European Twinning for research in Solar energy to (2) water (H2O) production and treatment technologies
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Sol2H2O

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UNIVERSIDADE DE ÉVORA
Università degli Studi di Palermo
itc INSTITUTO TECNOLÓGICO DE CANARIAS
Ciemat PSA

Fast Track School #2

Beyond State of the Art in Solar-driven Water production & Treatment technologies and brine treatment processes

CANARIAS, 25.-26.09.2024

Sol2H2O

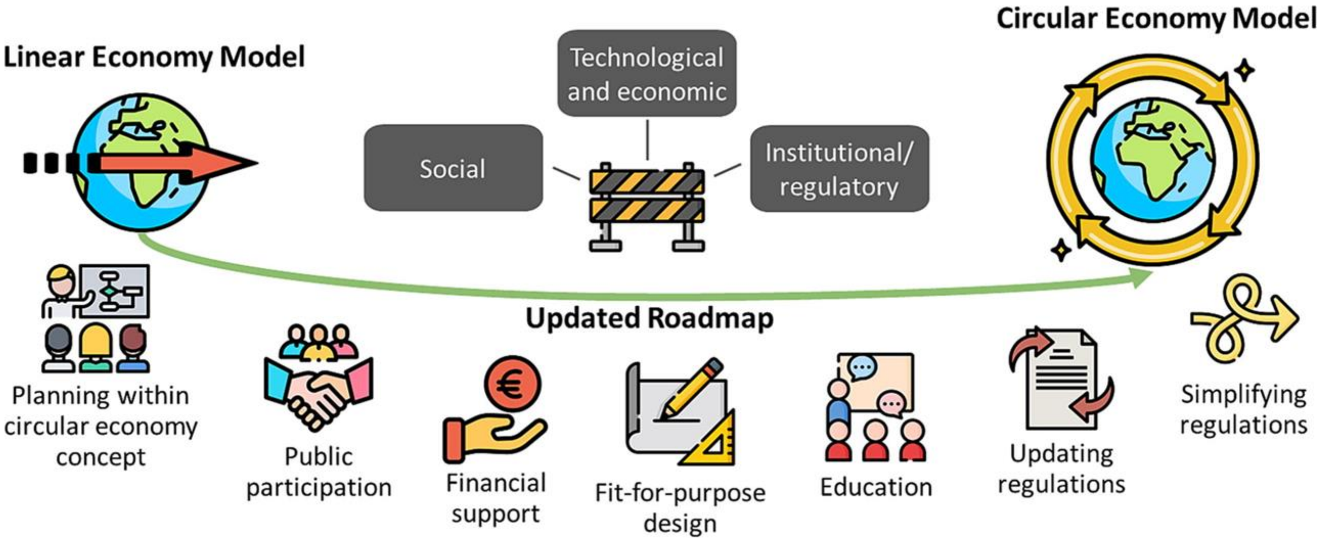
Isabel Oller Alberola; ioller@psa.es

Beyond SoA of Solar water treatment, integration of technologies for WW regeneration

CANARIAS, 25.-26.09.2024

Circular economy in water reuse

The availability of water is crucial for economic development since sectors like agriculture, tourism, and all kind of production consume water. The **agricultural sector** is responsible for **70 % of the world's water consumption** (UN-Water, 2021).
As the stress caused by climate change on water resources accelerates the transition towards a **circular economy**, the reuse of treated water, which ensures the circularity of water, in agriculture is becoming increasingly common. Nowadays, **wastewater is seen as a resource rather than a waste.**



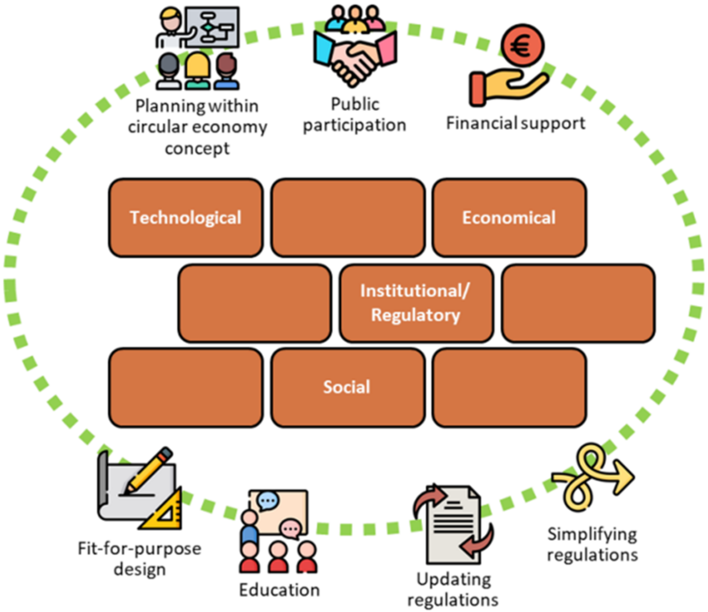
Source: https://doi.org/10.1016/j.biortech.2022.127951

Circular economy in water reuse

In the **new Circular Economy Action Plan** water connects agricultural, industrial, and municipal systems. The ubiquity of water makes it very important in realizing the circular economy model.
Water reuse in agriculture was included in "Food, water and nutrient" product value chain of the new plan.

