LIFE PHOENIX

Development and results of solar technologies for small populations

Design, construction and operation of a solar photo-Fenton treatment plant *for micropullutant removal in raceway pond reactors operated in continuous flow mode*

José Luis Casas López
Solar Energy Research Centre (CIESOL)
Joint Centre University of Almería - CIEMAT
Almería, Spain

The **Solar Energy Research Center (CIESOL)** 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

www.ciesol.es

Ciemat PSA

UNIVERSIDAD DE ALMERÍA

Interdisciplinarity: physicists, chemists, biologists, industrial engineers and chemical engineers. Aimed to various industrial sectors:

- **Medium and high temperature solar thermal energy**
- **Integration of thermal and photovoltaic energy in buildings**
- **Water treatment (desalination, decontamination, microalgae)**
- **Control, modelling and optimization of solar processes**

Innovative cost-effective multibarrier treatments for reusing water for agricultural irrigation. LIFE19 ENV/ES/000278

LIFE PHOENIX is a project co-funded by the European Union under the LIFE Programme Grant Agreement no. LIFE19 ENV/ES/000278

COORDINATOR

aqualia

PARTNERS

DIPUTACIÓN DE ALMERÍA

ÁGUAS DE PORTUGAL

CIESOL Centro de Investigación en Energía Solar Centro Mixto UAL - PSA CIEMAT

CETIM Technological Centre

microLAN On-line Biomonitoring Systems

Newland EnTech Europe Ozone & UV Technology

chg

Life Program Priority Area: Environment and Resource Efficiency project application

Sector: Water including the marine environment

Coordinator: AQUALIA
Partners: AdP, CETIM, CHG, DIPALME, NEWLAND, UAL- CIESOL, microLAN
Budget: 3,390,078 €

EU Contribution: 1,855,113 €

Duration: 09/2020 – 02/2024 (42 months)

INDEX

FUNDAMENTALS

JUSTIFICATION

WWTP El Toyo
Almería, Spain

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Water Regeneration

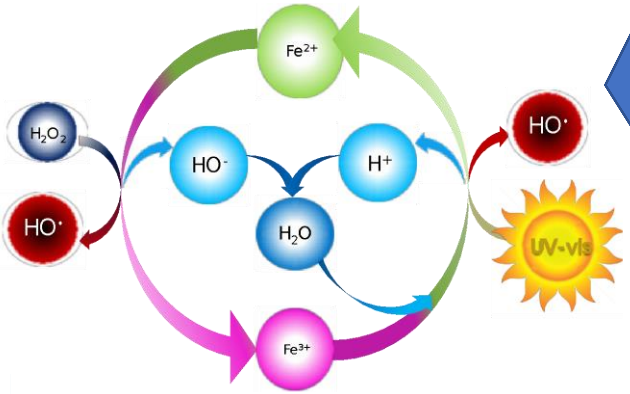
Pathogens

Contaminants of emerging concern (CECs)

Current tertiary treatments

New EU regulation involves pathogen and micropollutant removal

Alternative Tertiary treatments needed



Solar Photo-Fenton

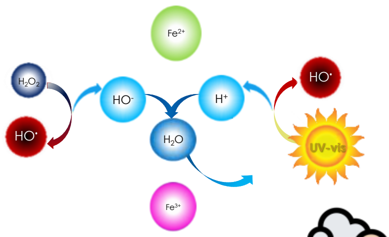
The Solar Photo Fenton process has demonstrated to be a competitive alternative to the current tertiary treatments removing pathogens and organic micropollutants

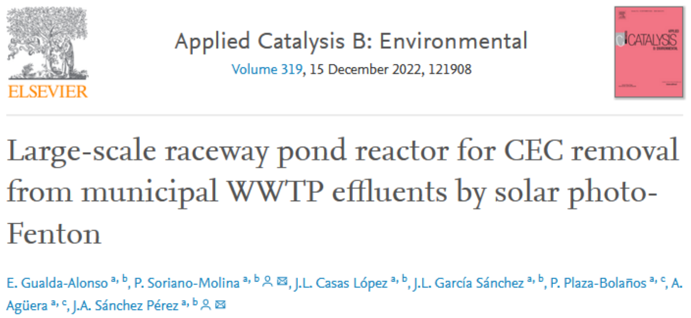
Photo-Fenton cycle

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^\bullet$ Very fast reaction (1894, H.J.H. Fenton)

$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + HO^\bullet + H^+$ Reaction rate dependent on the UV

MP removal: $C + HO\bullet \rightarrow MX$





Applied Catalysis B: Environmental
Volume 319, 15 December 2022, 121908

Large-scale raceway pond reactor for CEC removal from municipal WWTP effluents by solar photo-Fenton

E. Gualda-Alonso [a, b], P. Soriano-Molina [a, b], J.L. Casas López [a, b], J.L. García Sánchez [a, b], P. Plaza-Bolaños [a, c], A. Agüera [a, c], J.A. Sánchez Pérez [a, b]

Acidic pH:

- ✓ Fe^{3+} photo-active and soluble at acidic pH
- ✓ Optimal pH ≈ 3

Neutral pH:

- ✓ Use of chelating agents to keep iron dissolved
- ✓ EDDS and NTA: soluble and stable complexes

HIGHLIGHTS & CHALLENGES

- **Environment (UV, T) dependent**
- **Solar cycles influence**
- **Absence of monitoring tools**
- **Influenced by water quality inlet**
  - **(CO_3^{2-}, NH^{4+}, PO_4^{3-})**
- **Monitoring and scaling-up**
- **Control system design**
- **Cost reduction**

Important progresses: a) **photo Fenton modelling** at acidic pH and neutral pH with EDDS and NTA b) **continuous operation** and c) **scale up in LOW COST RPR**

Sánchez Pérez et al. 2017 *Chem. Eng. J.* 310, 464-472

Soriano-Molina et al. 2018 *Appl. Catal. B-Environ.* 233, 234-242

Gualda-Alonso et al. 2022 *Appl. Catal. B-Environ.* 318, 121795

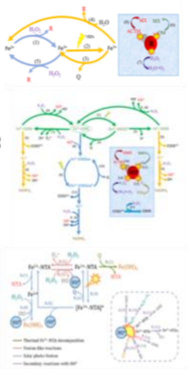


PHOTO FENTON PROCESS DESIGN

Strategy for the design and scale up of the process

Characteristics of wastewater → **Model development /calibration**

Environmental conditions (T, UV) → **Model Validation**

Historical Records (T, UV) → **Model application Reactor Design**

Demonstration-scale plant

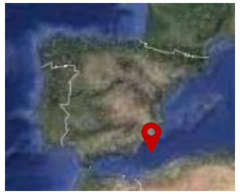
GOAL OF TREATMENT m^3/day

Photo-Fenton Process Design

Indoor
Lab scale

Outdoor
Pilot plant scale

Plant location
Demo-scale plant



FROM THE LAB TO THE DEMO PLANT

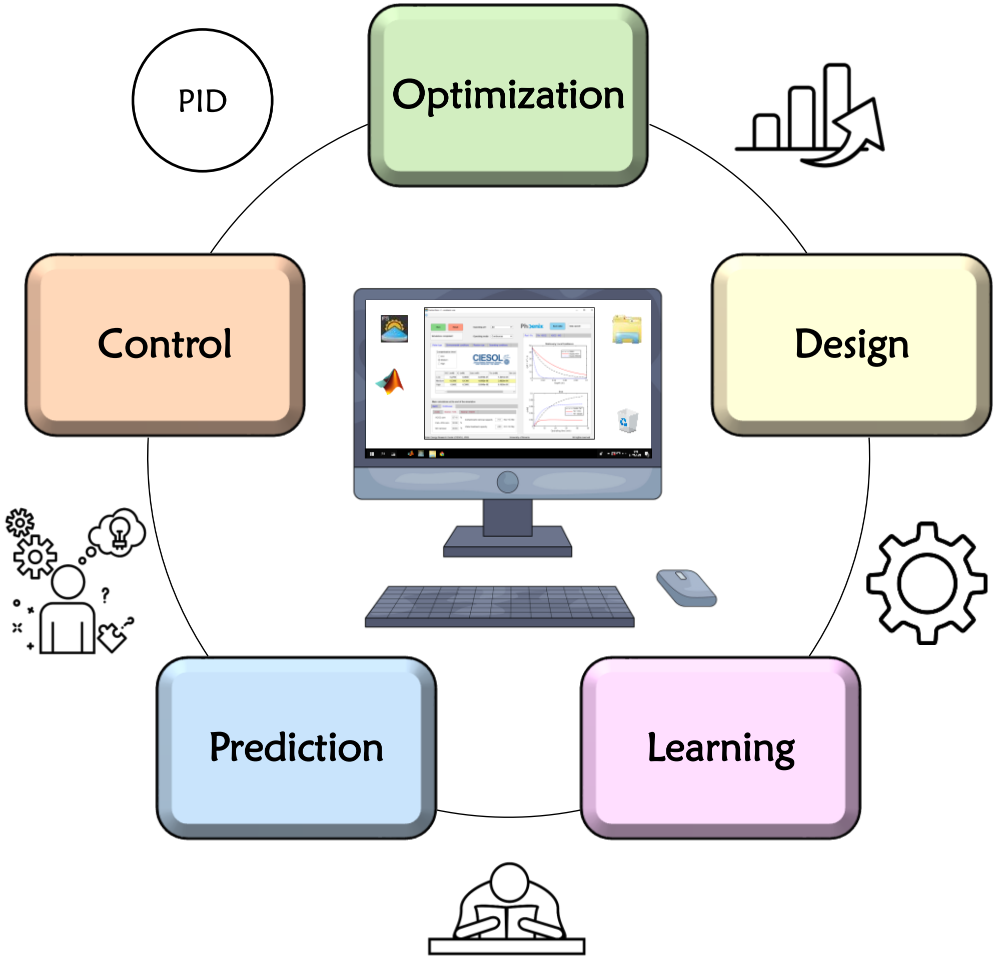
Automation and control of the plant is required

Interactive simulating tool for Design and optimization purposes

FentonSims

Free download!

Scan me!



FentonSims®

Development software:

Matlab® App

Designer R2021.b

Interactive simulating tool for Design and optimization purposes

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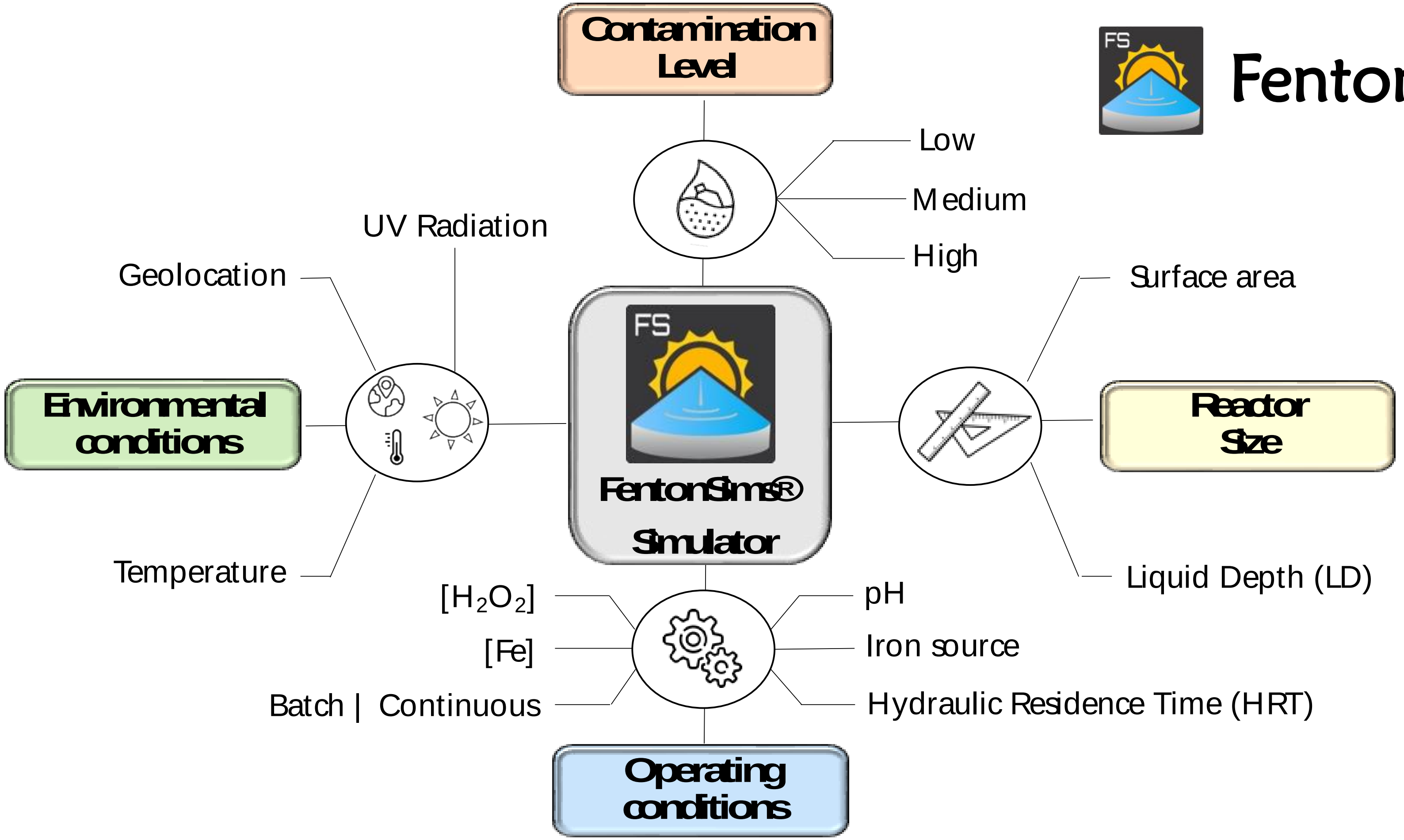


