$
- **$H_2O_2/Fe^{2+}$ ($Fe^{3+}$ )/UV (Photo-Fenton):** $Fe^{3+} \xrightarrow{h\nu} Fe^{2+} + HO^\bullet$
- **$TiO_2/h\nu/O_2$ (Photocatalysis):** $TiO_2 \xrightarrow{h\nu} e^- + h^+$

  $h^+ + H_2O \rightarrow {}^\bullet OH + H^+$
- **$O_3$/ $H_2O_2$:** $H_2O_2 \xleftrightarrow{H^+} HO^- + O_3 \rightarrow O_2 + HO_2^-$ $\quad HO_2^- + O_3 \rightarrow HO_2^\bullet + O_3^{\bullet -}$

  $HO_2^\bullet \Leftrightarrow H^+$ … $H^+ \rightarrow HO_3^\bullet$

  $HO_3^\bullet \rightarrow HO$ …




- **$O_3$/ UV:** $O_3 \xrightarrow{h\nu} O^1$ … $H_2O_2 \xrightarrow{h\nu} 2HO^\bullet$
- **$H_2O_2$/UV:** $H_2O_2 \xrightarrow{h\nu}$ …

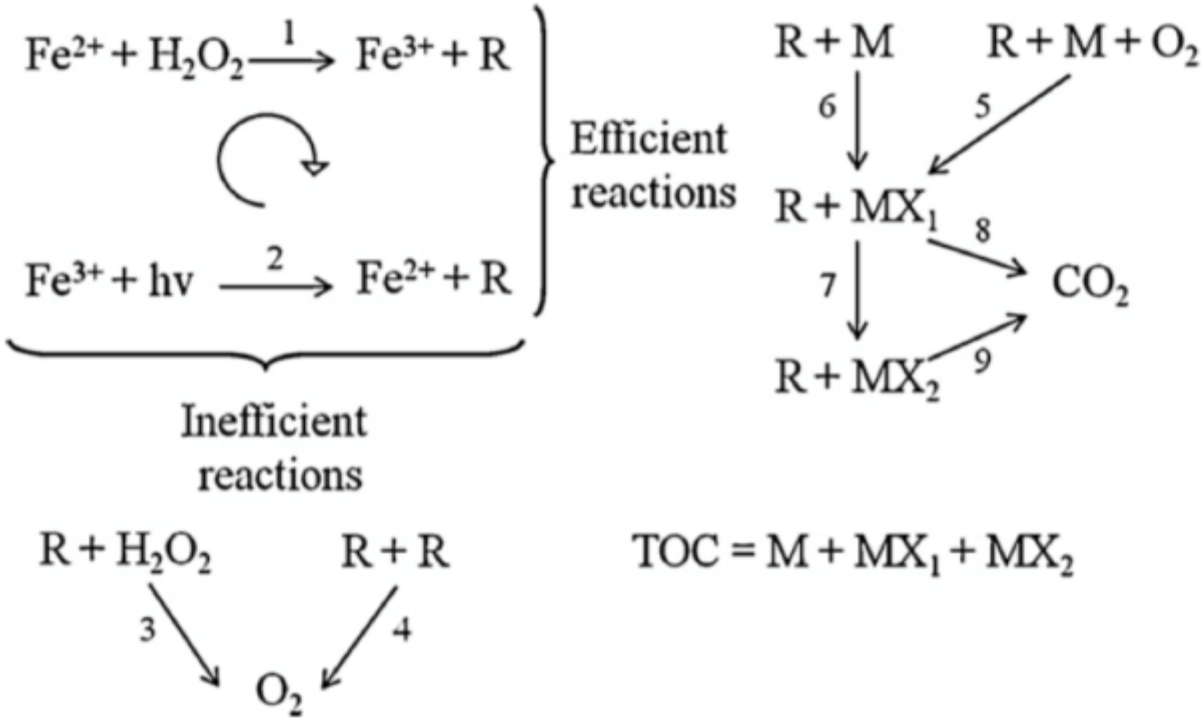
Malato et al., Catalysis Today 147: 1 (2009)

# THE SOLAR PHOTO-FENTON PROCESS

is especially interesting since it is much faster than $TiO_2$ photocatalysis for the removal of persistent organic contaminants and bacteria inactivation in complex media