Barriers to the widespread use of reclaimed water in agriculture.

Actions to be done to overcome such barriers



Water microbial contamination

BACTERIA

Prokariotic- Unicellular organism without protoplasm differentiated into nucleus and cytoplasm

Diameter: 1-20 µm

FUNGI

Eukariotic- Unicellular organism with protoplasm differentiated into nucleus and cytoplasm

Diameter: 2-10 µm

PROTOZOA

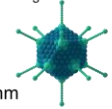
Eukariotic- Unicellular organism with protoplasm differentiated into nucleus and cytoplasm

Diameter: 2-100 µm

VIRUS

DNA or RNA enclosed in a simple protein shell known as a capsid – Non living cell

Diameter: 10 - 100 nm

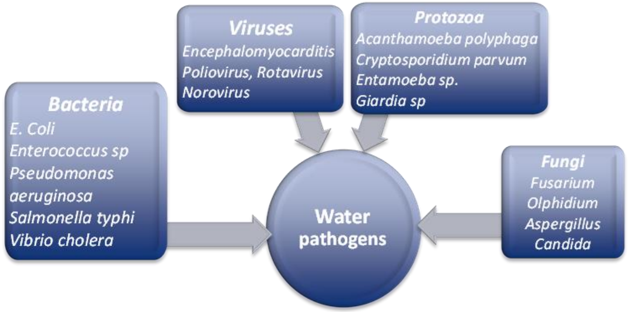


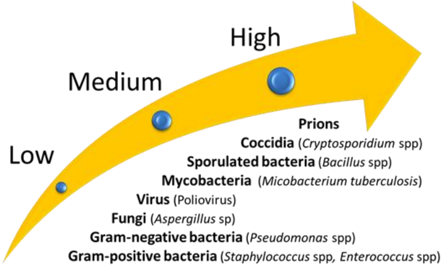
Well

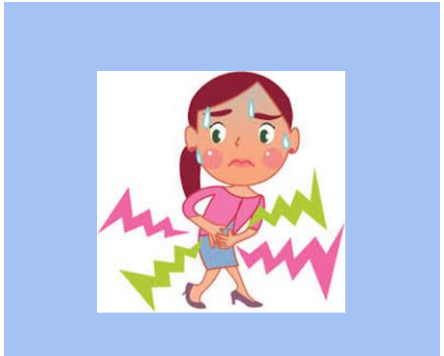
Reservoir

Rivers

Lakes



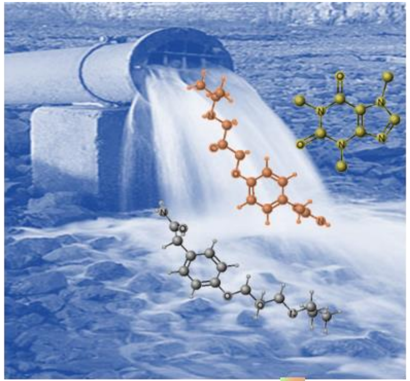




ANTIBIOTIC RESISTANT BACTERIA

Summary of priority pathogen list reported by the WHO (Publication date: 27 February 2017) (http://www.who.int/medicines/publications/global-priority-list-antibiotic-resistant-bacteria/en/)

Chemical contamination: CECs, mobile compounds…



Characterization

(QTRAP LC-MS/MS)

29/62 Compounds with high presence in the effluent of the MWWTP

contaminant	average [ng L-1]	min [ng L-1]	max [ng L-1]	detected [-]
C				
4				
P				
4				
N				
C				
Ib				
G				
F				
4				
H				
4				
N				
D				
O				
A				
R				
C				
S				
A				
Is				
C				
A				
D				
K				
Trimethoprim*	331.7	26	596	10
Venlafaxime	330.2	150	411	9
Azithromycin	262.7	75	405	6
Sulfapyridine*	241.0	50	734	10
Sum of ECs < 240 ng L-1	2589.0	846	5007	-

❖ **Downstream urban areas,** the surface water is often impacted by the discharge of wastewater treatment plant (WWTP) effluents → a continous entry of pharmaceuticals (P) and transformation products (TPs) into the environment

❖ When such a surface water is used for crop irrigation (**unplanned water reuse**)