Interactive simulating tool for Design and optimization purposes

FentonSims®

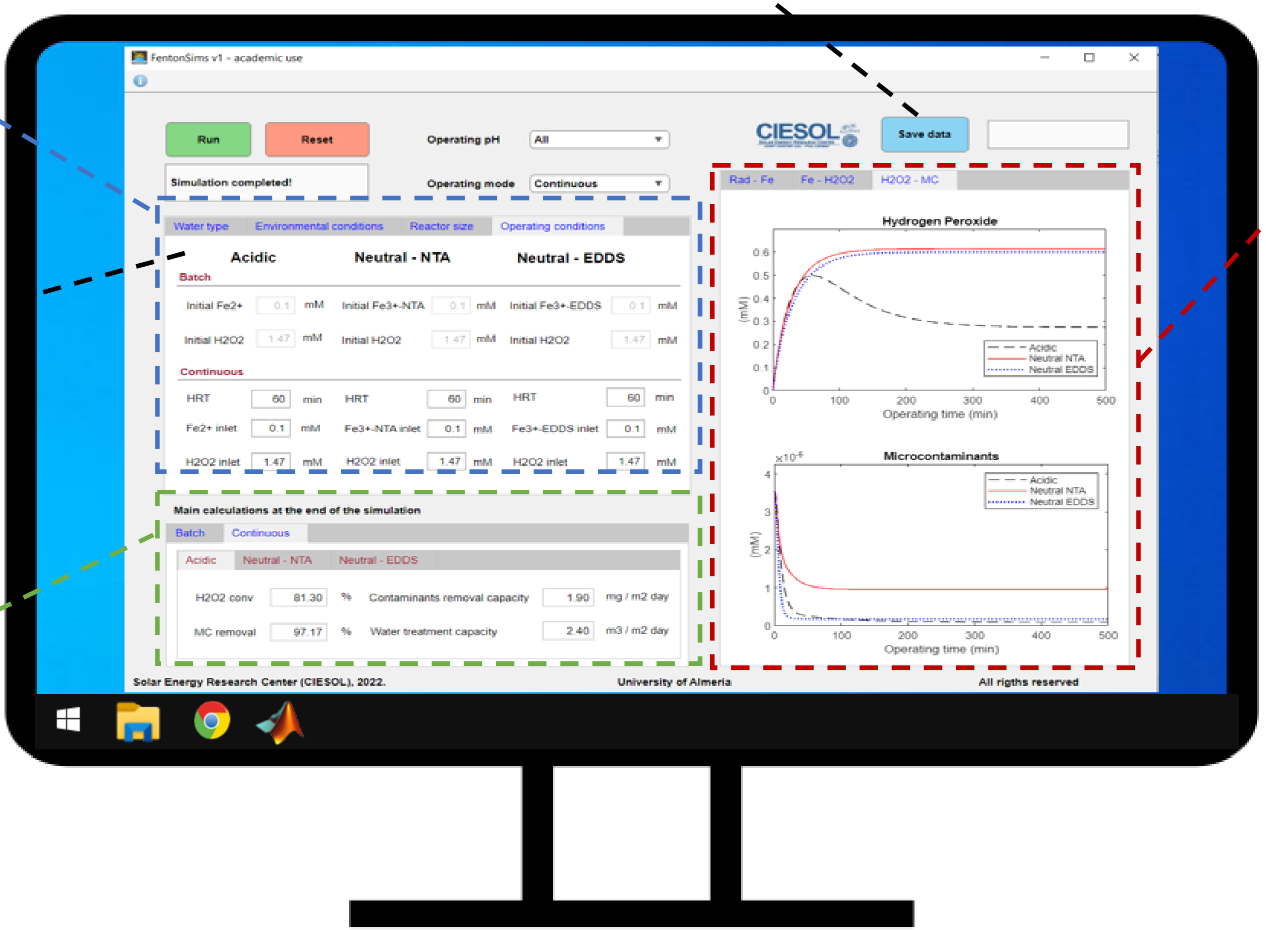
FentonSims® allows simulating with constant or variable radiation along the simulated experiment

User-Defined Parameters

Operating conditions

Main calculations

Data saving



Graphical results

Profiles of:

- Radiation
- Fe
- H_2O_2
- Microcontaminants

The possibility to work simultaneously with the 3 models is available

Photo Fenton plant construction

Photo Fenton plant construction

ULISES Solar photo Fenton tertiary plant final design

- ✓ RPR area: 100 m^2
- ✓ L/W: 25/2 > 10
- ✓ Liquid depth: 10 – 18 cm
- ✓ Inlet Flow: 10 – 37,5 m^3/h
- ✓ Operating hours: 6 – 10 h
- ✓ HRT: 45 – 60 min
- ✓ Treatment capacity: 0.8 – 1.9 m^3/m^2d

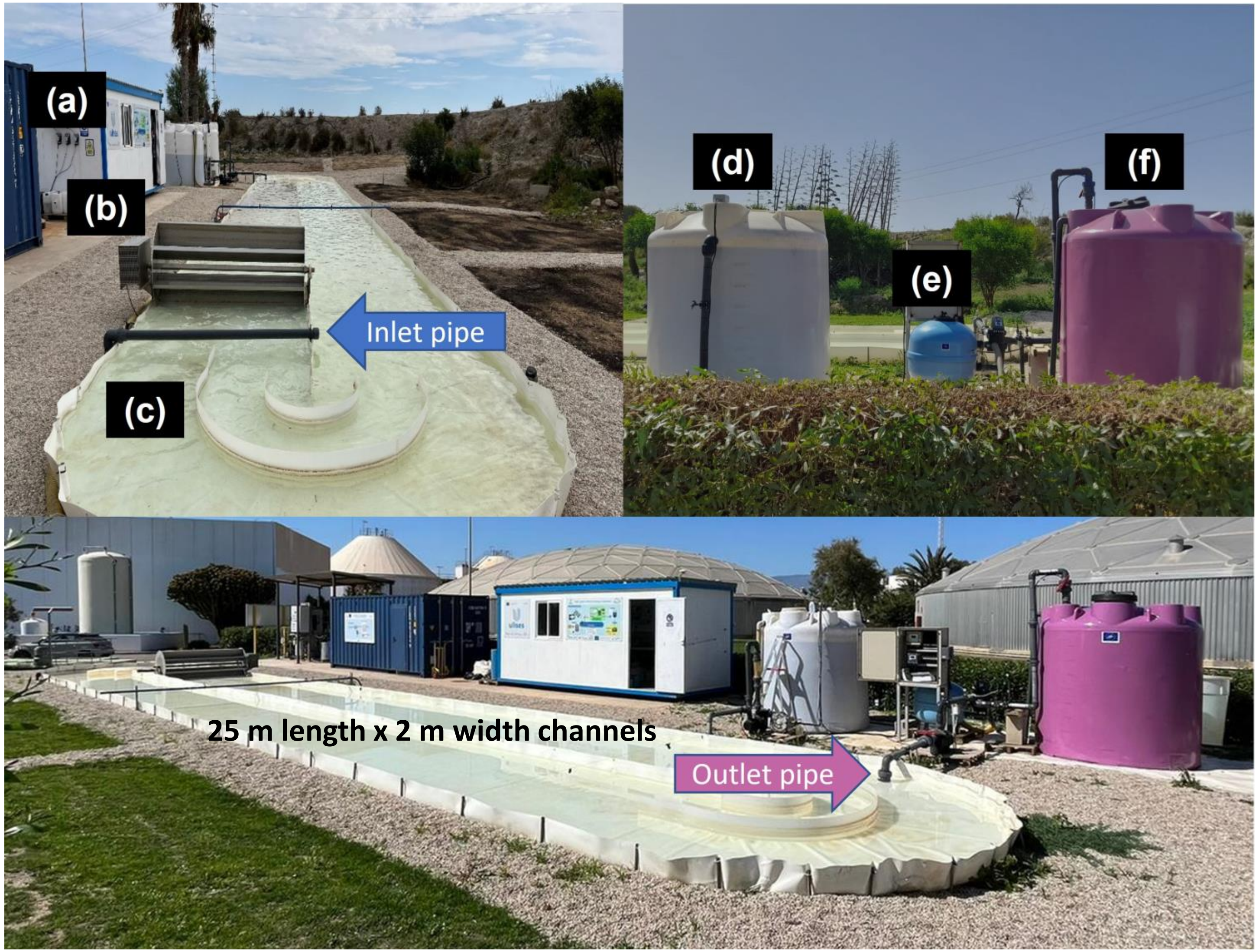
100 m^2 raceway pond reactor

Liquid depth: 10 – 18 cm

Secondary effluent from WWTP El Bobar, Almería, 200,000 inhabitants

ulises

Photo Fenton plant construction



'El Bobar' WWTP, Almeria (Spain)

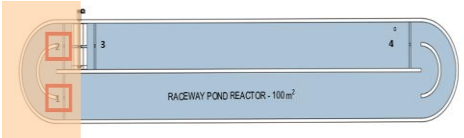
ulises aqualia

Low Cost construction

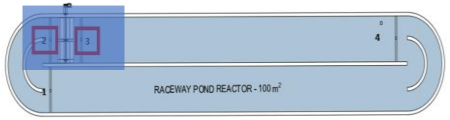
(a) dosing pumps (3x)
(b) paddlewheel
(c) raceway pond reactor
(d) conditioning tank
(e) calcium carbonate filter
(f) storage tank

Fluid dynamics characterization

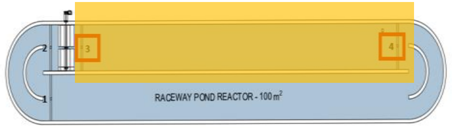
Section 1: Bend mixing



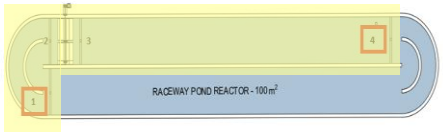
Section 2: Paddle-wheel mixing



Section 3: Longitudinal mixing



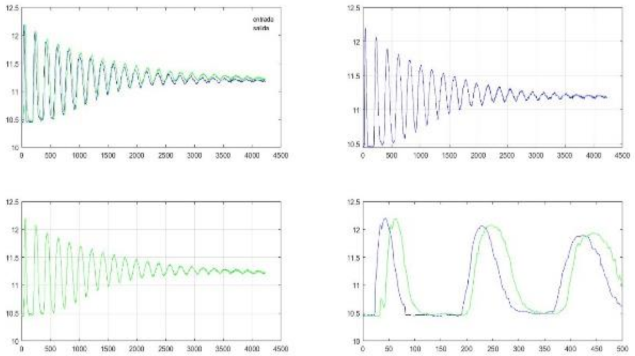
Section 4: Bend & longitudinal mixing



The overall behavior of the reactor is plug flow.

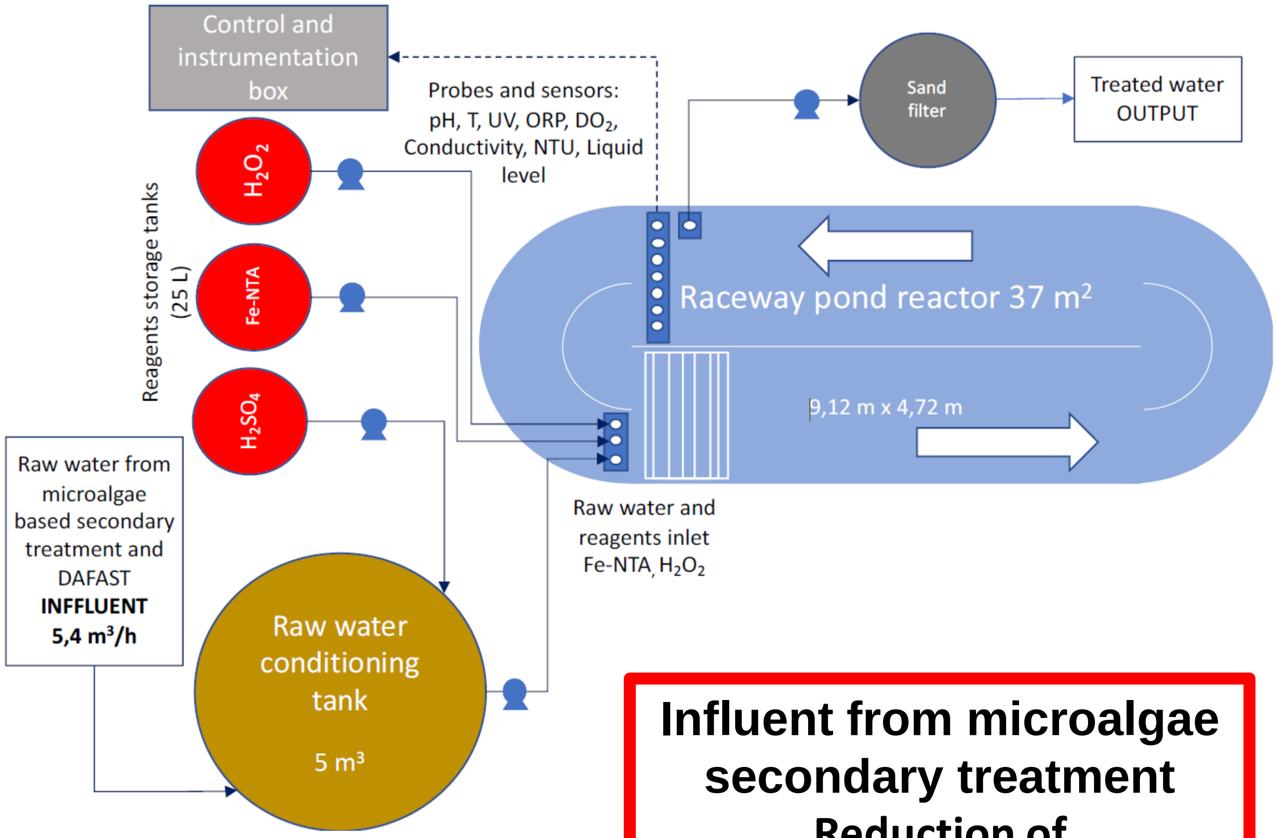
Characterization of the reactor

Recorded data



	Motor frequency (Hz)	Paddlewheel speed (rpm)	Circulation speed (m/s)	Cycling time (min)	Mixing time (min)	Power consumtion (W/m3)
18 cm	15	5.6	0.15	5.4	72	17.26
	25	8.4	0.27	3.2	58	21.58
	35	**10.6**	**0.33**	**2.5**	**46**	**29.35**
10 cm	15	6.3	0.11	7.5	99	26.41
	25	10.6	0.16	5.3	71	31.07
	35	15	0.19	4.4	64	35.11

Photo Fenton plant construction



Influent from microalgae secondary treatment
Reduction of
(CO_3^{2-}, NH^{4+}, PO_4^{3-})

Phoenix

- ✓ RPR area: 37 m²
- ✓ L/W ratio = 2
- ✓ L=9,1 m; W=4,6 m
- ✓ Liquid depth: 10 – 20 cm
- ✓ Inlet Flow: 3.7 – 9.8 m³/h
- ✓ Operating hours: 6 – 10 h
- ✓ HRT: 15 - 60 min
- ✓ Treatment capacity:
  - ✓ 0.8 – 1.9 m³/m²d
- ✓ Material: HDPE (10 mm)

Optimizing the reactor geometry is recommended to improve the operating conditions.