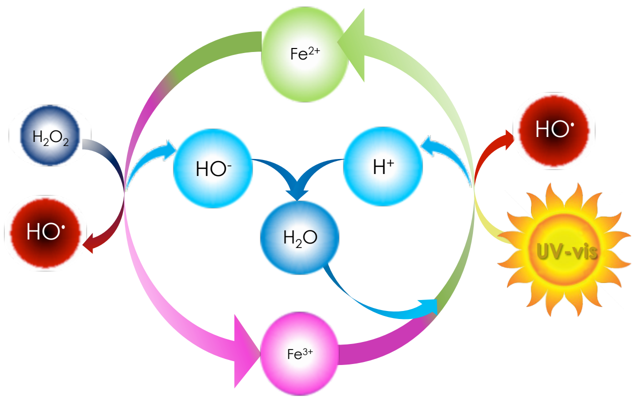
$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{-} + HO^{\bullet}$ Eq. 1

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




Cabrera et al., App Cat B: Environ. 119-120: 132-138 (2012)

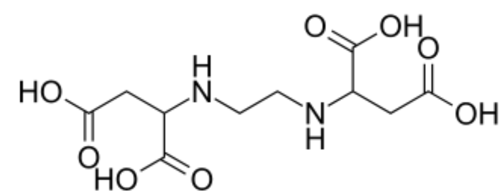
# THE SOLAR PHOTO-FENTON PROCESS



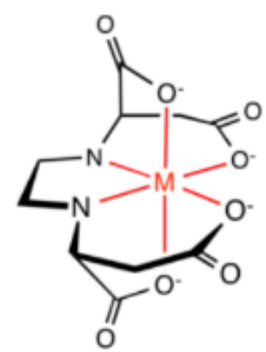

## Dependent on pH

- ✓ $Fe^{3+}$ is photoactive and soluble at acidic pH
- ✓ pH 2.8 reported to be the optimal

## At neutral pH

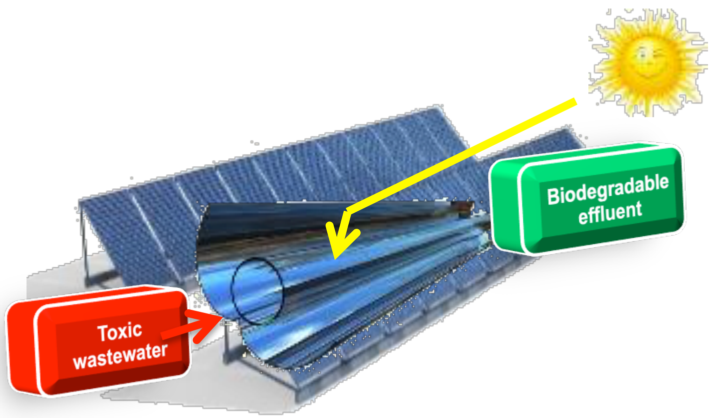


- ✓ Iron precipitation and presence of $HCO_3^-$
- ✓ Use of complexing agents to keep $Fe^{3+}$ dissolved
  $Fe^{3+}$-carboxylate complexes (citrate, oxalate...)
- ✓ EDDS: stable soluble complex with $Fe^{3+}$
  (S,S)-ethylenediamine-N,N`-disuccinic acid



De la Obra et al., Catalysis Today 287: 10-14 (2017)

# FACTORS TO CONSIDER WHEN DESIGNING A PHOTO-FENTON REACTOR




| Inputs: | Outputs: |
|---|---|
| UV-A radiation | Solar collector surface area |
| Operating pH | Reaction time |
| Fe concentration | Reactant consumption |
| $H_2O_2$ concentration | Cost |

Wastewater → Decontaminated water

Tubular reactors equipped with compound parabolic collectors, CPC

- ✓ 5 cm-diameter tubular loop
- ✓ Tube evenly illuminated
- ✓ Low illuminated volume/surface ratio, ~10 $L/m^2$

150 $m^2$ CPC detoxification plant, Almería, Spain

ELSEVIER

Science of The Total Environment
Volume 648, 15 January 2019, Pages 601-608

## Solar photo-Fenton reactors

# Comparison of different detoxification pilot plants for the treatment of industrial wastewater by solar photo-Fenton: Are raceway pond reactors a feasible option?