"Necessity of providing solid data on the uptake of contaminants by crop plants under actual farming conditions"

Water decontamination and disinfection techniques

Physical removal

- ✓ *Coagulation and sedimentation*
- ✓ *Filtering*
  - ▪ *Fast filtering*
  - ▪ *Sand filtering*
  - ▪ *Active carbon*
  - ▪ *Membrane filtering*

✓ Widely used
× Expensive
× Do not really destroy microorganisms

Degradation/Inactivation (death)

- ✓ *Chlorination*
- ✓ *Ozonation*
- ✓ *UV(C) disinfection*
- ✓ *Solar water disinfection (SODIS)*
- ✓ *Advanced Oxidation Processes (AOPs)*
  - ▪ *Photocatalysis*
  - ▪ *Electrophotocatalysis*
  - ▪ H_2O_2*-UVC*
  - ▪ H_2O_2*-Ozone*

✓ High efficiency for virus and bacteria
✓ Widely used and investigated
× THM and other carcinogenic compounds
× Flavor to water
× Expensive

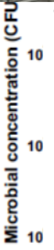
***<u>Definition of water treatment</u>**: is a process that makes water more acceptable for an end-use, which may be drinking, industry, or medicine. A water treatment should remove existing water contaminants or so reduce their concentration that their water becomes fit for its desired end-use, which may be safely returning used water to the environment.*

Solar heterogeneous photocatalysis: enhancement strategies

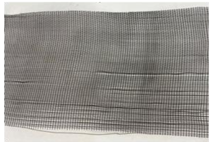
IMMOBILIZATION OF THE CATALYST IN SUBSTRATES

Uncoated external,
TiO_2 coated internal

- ➢ Lower microbial reduction efficiency than with suspended catalyst
- ➢ Scaling-up challenge



Commercial ZVI nanoparticles developed by **SMALLOPS S.L.** (Extremadura, Spain) from olive mill wastewater (ZVI-OMW) and supported on a polypropylene mesh (ZVI-MESH)



Cata

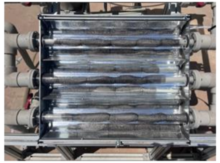
ZVI-OMW

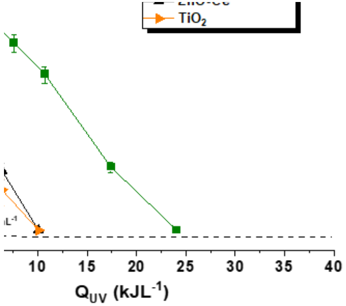
ZVI-MESH

- ✓ particle size 150 nm ± 50 nm
- ✓ 44.5 % total Fe
- ✓ 2.5 % ZVI

- ✓ 0.44 % total Fe

PILOT PLANT SCALE





- ✓ 3 tubes available
- ✓ Irradiated area: 0.09 m² (1 tube) and 0.28 m² (3 tubes)
- ✓ Irradiated volume: 0.4 L (1 tube) and 1.2 L (3 tubes)
- ✓ ZVI-OMW: 55 cm x 15 cm = 0.06 mM Fe
- ✓ Total volume: 12 L

Catalyst holder

UV-Solar oxidative agents

H_2O_2

$$H_2O_2 \xrightarrow{UVC} 2HO^{\bullet}$$

(Goldstein et al., 2007)

Chlorine

$$HClO \xrightarrow{UVC} HO^{\bullet} + Cl^{\bullet}$$

$$ClO^{-} \xrightarrow{UVC} O^{\bullet -} + Cl^{\bullet}$$

$$O^{\bullet -} + H_2O \rightarrow HO^{\bullet} + OH^{-}$$

(Chuang et al., Environ Sci Technol, 2017. 51(23) 13859-13868.)

Persulfate / Peroxymonosulfate

$$S_2O_8^{2-} \xrightarrow{UVC} 2SO_4^{\bullet -}$$

$$SO_4^{\bullet -} + H_2O \rightarrow HO^{\bullet} + SO_4^{2-} + H^{+}$$

$$HSO_5^{-} \xrightarrow{UVC} SO_4^{\bullet -} + HO^{\bullet}$$

$$HSO_5^{-} + H^{\bullet} \rightarrow SO_4^{\bullet -} + H_2O$$

(Sánchez-Montes et al. Environ. Sci.: Water Res. Technol., 2020, 6, 2553–2566)
(Guerra-Rodríguez et al., Water 2018, 10, 1828)

- $SO4^{\cdot -}$ has a high oxidation potential (2.5–3.1 V) comparable or even higher than $^{\cdot}OH$
- Reacts more selectively and efficiently with organic compounds that contain unsaturated bonds or aromatic π electrons
- Half-life of sulfate radicals is supposed to be 30–40 μs
- Chlorine radicals oxidation potential 1.5V. High half-life

Photochemical processes

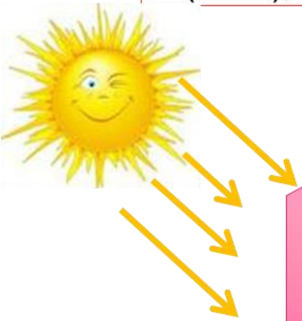
UV-C

- Low efficiency in CEC and OMC elimination.