L/W ratio = 2

The design included a new drain to work at different liquid level

Photo Fenton plant construction

Paddle wheel before be assembled

Raceway Pond Reactor Vessel

El Toyo WWTP

aqualia Phoenix

- ✓ RPR area: 37 m^2
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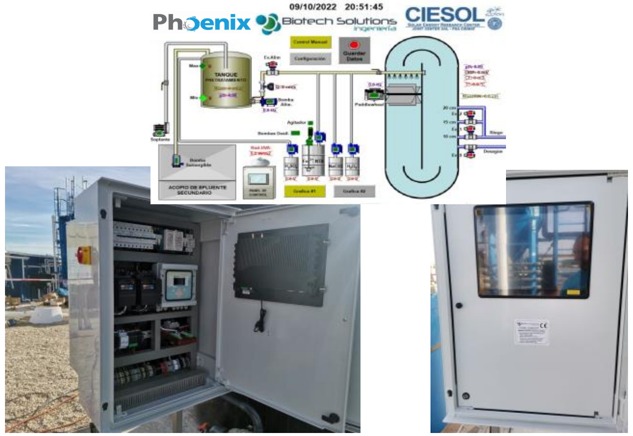
  - ✓ 0.8 – 1.9 m^3/m^2d
- ✓ Material: HDPE (10 mm)

Photo Fenton plant construction

Raceway Pond Reactor

Conditioning tank



SCADA and control box

Phoenix

aqualia

El Toyo WWTP

Dosing pumps

Dosing points

Fluid dynamics characterization

WWTP *EL Bobar*

Demo plant 100 m^2 (18 m^3)

Motor frequency (Hz)	Liquid depth (cm)	Paddlewheel rotational speed (rpm)	Circulation time (min)	Mixing time (min)
15	10	6.3	7.5	99
25		11	5.3	71
35		15	4.4	64
15	18	5.6	5.4	72
25		8.4	3.2	58
35		11	2.5	46

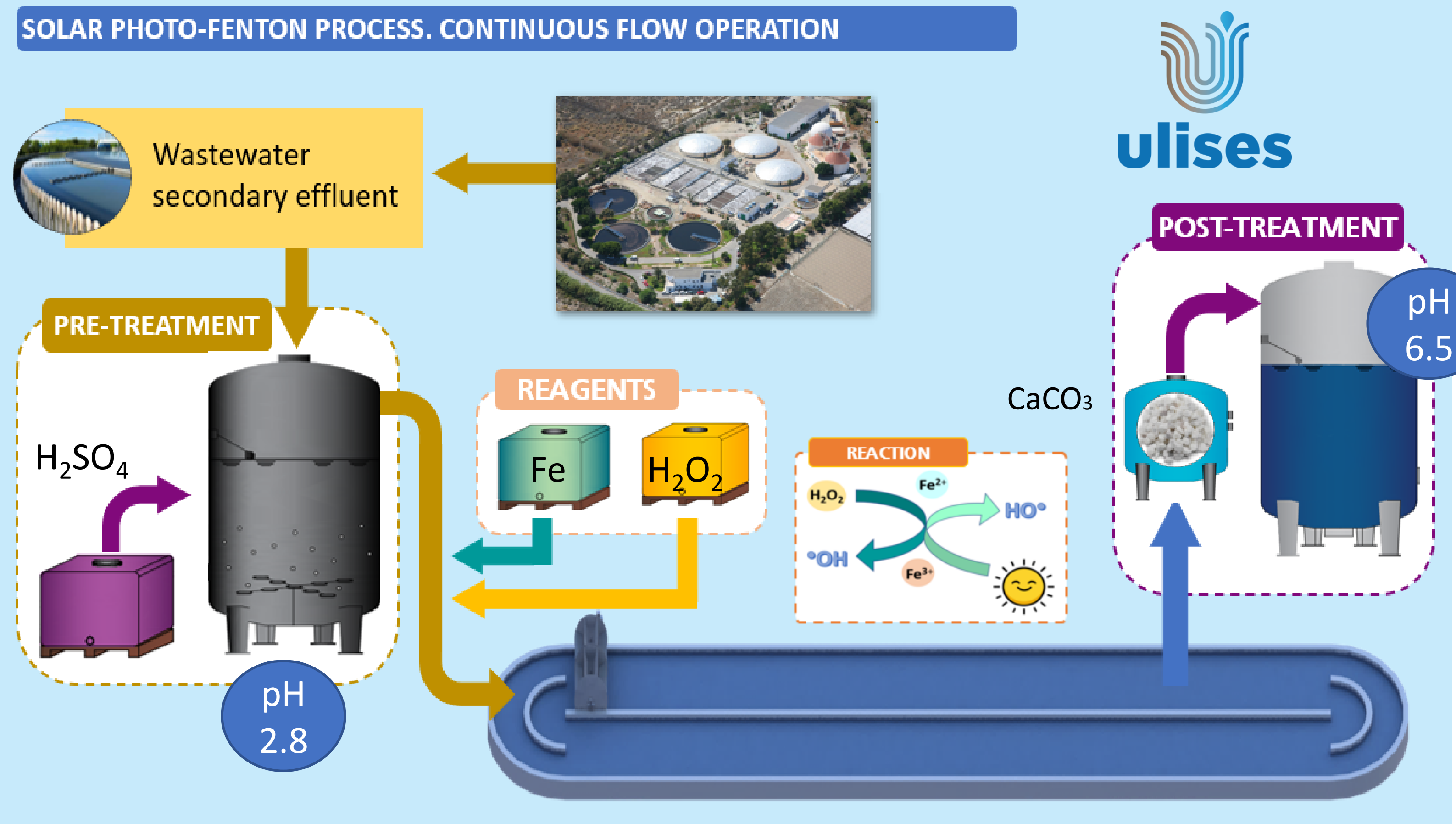
WWTP *El Toyo*

Automatic demo plant *37* m^2 (7.4 m^3)

Liquid Depth (cm)	*Paddlewheel Engine Frecuency (Hz)*	*Mixing time (min)*
10	15	30
	25	25
	35	15
20	15	20
	25	10
	35	-

Plant operation

Continuous flow operation. Acidic pH



Gualda-Alonso et al., 2022

Appl. Catal. B-Environ. 319, 121908

Applied Catalysis B: Environmental 319 (2022) 121908

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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

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[a] Solar Energy Research Centre (CIESOL), Ctra. de Sacramento s/n, Almería 04120, Spain
[b] Chemical Engineering Department, University of Almería, Almería 04120, Spain
[c] Department of Chemistry and Physics, University of Almería, Almería 04120, Spain

Inlet TIC: 90 mg/L

TIC removed with H_2SO_4
85% H_2SO_4 consumed to broke carbonate buffer and reduce TIC. 15% to drop pH.

Important to reduce the scavenger effect of the carbonates

Acidic pH 2.8

1.47 mM H_2O_2
0.1 mM Fe

HRT
60 min
45 min

10 cm - Winter
18 cm - Summer

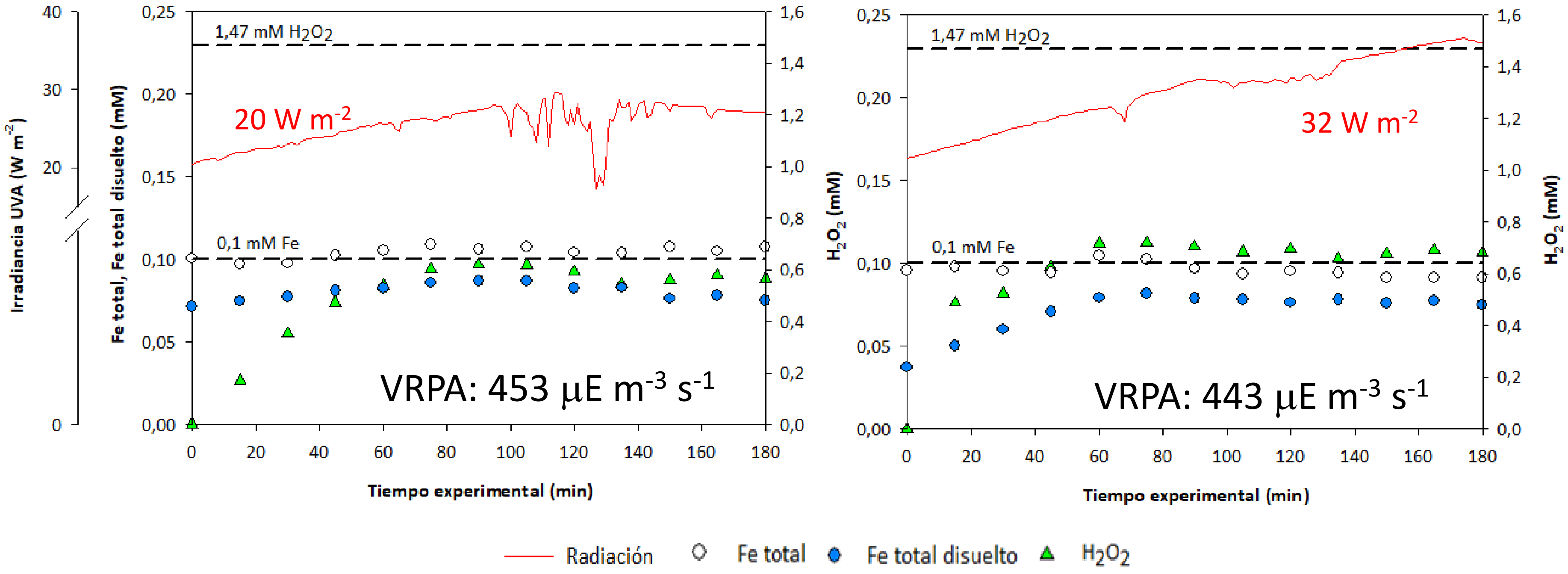
Continuous flow operation. Acidic pH

Acidic pH

0,1 mM $FeSO_4$
1,47 mM H_2O_2

Winter
10 cm, 60 min

Summer
18 cm, 45 min



Constant Flows of Reagents

Higher irradiance in summer allows working at higher liquid depth

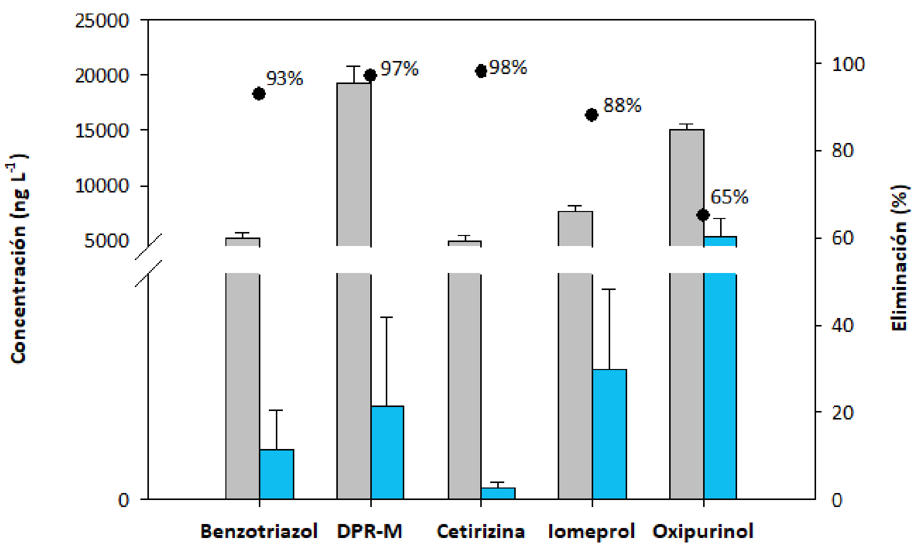
Micropollutant removal

Efluente secundario | Agua tratada | % Eliminación

Acidic pH

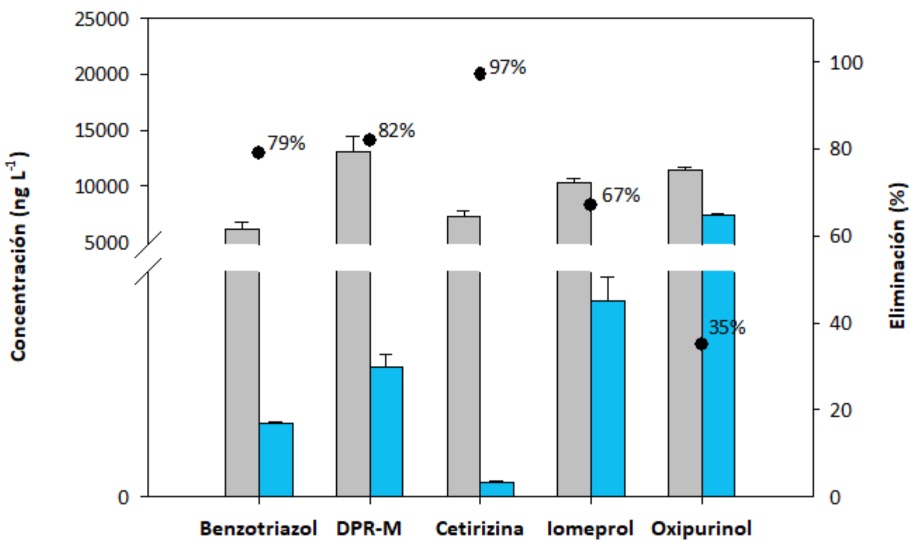
> 80% total CEC load removal

Winter



Total CECs load: 125 µg L^{-1}
Removal: **85%**
Treatment capacity: 800 L m^{-2} d^{-1}