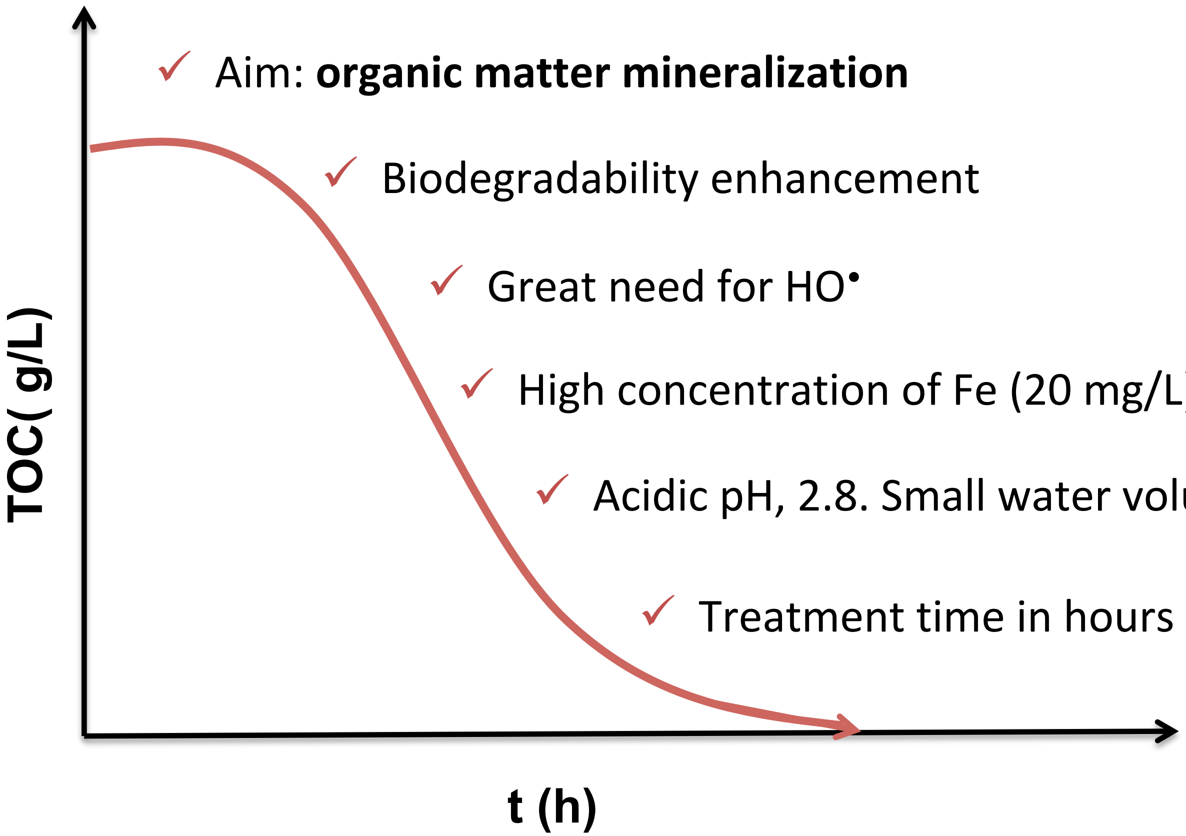
A. Cabrera-Reina [a], S. Miralles-Cuevas [a], G. Rivas [b, c], J.A. Sánchez Pérez [b, c]

To reduce costs, **low-cost reactors** such as Raceway Pond Reactors (RPRs) are used, in which the liquid depth can be varied according to the availability of UV radiation