Free Chlorine (Chlorination)

- Low efficiency in CEC and OMC elimination.
- Generation of toxic by-products: trihalomethanes (THM), haloacetic acids.

In crop irrigation, regenerated wastewater is normally stored along hours/days before being used.

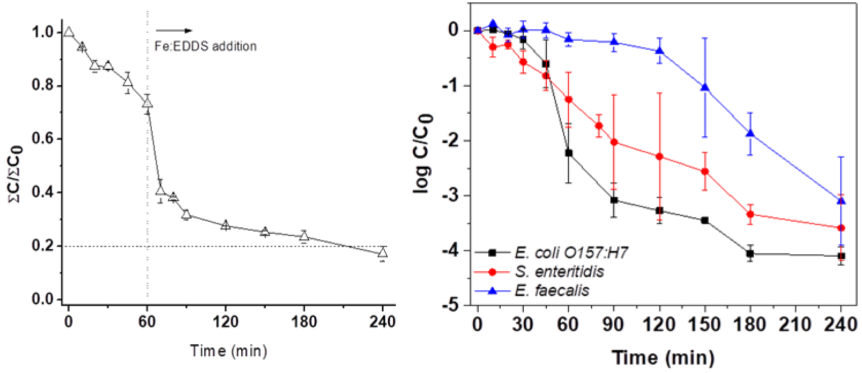


UV-C/ free Chlorine

- **Low studied combination for CEC and OMC elimination.**
- **Effect of UVC in THM formation.**

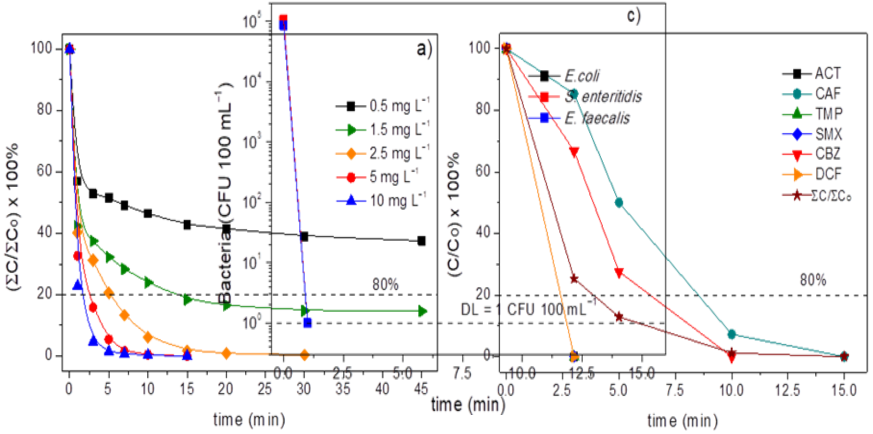
Simultaneous water decontamination & disinfection

SWWTP effluent with 200 mg/L of $S_2O_8^{2-}$ using solar radiation and neutral pH, adding 0.1 mM of Fe^{3+}:EDDS



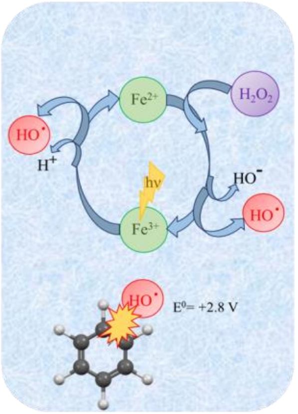
∑**MCs** decreased 29-34% during the first 60 min
When Fe^{3+}:EDDS (1:1) is added, MCs sharply decreased till **70% (90 min** of whole treatment) & **80% after 240 min**.
E. coli DL (1 CFU/ 100 mL) after 240 min.

Solar/free chlorine treatment of NW

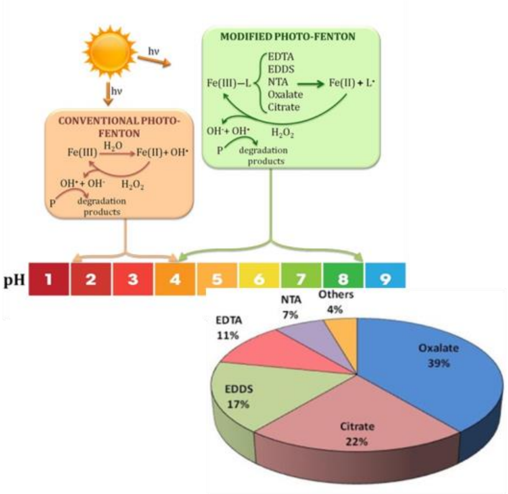


In the presence of free chlorine, regrowth was not observed after the treatment for all times analyzed (24, 48, and 144 h). The residual free chlorine concentration remained constant (0.5 mg L^{-1}) in the dark until 144 h of storage.