Summer

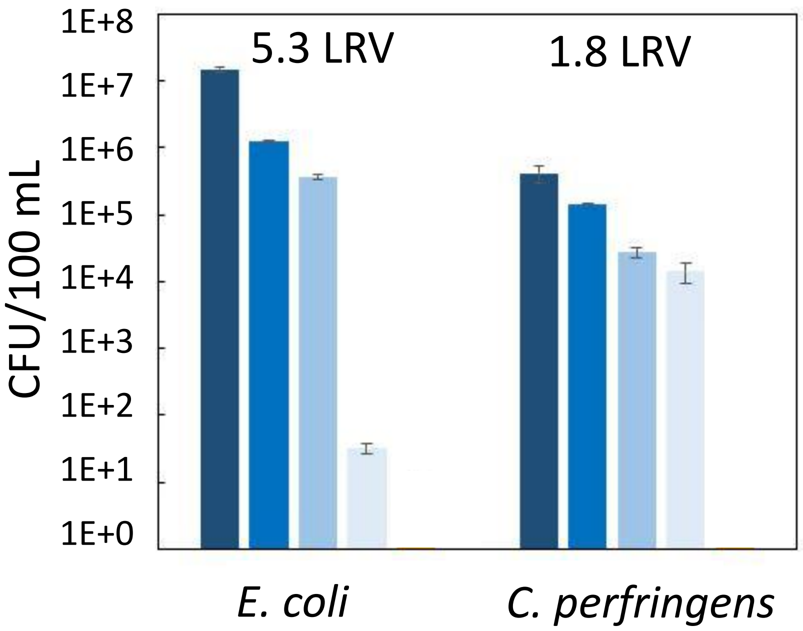


Total CECs load : 92 µg L^{-1}
Removal: **79%**
Treatment capacity: 1.920 L m^{-2} d^{-1}

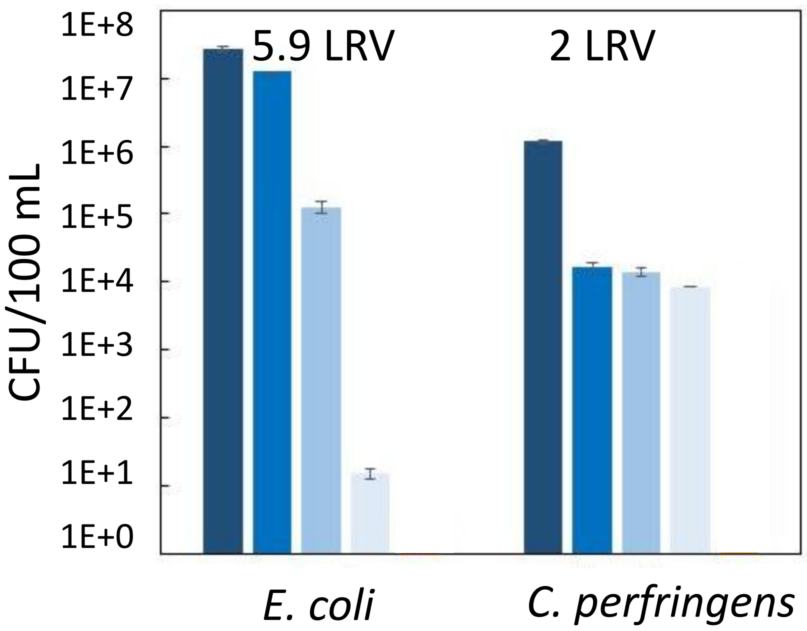
Continuous flow operation. Acidic pH

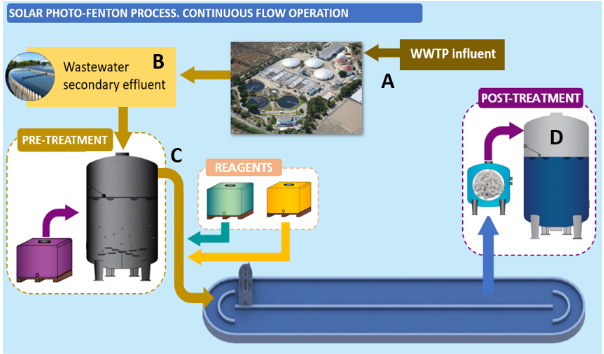
Disinfection

Winter



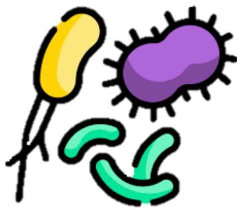
Summer





A : WWTP influent
B : WW secondary effluent
C : Conditioning tank
D : Treated water

LRV (log_{10} reduction value)



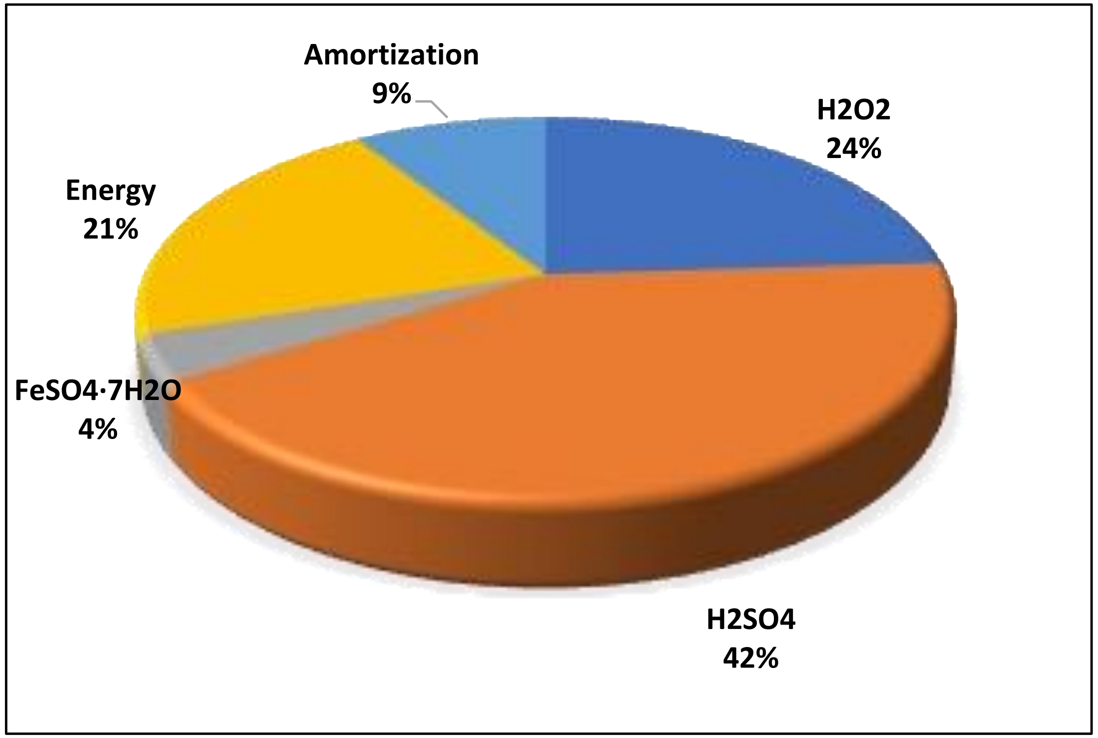
- ✓ Only 2 LRV was attained for *Clostridium perfringens* after treatment
- ✓ *Escherichia coli* concentration was within the monitoring requirements for reclaimed water quality Class A (≤ 10 CFU/100 mL) in EU 2020/741 regulation