# IMPACT OF POLLUTANT CONCENTRATION

**Highly polluted effluents: toxic wastewater, industrial wastewater**

**Contaminant concentration in the range mg/L - g/L**

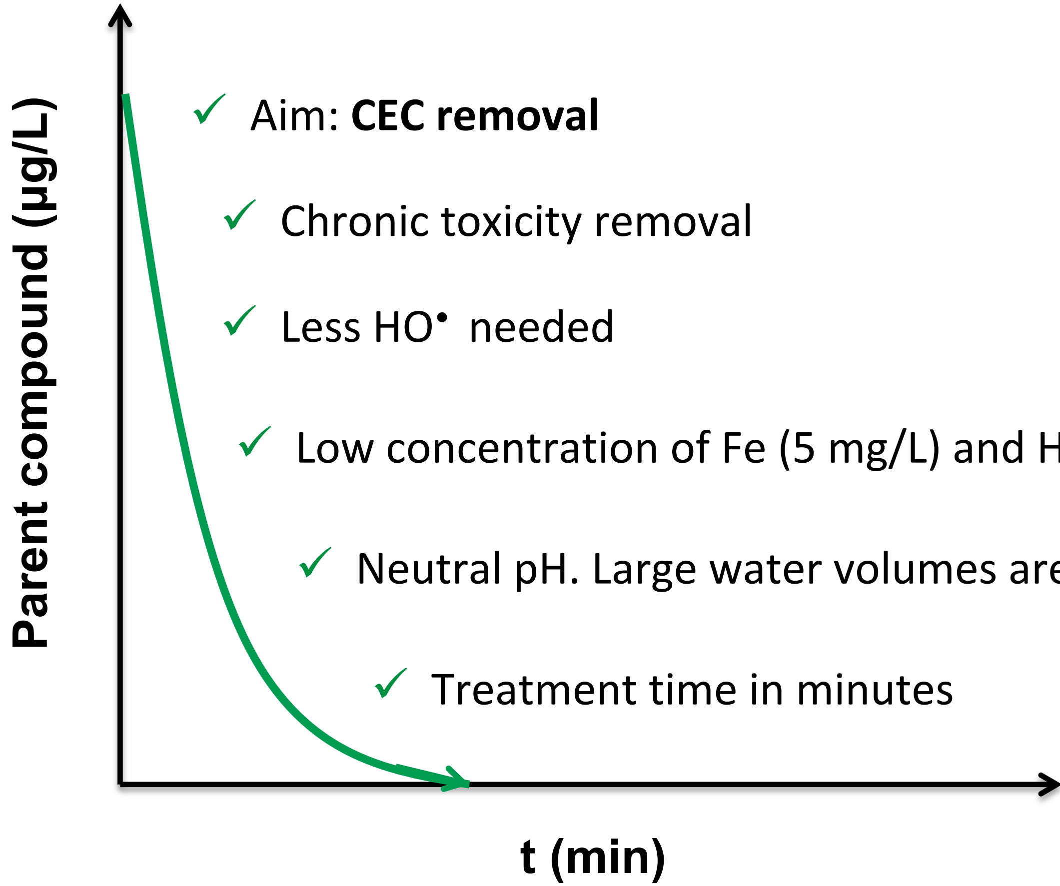



- ✓ Aim: **organic matter mineralization**
- ✓ Biodegradability enhancement
- ✓ Great need for $HO^{\bullet}$
- ✓ High concentration of Fe (20 mg/L) and $H_2O_2$ (1000 mg/L)
- ✓ Acidic pH, 2.8. Small water volumes are treated
- ✓ Treatment time in hours

# IMPACT OF POLLUTANT CONCENTRATION

Effluents containing microcontaminants: treated urban wastewater, treated agro-food industrial wastewater

Contaminant concentration in the range ng/L - µg/L




- ✓ Aim: **CEC removal**
- ✓ Chronic toxicity removal
- ✓ Less $HO^{\bullet}$ needed
- ✓ Low concentration of Fe (5 mg/L) and $H_2O_2$ (30-50 mg/L)
- ✓ Neutral pH. Large water volumes are treated
- ✓ Treatment time in minutes