Solar photo-Fenton at neutral pH

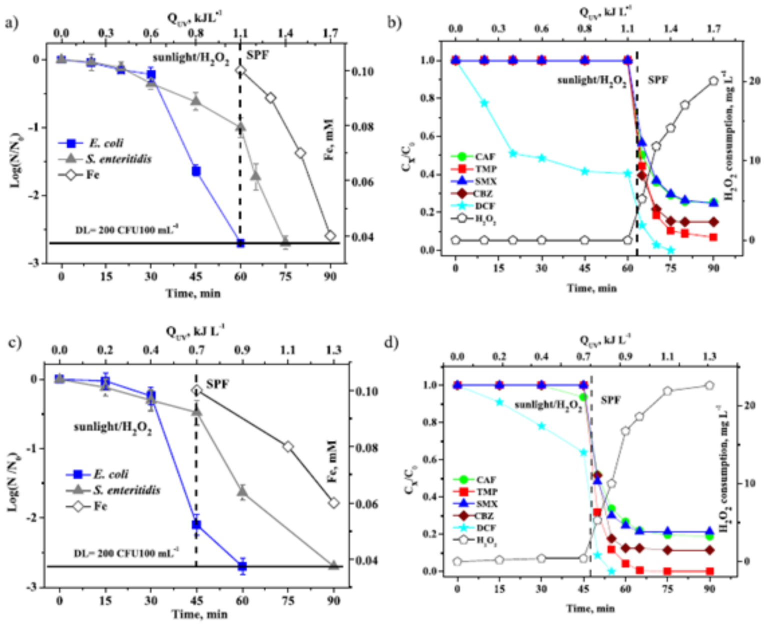


Neutral pH → $Fe(OH)_3$ ↓



Generation of photoactive Fe^{3+} complexes:

- **Fe^{3+} in solution in a wide range of pHs.**
- **Could present higher quantum efficiencies than those complexes generated between Fe^{3+} and water.**
- **Formatio of aditional oxidant species.**



Bacteria inactivation and CECs degradation in SUWWE by sequential treatment with sunlight/H_2O_2 (H_2O_2 =50 mg L^{-1}) with subsequent addition of Fe:EDDS (0.1 mM Fe:EDDS) at several dosing times: 60 min (a, b), 45 min (c, d) in RPR.

Journal of Hazardous Materials 436 (2022) 129134.

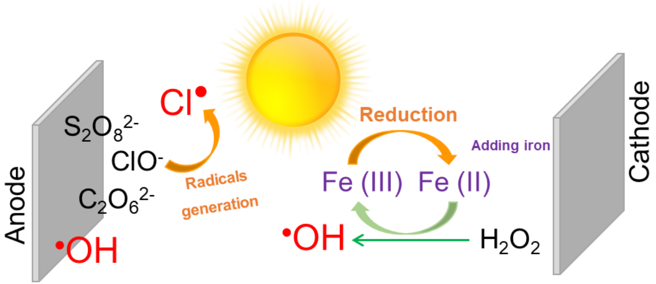
Electrochemical treatments

Electrochemical processes

- Electrocoagulation
- Electroflotation
- Electroreduction
  - Halogenated compounds
  - Nitrates
- Electrodialysis
- Capacitive deionization
- Electro-oxidation
- Electro-Fenton y photo-electro-Fenton
- Photo-electro-catalysis

(Electro-oxidation, Electro-Fenton y photo-electro-Fenton, Photo-electro-catalysis:) Assisted by light

- ✓ Easy to operate and automate
- ✓ No addition of reagents and so the risks associated to their storage.
- ✗ High electric consumption