Economic evaluation

> 80% total CEC load removal

0,33 € m^{-3}

Constant Flows of Reagents



1.47 mM H_2O_2
0.1 mM Fe

60 min
45 min

10 cm - Winter
18 cm - Summer

Process control and optimization

Strategy for the design and scale up of the process

Characteristics of wastewater → **Model development**

Environmental conditions (T, UV) → **Model Validation**

Historical Records (T, UV) → **Model application Reactor Design**

Demonstration-scale plant

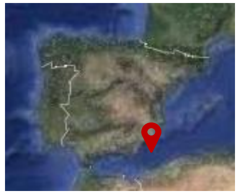
GOAL OF TREATMENT m^3/day

Photo-Fenton Process Design

Indoor
Lab scale

Outdoor
Pilot plant scale

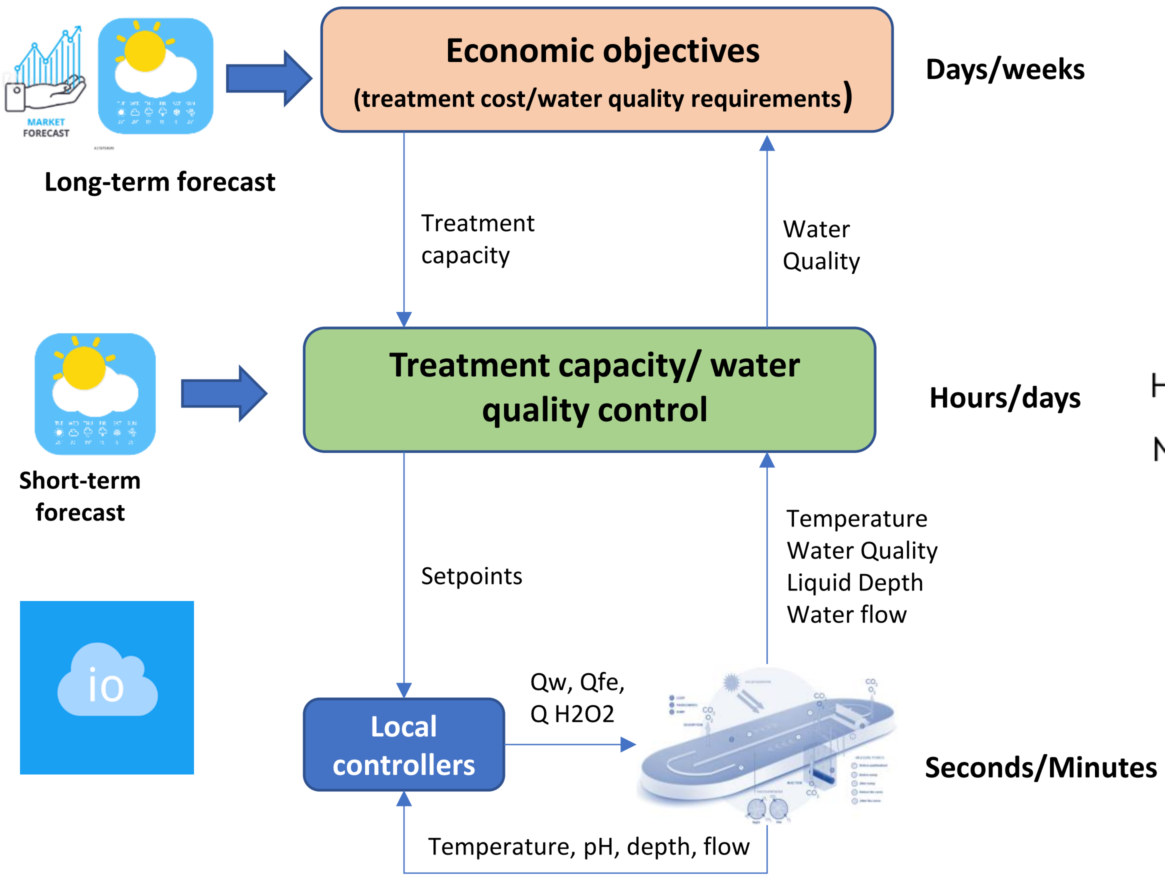
Plant location
Demo-scale plant

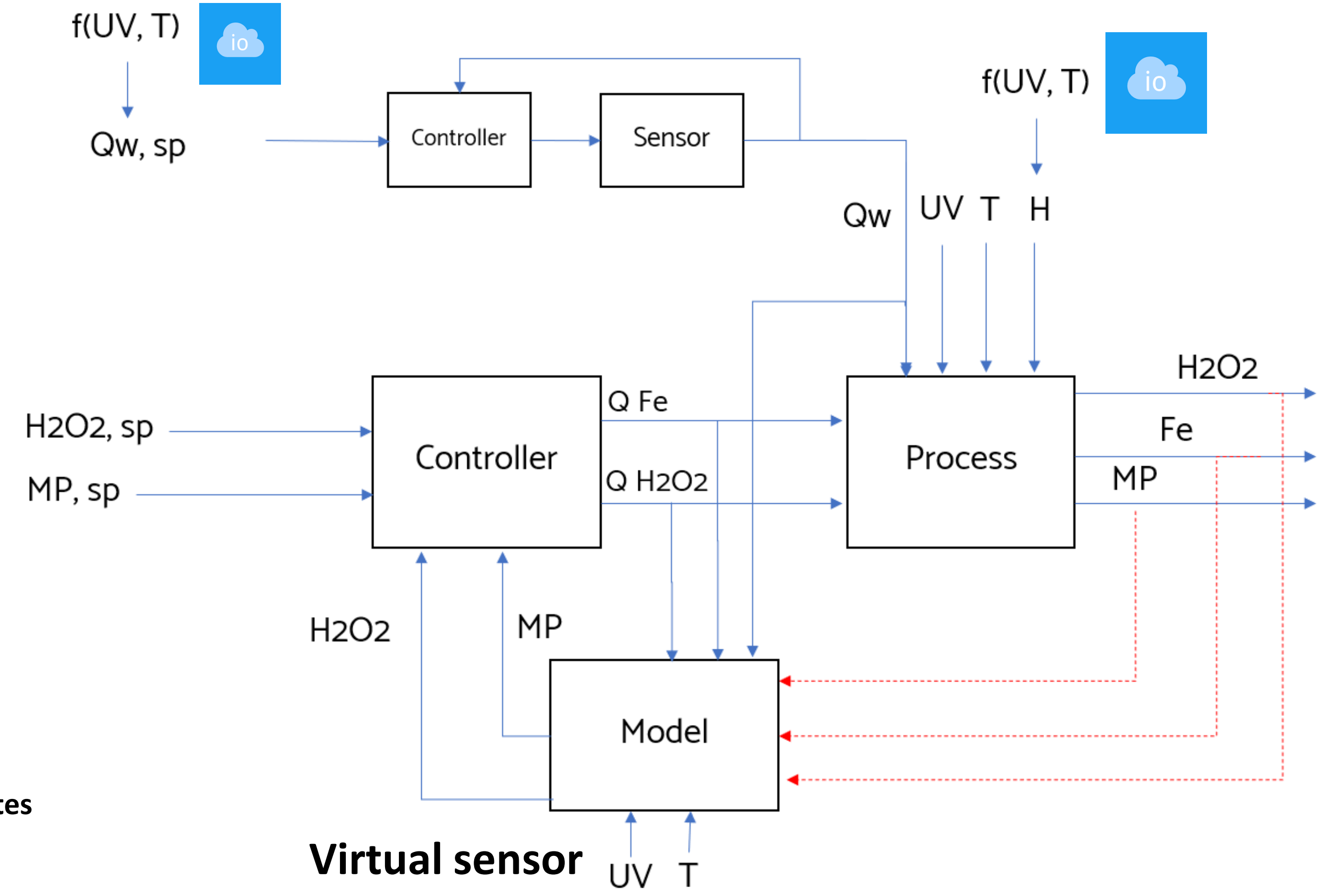


FROM THE LAB TO THE DEMO PLANT

Automation and control of the plant is required

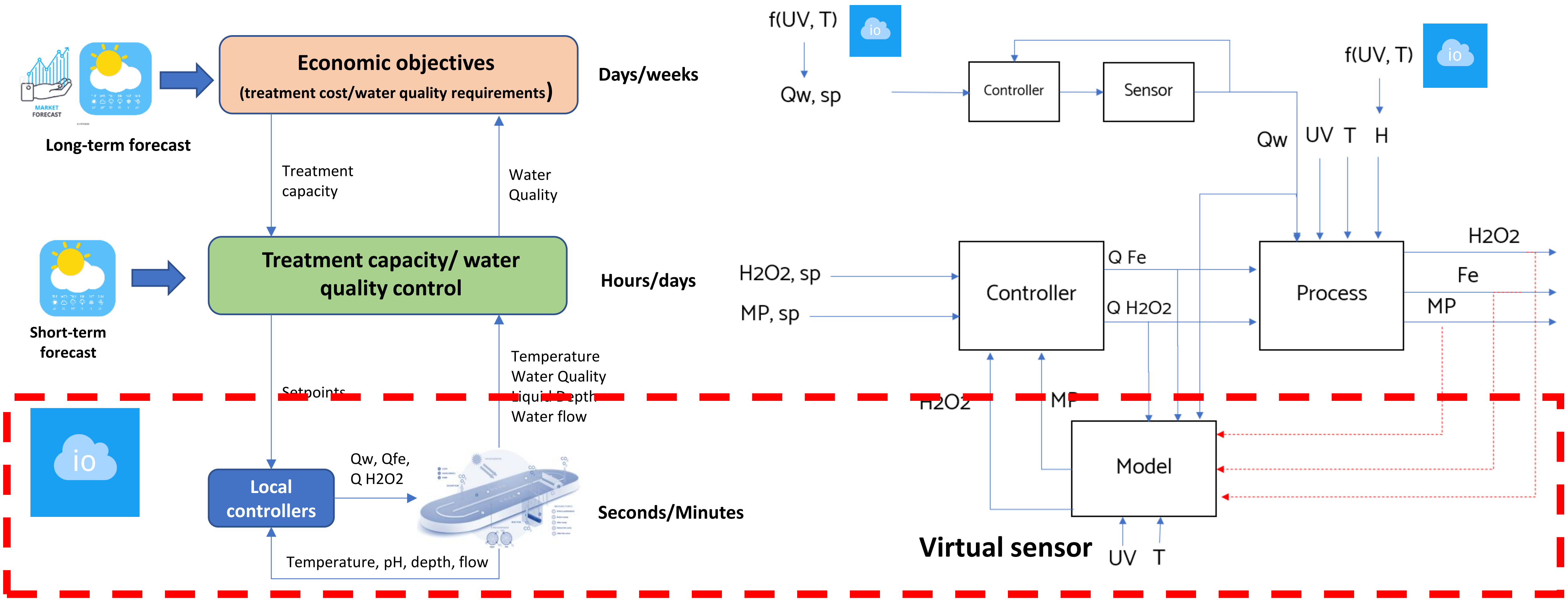
PHOTO FENTON PROCESS CONTROL





Virtual sensors

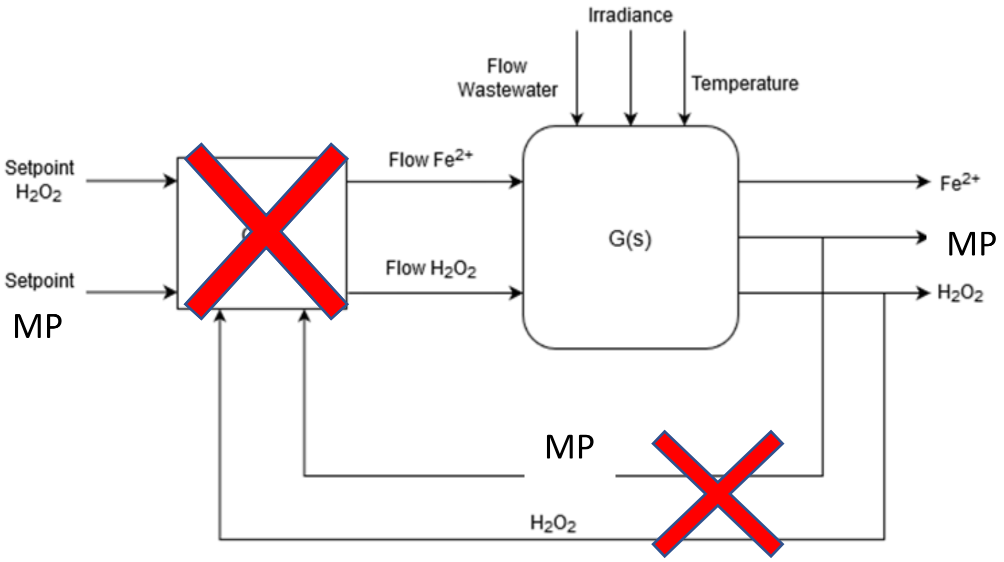
PHOTO FENTON PROCESS CONTROL



OPEN LOOP

Manual operation

Inlet flows of iron and H_2O_2 constants

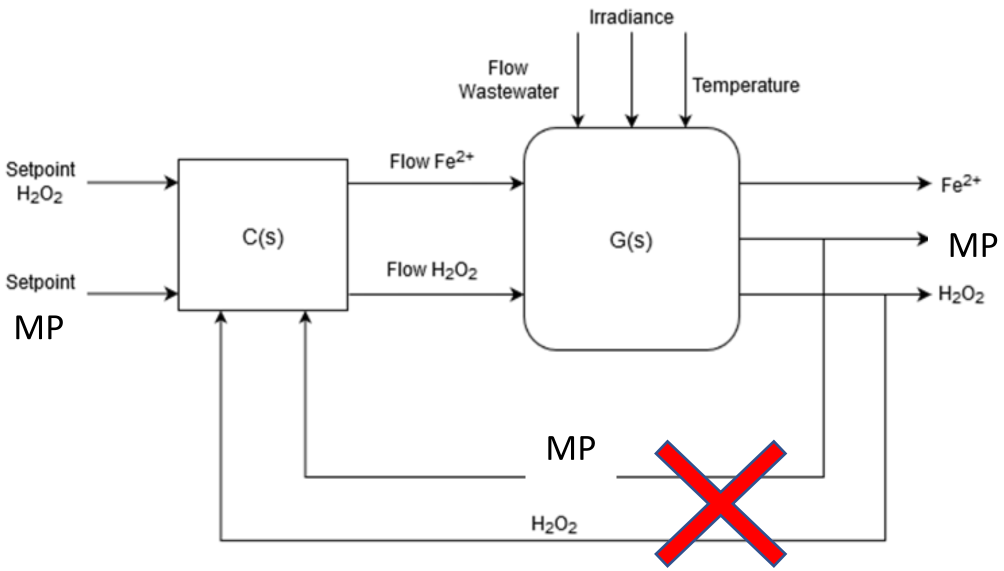