CEC: contaminants of emerging concern

- Pharmaceuticals
- Personal care products
- Pesticides

Catalysis Today 313 (2018) 72–78

Contents lists available at ScienceDirect

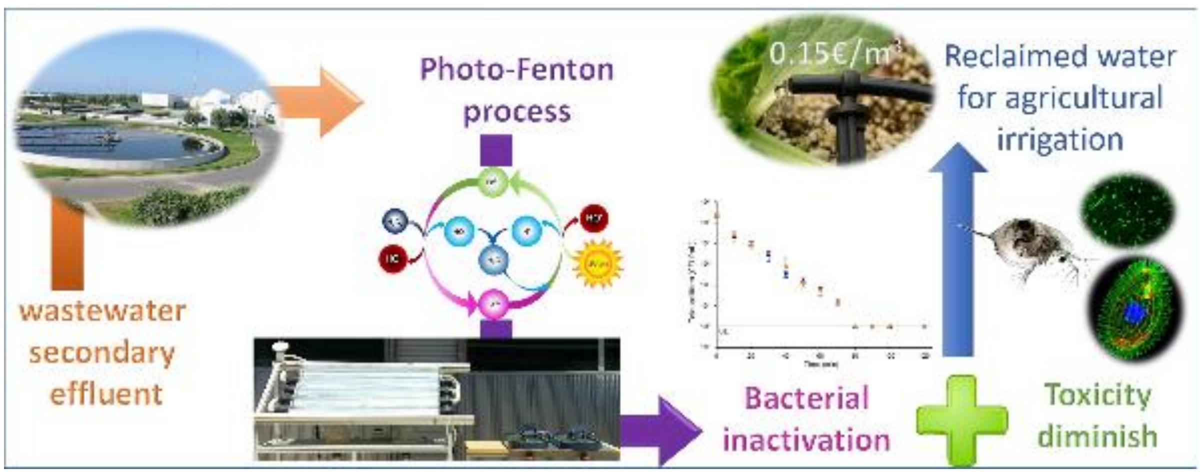
Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Wild bacteria inactivation in WWTP secondary effluents by solar photo-fenton at neutral pH in raceway pond reactors

B. Esteban García[a,b], G. Rivas[a,b], S. Arzate[a,b], J.A. Sánchez Pérez[a,b,*]

# Wastewater disinfection in raceway pond reactors




✓The disinfection process was similar in RPR and CPC at neutral pH

✓Treatment time was around 60 min for *E. coli* inactivation to the detection limit (1 CFU $mL^{-1}$)

✓RPRs are efficient for bacterial inactivation in real WWTP effluents by solar photo-Fenton with 20 mg/L $FeSO_4$ and 50 mg/L $H_2O_2$

Chemical Engineering Journal
Volume 366, 15 June 2019, Pages 141-149

# CEC removal by solar photo-Fenton at neutral pH

## Assessment of solar raceway pond reactors for removal of contaminants of emerging concern by photo-Fenton at circumneutral pH from very different municipal wastewater effluents

P. Soriano-Molina [a, b], P. Plaza-Bolaños [a], A. Lorenzo [a], A. Agüera [a], J.L. García Sánchez [a, b], S. Malato [a, c], J.A. Sánchez Pérez [a, b]


- ✓ Photo-Fenton with $Fe^{3+}$-EDDS removes CECs regardless water composition
- ✓ 80% CEC removal after 15 min in 5 real WWTP effluents using:

  0.1 mM $Fe^{3+}$-EDDS (1:1) and 0.88 mM $H_2O_2$ (5 mg/L Fe and 30 mg/L $H_2O_2$)

# The short treatment times make it necessary to move from batch wise operation towards continuous flow operation

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Applied Catalysis B: Environmental

Volume 247, 15 June 2019, Pages 115-123

## Continuous flow disinfection of WWTP secondary effluents by solar photo-Fenton at neutral pH in raceway pond reactors at pilot plant scale

I. De la Obra Jiménez [a, b], B. Esteban García [a, b], G. Rivas Ibáñez [a, b], J.L. Casas López [a, b], J.A. Sánchez Pérez [a, b]

Solar photo-Fenton process was operated in continuous flow to disinfect wastewater

Applied Catalysis B: Environmental 256 (2019) 117801

Contents lists available at ScienceDirect

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Applied Catalysis B: Environmental