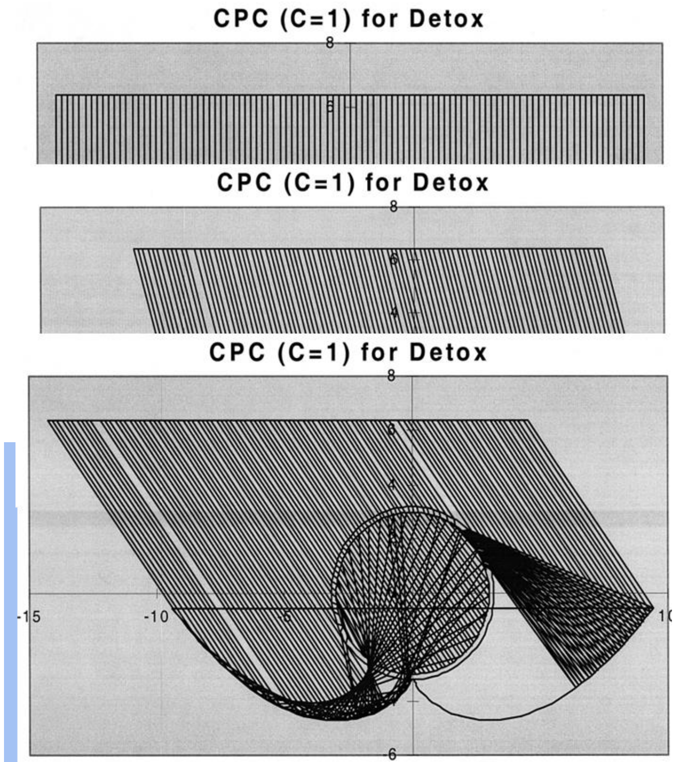


Anodic oxidation (AO) + Fenton = electro-Fenton (EF)

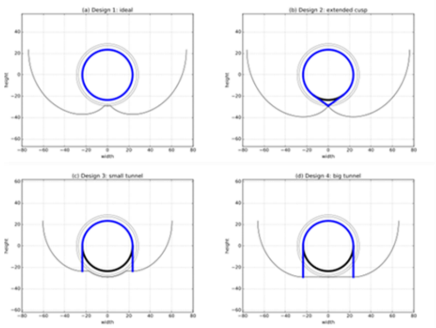
Electro-oxidation + activation of chlorine species+ photo-Fenton = Solar photo-electro-Fenton (SPEF)

Thanks to the photons, the amount of radicals increase due to the continuous regeneration of iron (II) and for the production of $Cl^{\bullet}$ from ClO^-.

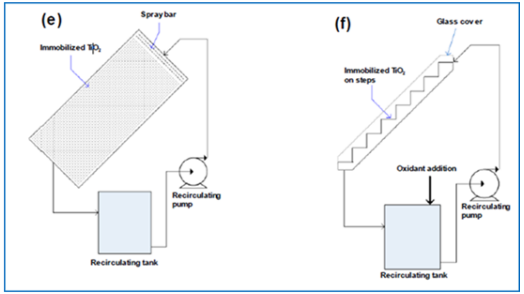
Design, improvement and optimization of solar photo-reactors



New reflector design



New photo-reactor design



Flat design solar reactor

Multi-step cascade

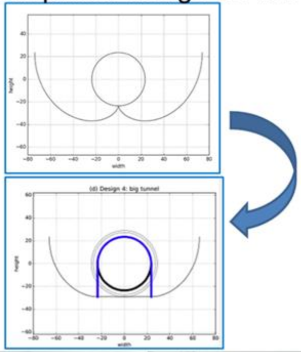
Inorganic coating with photocatalytic material in all steps of the cascade reactor.

Appl. Catal. B: Environ., **37**, 1-15, 2002.
Most cited paper 2002-2006.

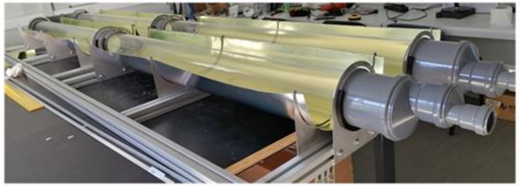
New solar photo-reactor design

One-Sun Compound Parabolic Collectors (CPC)

simplified design for low cost production ("big tunnel"), Osório et al. (2019)



Solar collector was obtained by molding the CPC-type profile over the receiver length