Unstable and inefficiency operation

CLOSED LOOP

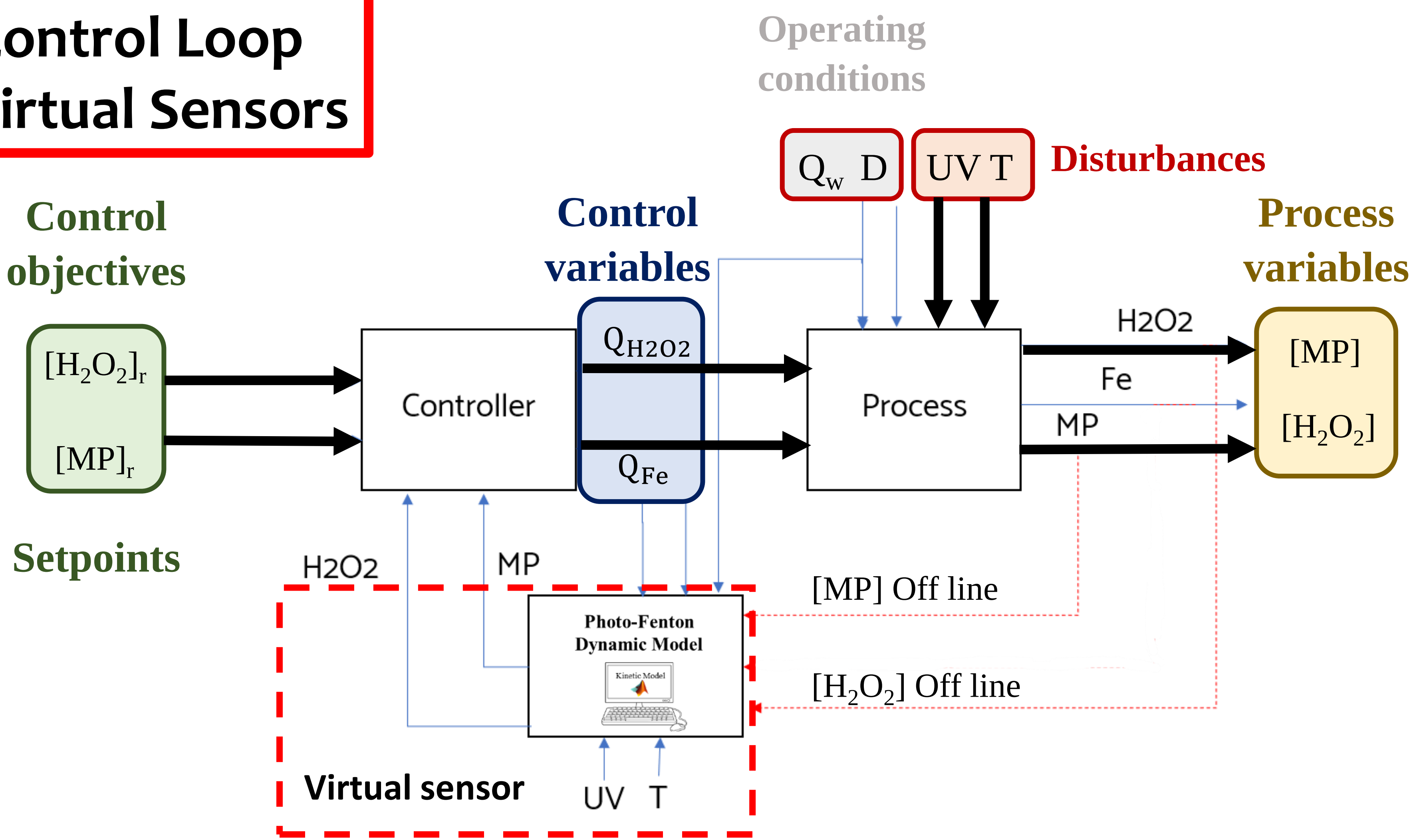
Automatic operation

Flows of iron and H_2O_2 are control variables

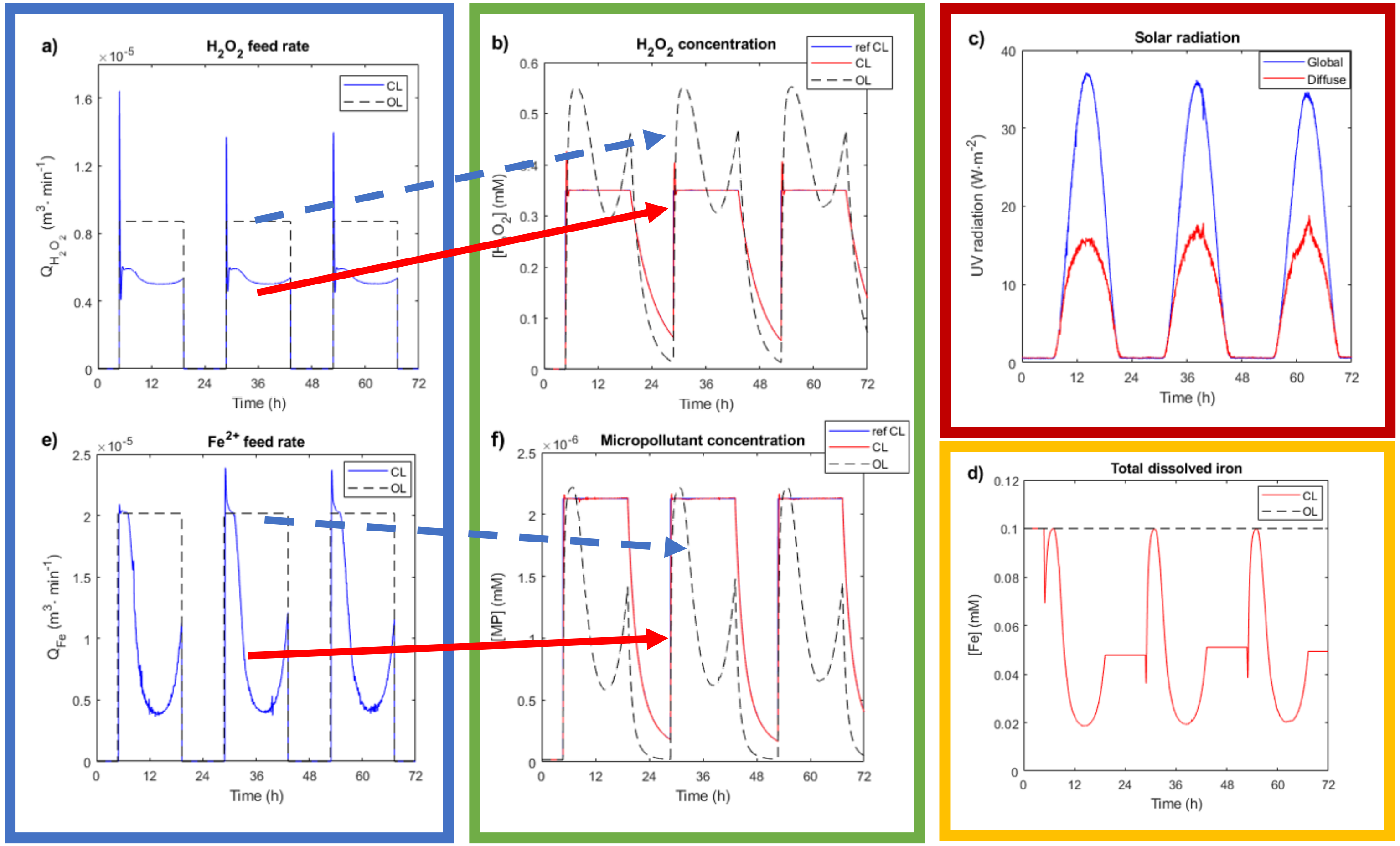


MP & H_2O_2 online probes not available

Closed Control Loop based in Virtual Sensors



OPEN LOOP vs CLOSED LOOP



Disturbance

Control Variables

Process Variables

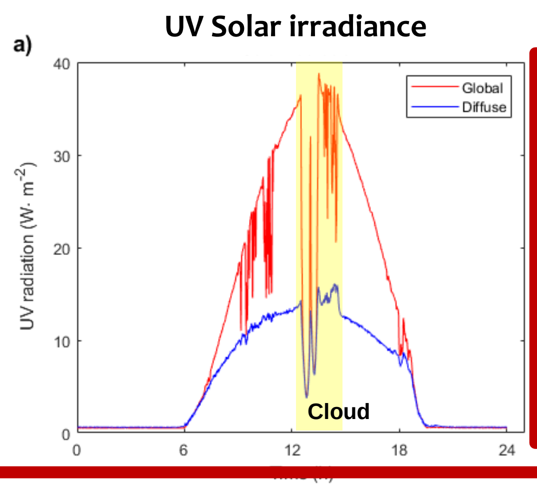
Model Input

Open Loop – – –
Closed Loop ———

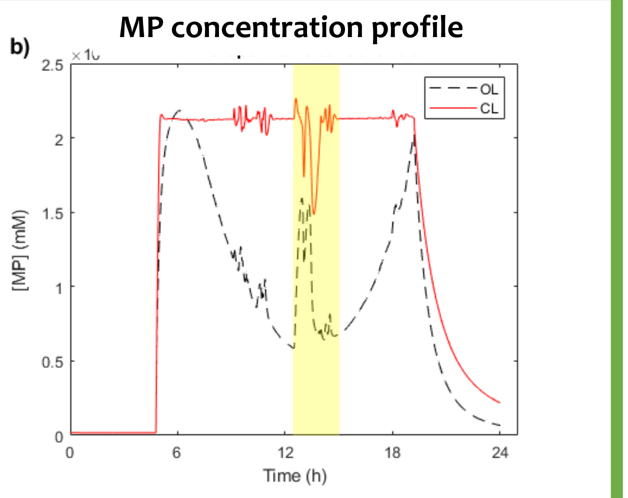
July 2021
D = 10 cm
HRT = 30 min

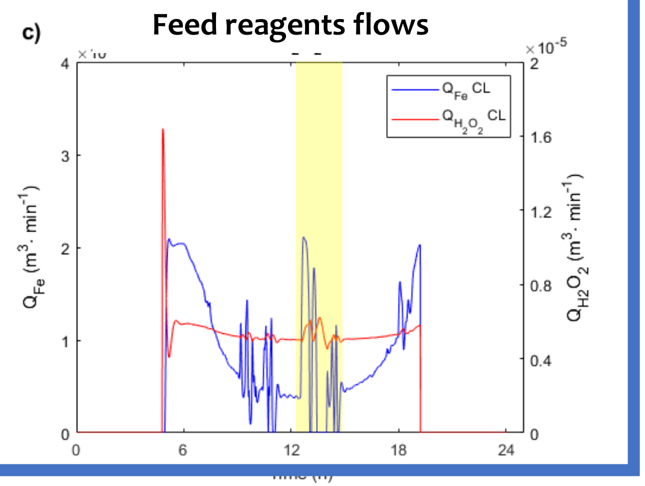
The control system adapt the operation of the process to the environmental conditions in a clear day giving a stable and robust behavior

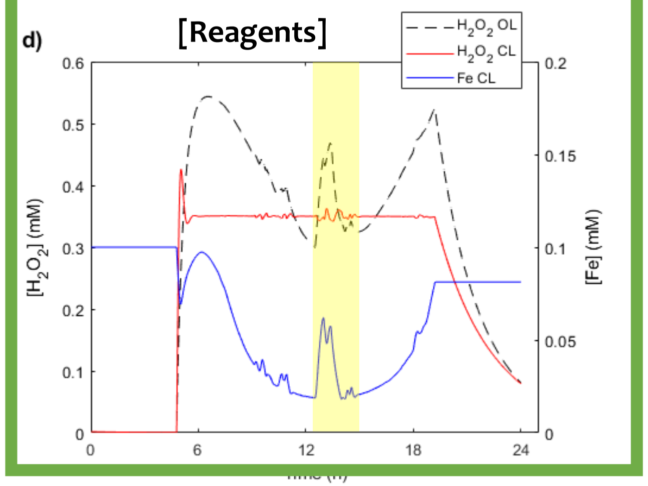
DISTURBANCE COMPENSATION



Disturbance







Control Variables

Process Variables

Simulation for a cloudy operating day. 1st June 2021.

Open Loop – – –

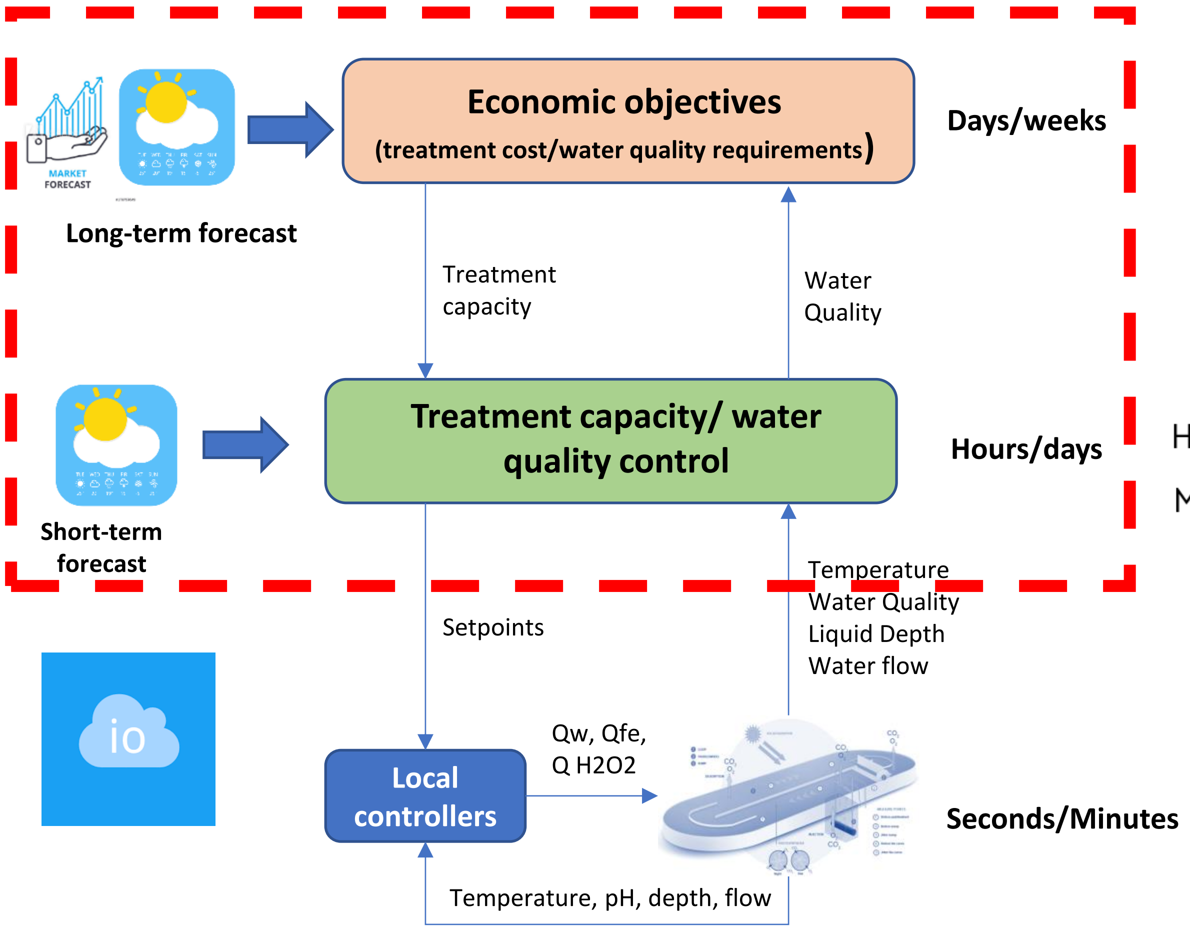
Closed Loop ——

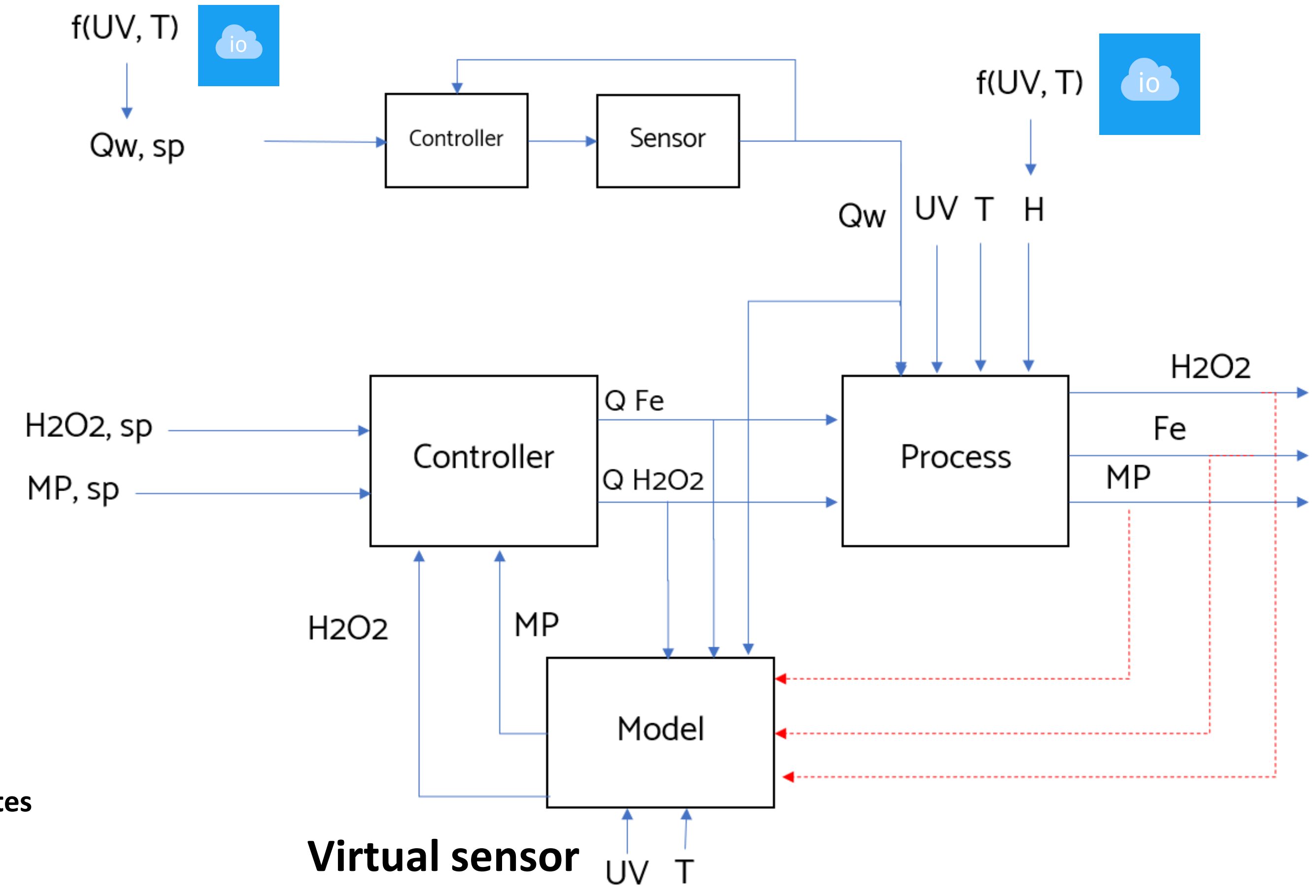
Control system remove the influence of the UV perturbation