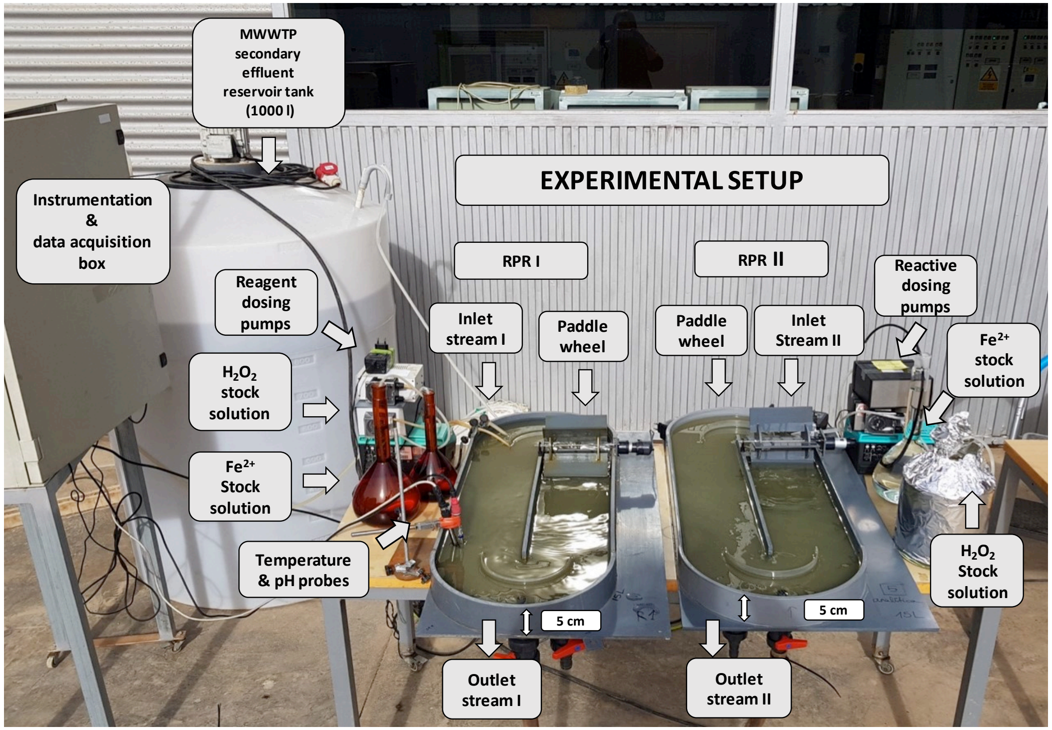
journal homepage: www.elsevier.com/locate/apcatb

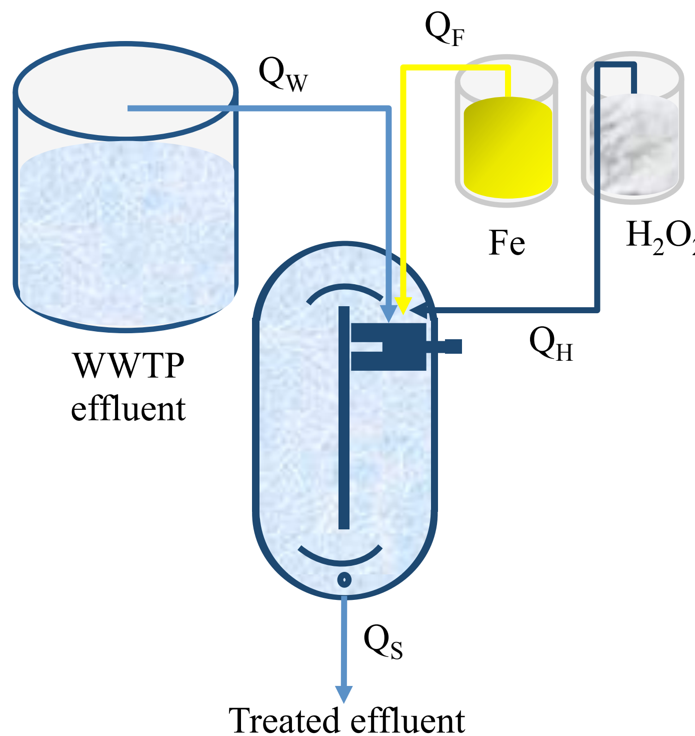
## On the design and operation of solar photo-Fenton open reactors for the removal of contaminants of emerging concern from WWTP effluents at neutral pH

P. Soriano-Molina[a,b], J.L. García Sánchez[a,b], S. Malato[a,c], P. Plaza-Bolaños[a], A. Agüera[a], J.A. Sánchez Pérez[a,b,*]

Solar photo-Fenton process was operated in continuous flow to remove CEC from wastewater

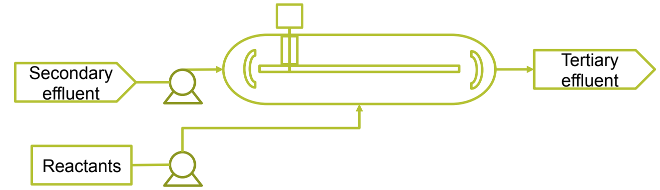
# CONTINUOUS FLOW OPERATION FOR WASTEWATER DISINFECTION




- ✓ Faecal microorganism models
  - Total coliform
  - *E. coli*
  - *Enterococcus* sp
- ✓ Winter and summer: UVA irradiance (13 - 40 $W{\cdot}m^{-2}$)
- ✓ Real WWTP secondary effluent
- ✓ HRTs (60 and 30 min)