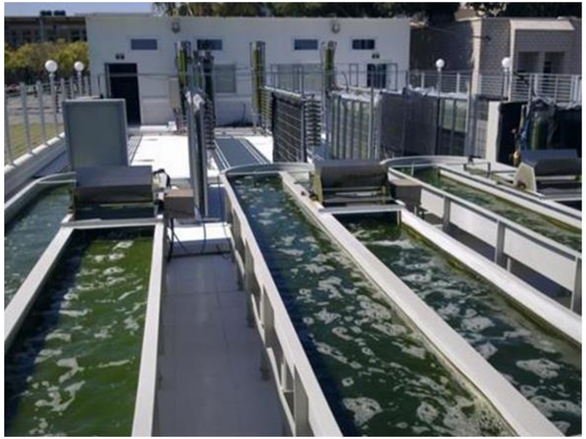
Tubular Receivers

The **horizontal receivers** are connected in series

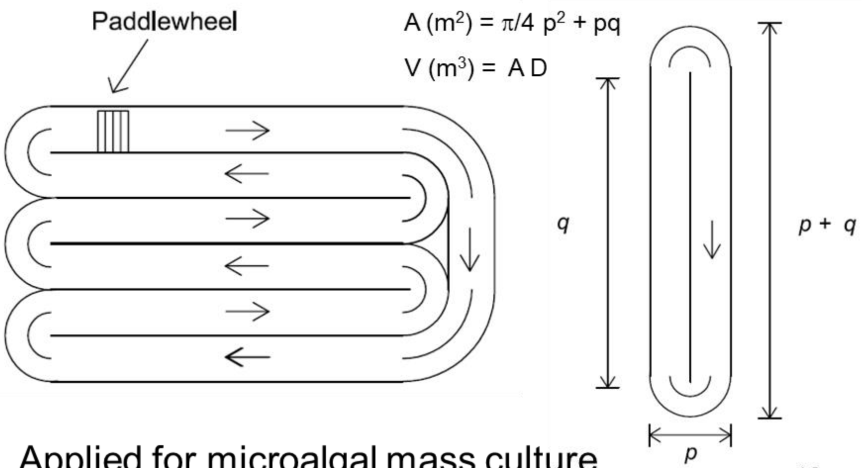
- 4 tubes
- borosilicate glass 3.3 DURAN®
- 125 mm outer diameter,
- 5 mm wall thickness and
- 1.5 m length
- with tubes and valves made of HDPE

New Solar photo-reactor design

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



Microalgal cultures in RPR and TPBR. Almería.



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

AQUACYCLE Project

AQUACYCLE Towards Sustainable Treatment and Reuse of Wastewater in the Mediterranean Region

ENI CBCMED
Cooperating across borders in the Mediterranean

Priority B.4.1 Water Efficiency

Support sustainable initiatives targeting innovative and technological solutions to increase water efficiency and encourage use of non-conventional water supply

Target
150
hectares of land irrigated with non-conventional water

Target
2,700,000
m³/year of non-conventional water supply used for domestic purposes