Stable and robust behavior of the simulated plant is achieved with the proposed control system schema

Event based robust control
Process optimization

PROCESS OPTIMIZATION





Closed loop optimization

Simulations

MATLAB®

6 Factor (5 levels) | 5^6 = 15625 simulations

- D → [0.10 0.15 0.20 0.25 0.30] m
- HRT → [15 30 45 60 75] min
- Rad → [10 20 30 40 50] $W \cdot m^{-2}$
- T → [15 20 25 30 35] ºC
- $[MP]_{setpoint}$ → [50 60 70 80 90] %
- $[H_2O_2]_{setpoint}$ → [5 10 15 20 25] $mg \cdot L^{-1}$

Response Variables

$Cost_{Total}$ ($€ \cdot m^{-3}$) (Cost Fe + Cost H_2O_2)

$Cost_{Efficiency}$ ($mg \cdot €^{-1} \cdot m^{-2}$)

MP removal is considered

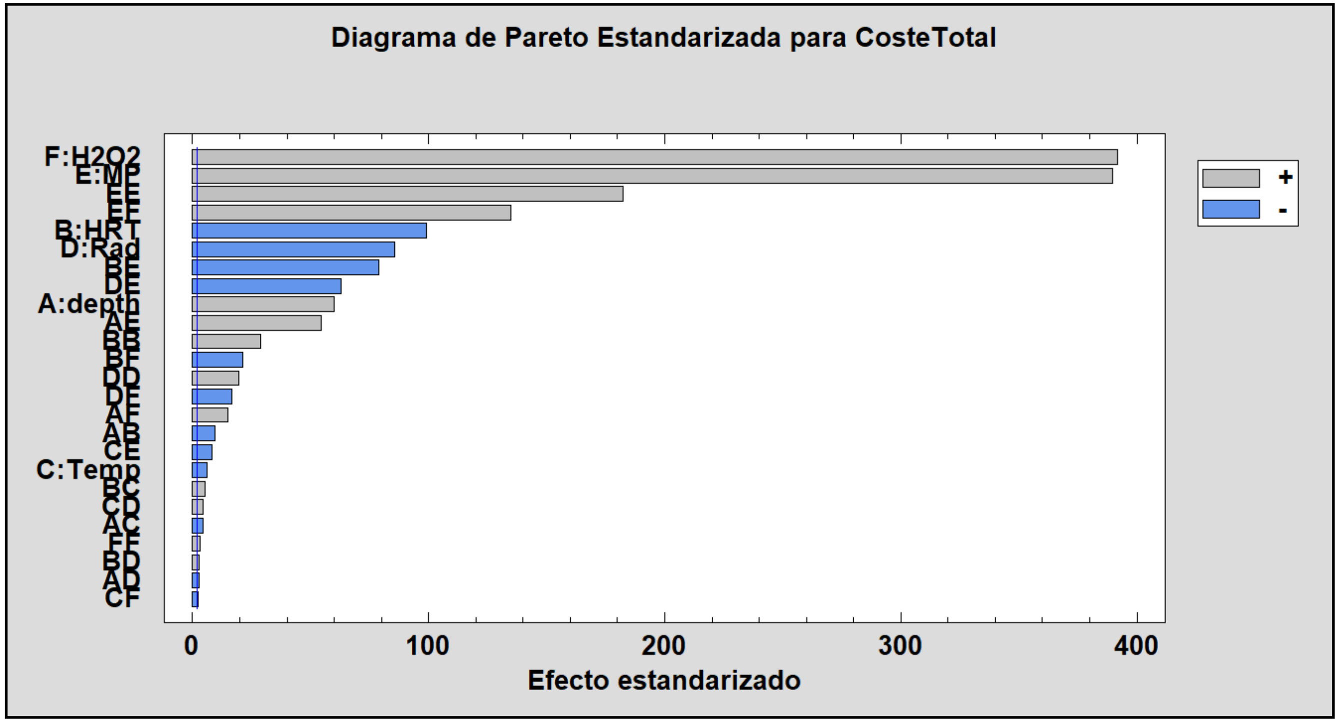
Only reagents cost are considered

Optimization based on total cost or efficiency cost ($€ \cdot m^{-3}$ or $mg \cdot €^{-1} \cdot m^{-2}$)

Models

1. $Cost_{Total}$ ($€\cdot m^{-3}$)

- Cuadratic model
- 26 parameters
- R^2 = 96 %



Analizar Experimento - CosteTotal

Coef. de regresión para CosteTotal

Coeficiente	*Estimado*
constante	0,209691
A:depth	-0,141819
B:HRT	0,000449961
C:Temp	0,000224027
D:Rad	0,000515817
E:MP	-0,00659086
F:H2O2	-0,00172982
AB	-0,00031482
AC	-0,000430923
AD	-0,000127935
AE	0,00271527
AF	0,00150445
BB	0,0000038268
BC	0,00000171896
BD	4,58407E-7
BE	-0,0000130733
BF	-0,00000699785
CD	0,00000216711
CE	-0,00000413828
CF	-0,00000221222
DD	0,00000584225
DE	-0,000015635
DF	-0,00000817373
EE	0,0000540954
EF	0,0000669937
FF	0,00000362448

El StatAdvisor

Esta ventana despliega la ecuación de regresión que se ha ajustado a los datos. La ecuación del modelo ajustado es

CosteTotal = 0,209691 - 0,141819*depth + 0,000449961*HRT + 0,000224027*Temp + 0,000515817*Rad - 0,00659086*MP - 0,00172982*H2O2 - 0,00031482*depth*HRT - 0,000430923*depth*Temp - 0,000127935*depth*Rad + 0,00271527*depth*MP + 0,00150445*depth*H2O2 + 0,0000038268*HRT^2 + 0,00000171896*HRT*Temp + 4,58407E-7*HRT*Rad - 0,0000130733*HRT*MP - 0,00000699785*HRT*H2O2 + 0,00000216711*Temp*Rad - 0,00000413828*Temp*MP - 0,00000221222*Temp*H2O2 + 0,00000584225*Rad^2 - 0,000015635*Rad*MP - 0,00000817373*Rad*H2O2 + 0,0000540954*MP^2 + 0,0000669937*MP*H2O2 + 0,00000362448*H2O2^2

en donde los valores de las variables están especificados en sus unidades originales. Para hacer que STATGRAPHICS evalúe esta función, seleccione Predicciones de la lista de Opciones Tabulares. Para graficar la función, seleccione Gráficas de Respuesta de la lista de Opciones Gráficas.

statgraphics 18 centurion

Optimization process

1. Response variable selection ⇨ Cost function ⇨ Model $Cost_{Total}$ $(€·m^{-3})$ / Model $Cost_{Efficiency}$ $(mg·€^{-1}·m^{-2})$
2. Minimal % removal MP ⇨ **Restriction:** $[MP] \geq \%Removal_{mín}$
3. Limits for set points ⇨
   - **Restriction:** $5\ mgL^{-1} \leq [H_2O_2]_{setpoint} \leq 25\ mgL^{-1}$
   - **Restriction:** $50\% \leq [MP]_{setpoint} \leq 90\%$
4. Minimal water Flow to treat ⇨ **Restriction:** $Qw_{mín}\ (m^3·min^{-1}) \leq \frac{S(m^2) \cdot D(m)}{HRT\ (min)}$
5. Limits for D and HRT ⇨
   - **Restriction:** $0.10\ m \leq D \leq 0.30\ m$
   - **Restriction:** $15\ min \leq HRT \leq 75\ min$
6. Environmental conditions ⇨ T(ºC) | Rad $(W·m^{-2})$ (Sensors)
7. To Solve optimization ⇨ Optimized Variables: D(m), HRT(min), $[MP]_{setpoint}$ & $[H_2O_2]_{setpoint}$

PROCESS OPTIMIZATION

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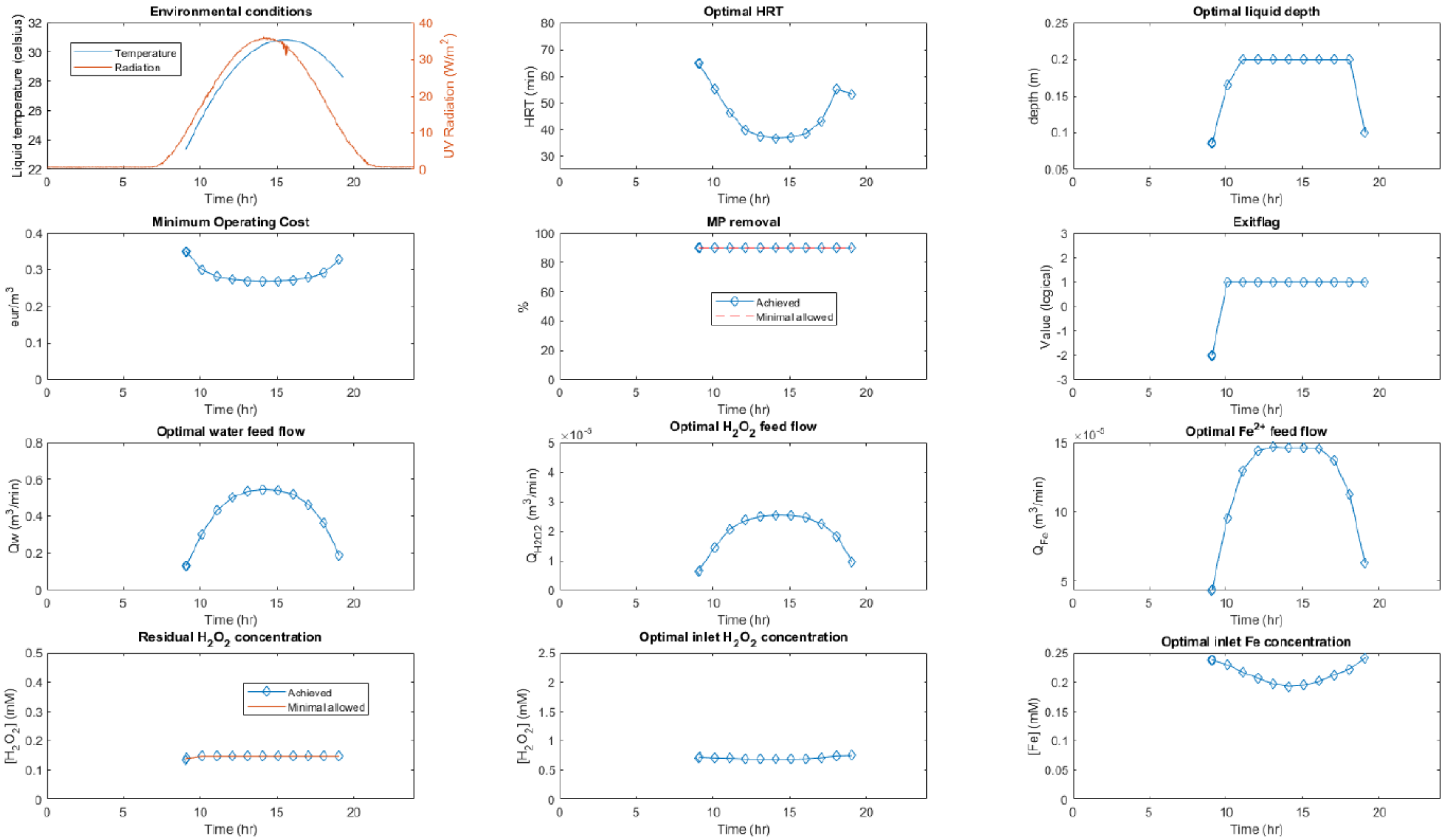
STATISTICAL OPTIMIZATION TOOLS