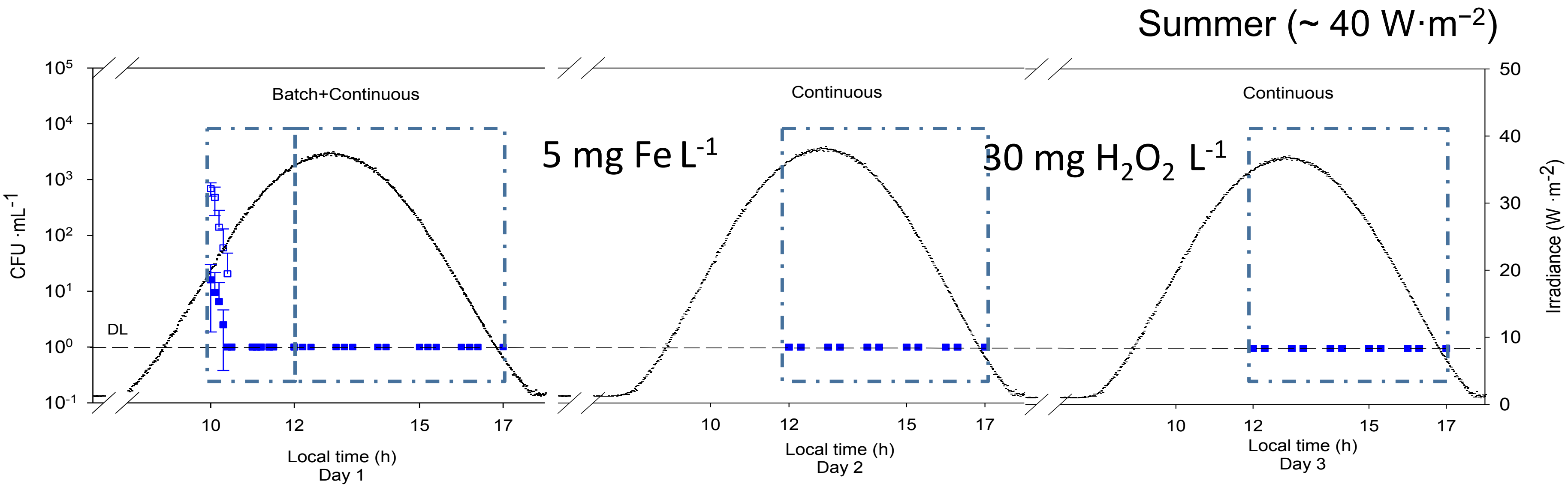
# Continuous flow operation at 30 min of HRT




The reactor start-up (batch) was carried out with 20 mg Fe $L^{-1}$ and 50 mg $H_2O_2$ $L^{-1}$

Next, the continuous supply of reactants in the inlet stream was set at 30 mg $H_2O_2$ $L^{-1}$ and iron concentration was reduced to 5 mg Fe $L^{-1}$

Disinfection was maintained at steady state with 35% CEC removal




Total *E. coli* ( ) Antibiotic resistant *E. coli* ( )