Event based robust control

90% CECs removal objective



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PROCESS OPTIMIZATION

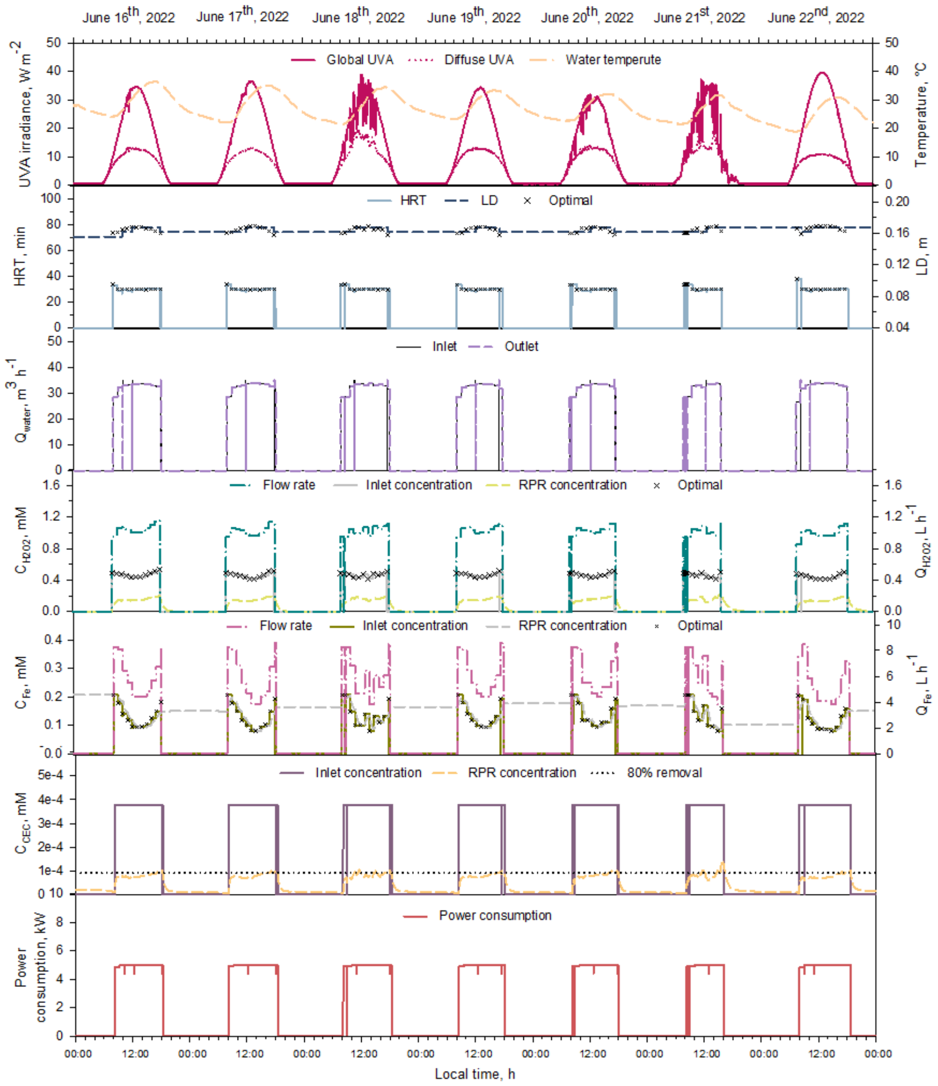
PUREAGROH2O Phoenix

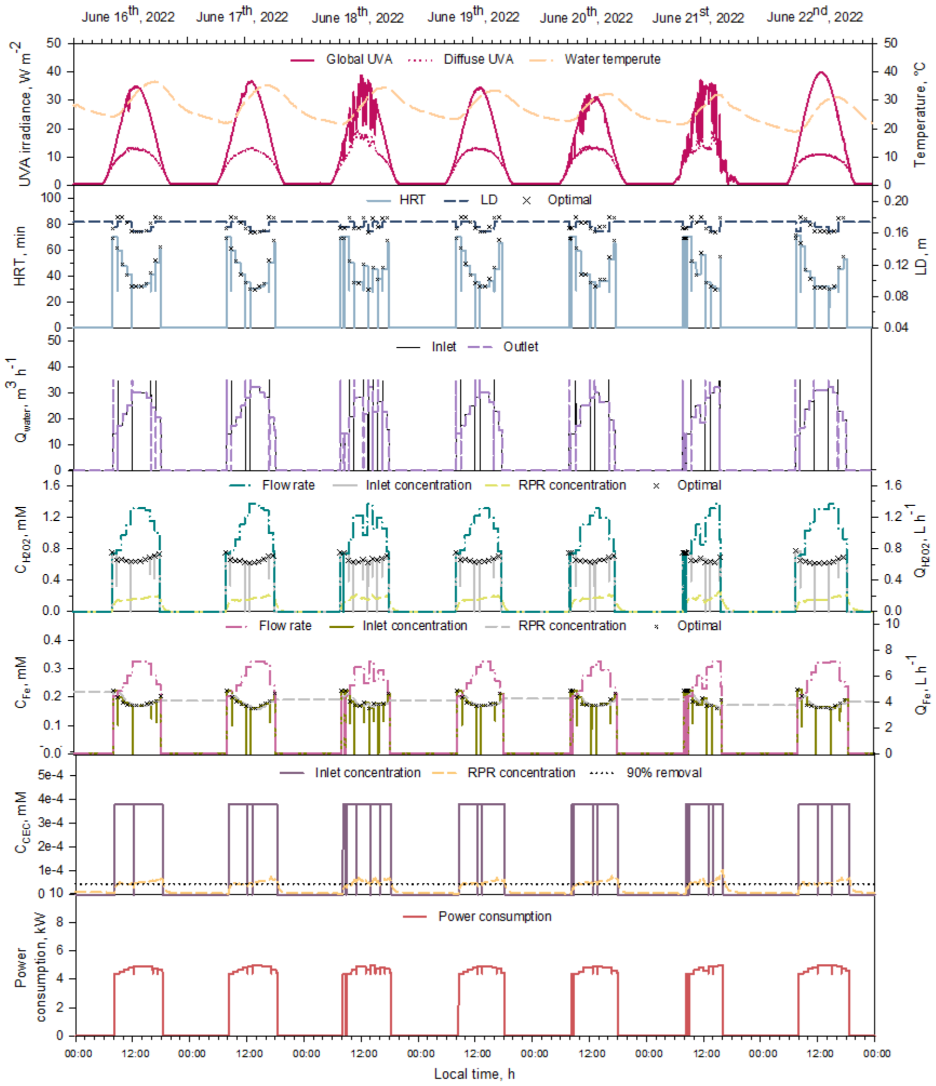
STATISTICAL OPTIMIZATION TOOLS

Daily operation simulation

Event based robust control

80 & 90% CECs removal objective





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Economic evaluation
Optimized process

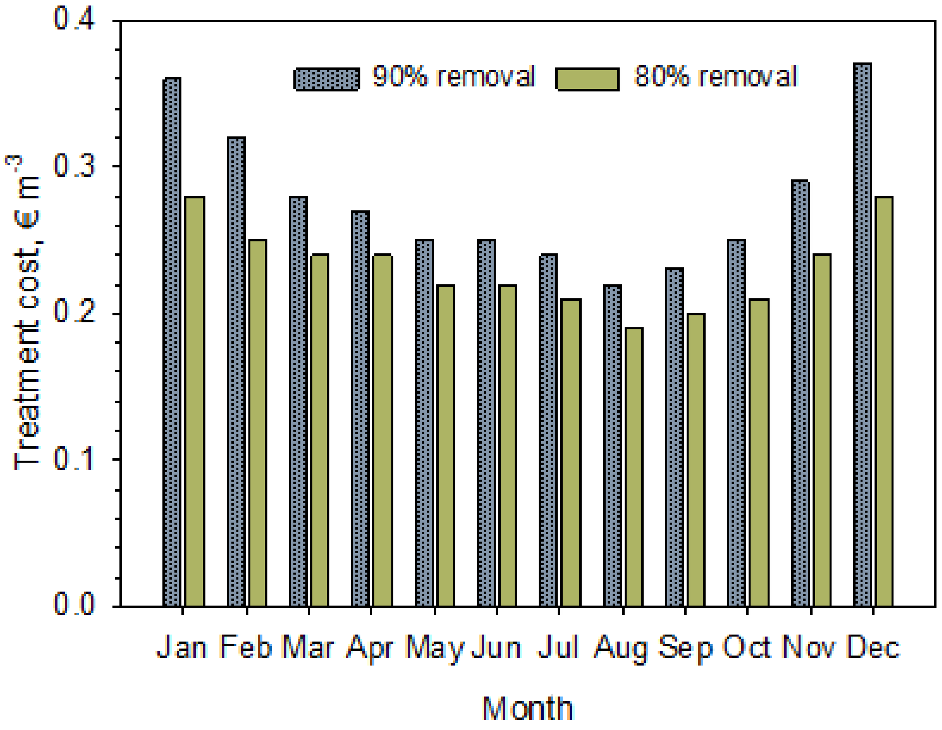
PROCESS EVALUATION

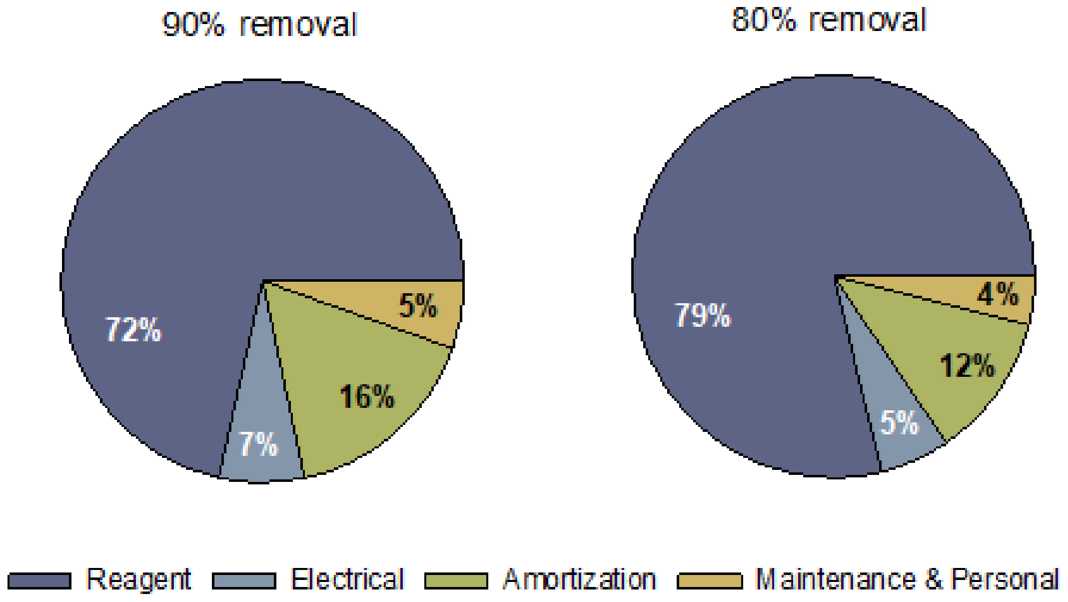
STATISTICAL OPTIMIZATION TOOLS

Annual operation simulation

Event based robust control

80 & 90% CECs removal objective



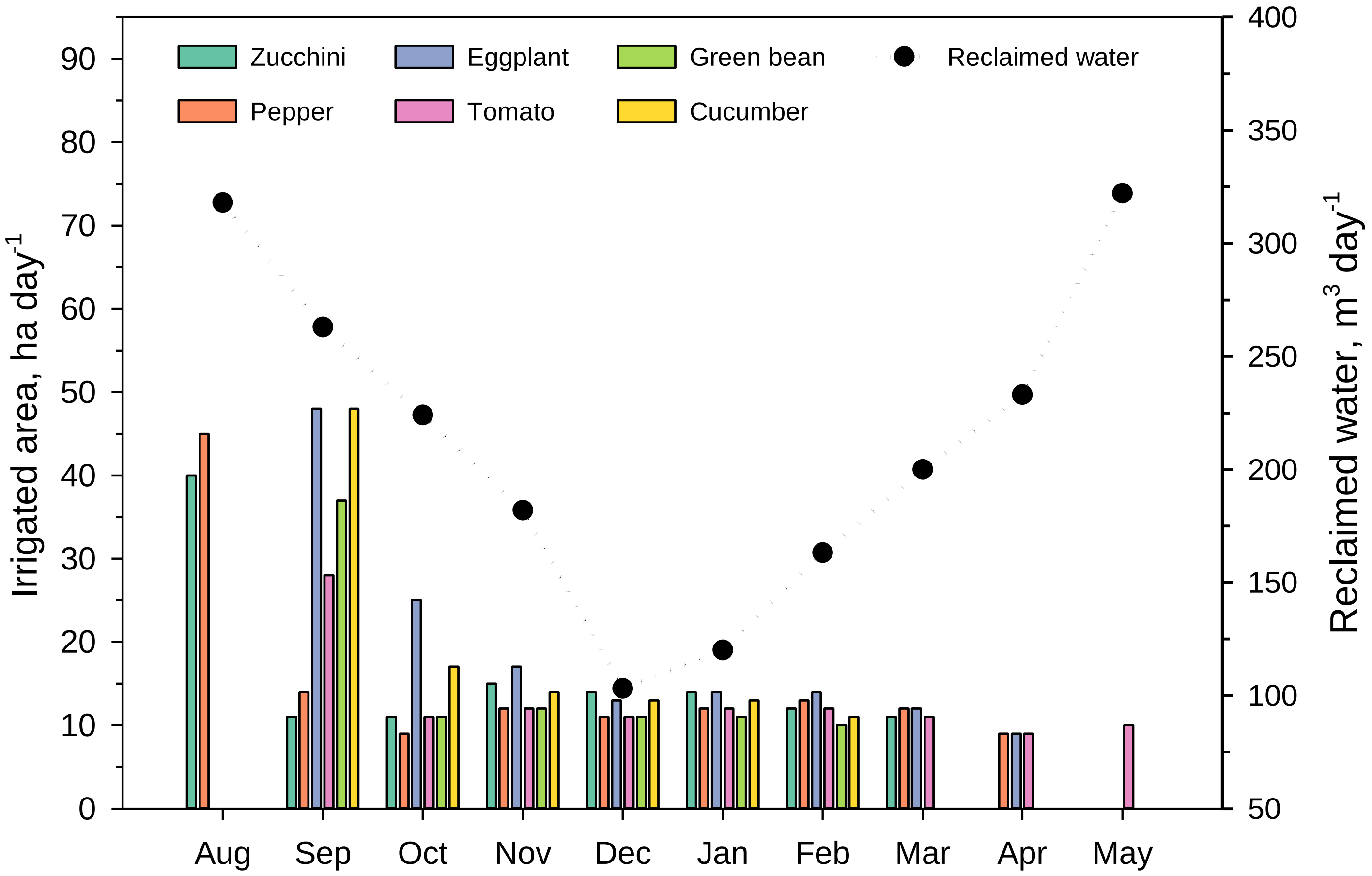


The annual treatment cost ranges from 0.19 to 0.28 € m^{-3} for 80% CEC removal and from 0.22 to 0.37 € m^{-3} for a 90% target

PROCESS EVALUATION

STATISTICAL OPTIMIZATION TOOLS

Annual simulation of crops irrigation requirements



In general, and conservative terms, the daily-water requirements of 1,000 m² of greenhouse-grown vegetables can be supplied per 1 m2 of RPR surface area.

CONCLUSIONS & FUTURE ACTIONS

CONCLUSIONS

- ✓ The solar photo-Fenton process in raceway pond reactors for micropollutant removal is feasible under real conditions at large scale.
- ✓ The operating conditions depends on the quality of water to be treated and the final quality to achieve.
- ✓ The use of kinetics model allows to design and optimize the process in a smart way of work.
- ✓ A control system based on virtual sensors has been designed and simulated for the continuous flow operation of the solar photo-Fenton process applied to MP removal.
- ✓ The stable operation of the plant and the capacity to compensate the effects of the perturbances has been demonstrated by simulation.
- ✓ The optimization of the process can be carried out using the models. This information can be applied for the event based robust control system.

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Innovative Cost-effective Multibarrier Treatments for Reusing Water for Agricultural Irrigation (LIFE PHOENIX)

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Upgrading Wastewater Treatment Plants by Low Cost Innovative Technologies for Energy Self-Sufficiency and Full Recycling. (LIFE ULISES)

Thanks a lot!

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