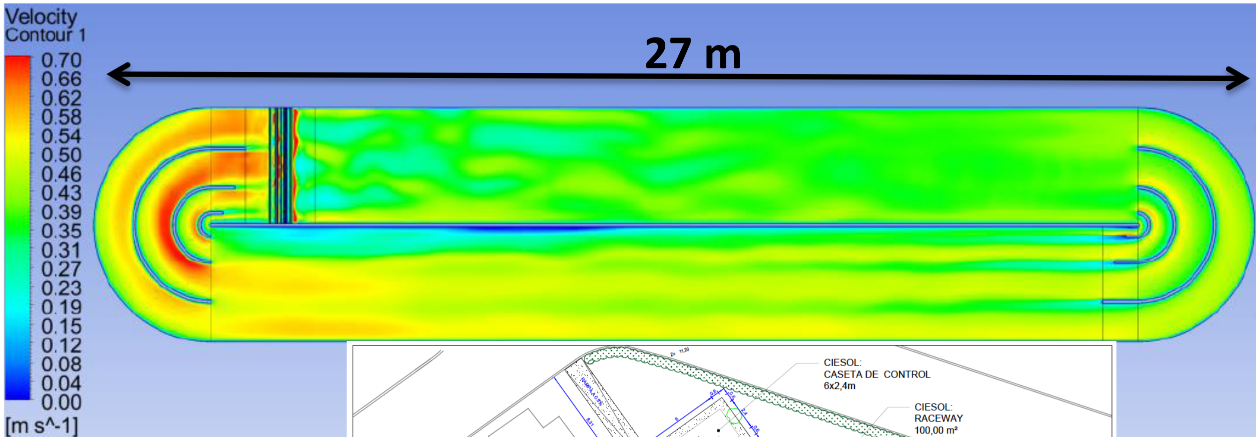
# ECONOMIC ASSESSMENT. COST ESTIMATION

Treatment flow rate:
400 $m^3$/day 5 cm-deep RPR

| | Operation conditions in continuous flow mode | | | |
|---|---|---|---|---|
| | CEC removal (35%) and disinfection | | CEC removal (80%) | Disinfection |
| | $FeSO_4$ | $Fe^{3+}$-EDDS | $Fe^{3+}$-EDDS | $FeSO_4$ |
| Iron (mM) | 0.36 | 0.10 | 0.10 | 0.10 |
| $H_2O_2$ (mM) | 1.47 | 0.88 | 0.88 | 0.88 |
| EDDS (mM) | -- | 0.10 | 0.10 | -- |
| HRT (min) | **60** | **40** | **15** | **30** |
| RPR volume ($m^3$) | 50 | 33 | 13 | 25 |
| Treatment capacity ($m^3/m^2\cdot day$) | 400 | 600 | 1600 | 800 |
| RPR surface ($m^2$) | 1000 | 667 | 250 | 500 |
| | COSTS (€/$m^3$) | | | |
| Amortization | 0.014 | 0.010 | 0.004 | 0.007 |
| Operation | 0.217 | 0.482 | 0.464 | 0.117 |
| Total | **0.23** | **0.49** | **0.47** | **0.12** |

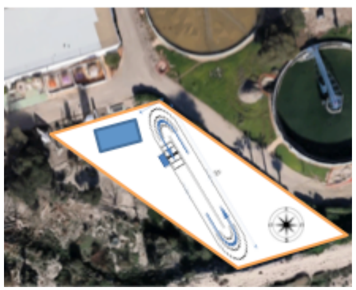
Soriano Molina et al., Catalysis Today (2019)
DOI: 10.1016/j.cattod.2019.11.028

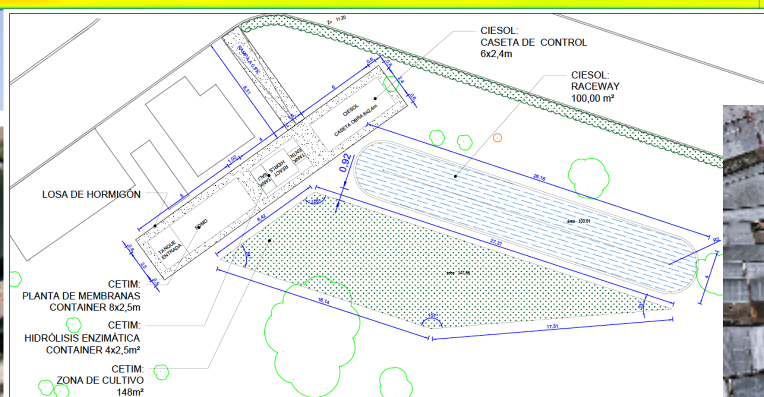
# Upgrading wastewater treatment plants by Low cost Innovative technologies for energy SElf-Sufficiency and full recycling




## Construction in 2020

RPR area: 100 $m^2$
Liquid depth: 5 – 10 cm
Inlet Flow: 12 - 35 $m^3/h$
Operating hours: 6 – 10 h
HRT: 30 – 20 min
$[Fe^{2+}]$: 5 ppm $[H_2O_2]$: 30 ppm







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