4 EU partners, 3 Mediterranean partners, and 4 Associated Partners from Greece, France, Algeria, Morocco

01.09.2019-31.10.2023

North Governorate of Lebanon

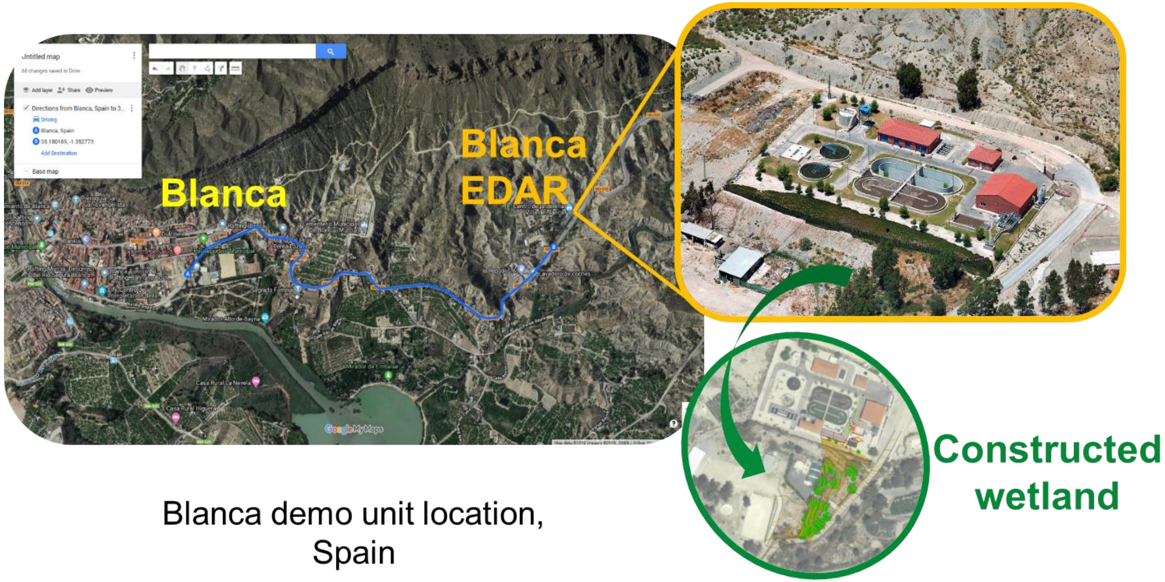
Murcia Region of Spain

Zaghouan Governorate of Tunisia

AQUACYCLE Project

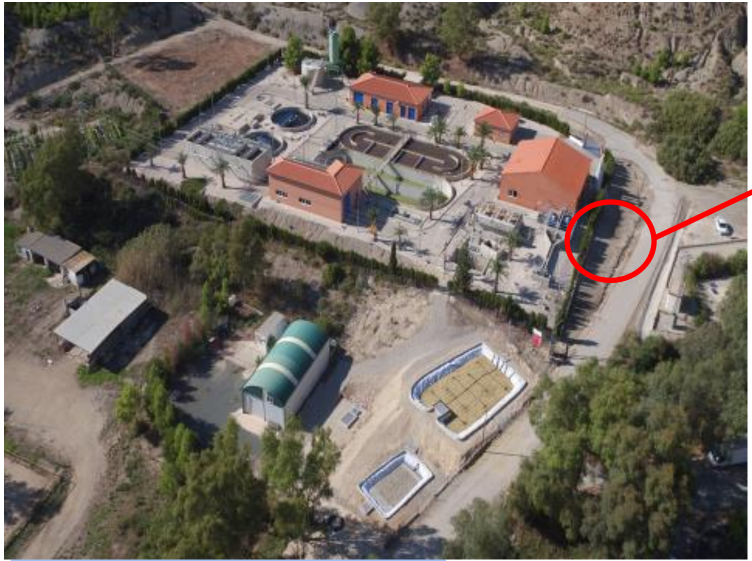
Demo plant in Blanca WWTP, operated by ESAMUR and CIEMAT-PSA

- ✓ Feed flow rate 5 m^3/d
- ✓ AD: existing ***Upflow Anaerobic Sludge Blanket*** (UASB) reactor
- ✓ CW: two CWs, connected in series, one ***subsurface vertical wetland*** and one ***subsurface horizontal wetland***
- ✓ PO: solar photoreactor in the form of a ***raceway pond (RPR)***

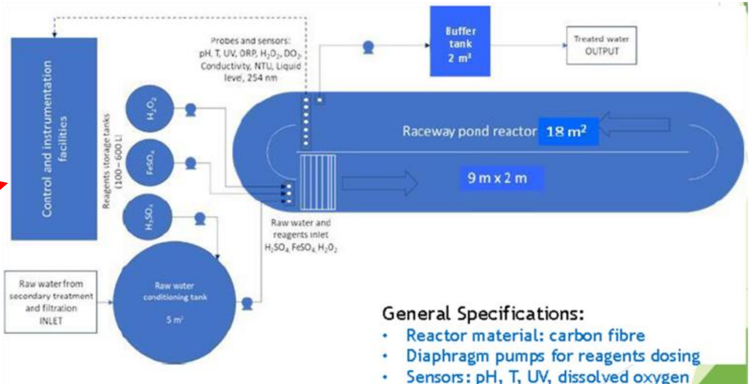


Blanca demo unit location, Spain

AQUACYCLE Project



Anaerobic biorreactor
(700 m³/day)



AQUACYCLE Project: Simultaneous water decontamination and disinfection

- To investigate and optimize an advanced solar quaternary treatment at pilot scale (90 L) based on the addition of H_2O_2, for further validation at demonstrative scale (2000 L) for compiling with the new EU regulation on minimum requirements for water reuse in agriculture.

EU Regulation 2020/741 *(June 2023)*

*Legislative Limit (Class A):
- *E. coli* ≤ 10 CFU/100mL
- Spore-forming SRB ≤ 20 CFU/100mL

*Technology validation:
- ≥ 5 LRV* *E. coli*
- ≥ 5 LRV* Spore-forming SRB

*LRV: Logaritm Reduction Value

Challenges on wastewater reclamation

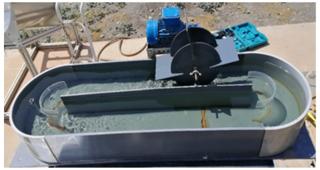
- Contaminants of Emerging Concern (CECs), persistent contaminants
- Microbial pathogens
- Antibiotic Resistance Bacteria and Genes (ARB, ARGs)
- Disinfection by-products

→ Crop irrigation water ⇒ Harmful to humans and ecosystems

AQUACYCLE Project: Simultaneous water decontamination and disinfection

Pilot Plant

✓ **Raceway Pond Reactor (RPR)**



- Total volume: 90 L
- Illuminated surface: 0.6 m^2

✓ **Microorganisms**

- *Escherichia coli*: 10^2 CFU/100 mL
- *Enterococcus* spp.: 10^3 CFU/100 mL
- Total coliforms: 10^5 CFU/100 mL
- Spore-forming SRB: 10^3 CFU/100 mL

✓ **Oxidant**

- $[H_2O_2]$: 50, 100 mg/L

✓ **CECs**

- ∑ 223: antibiotics, pesticides, insecticides, etc.

Demo Plant

1. Vertical wetland

Surface: 124 m^2

2. Horizontal wetland

Surface: 32 m^2

Raceway Pond Reactor (RPR)

Total volume: 2000 L

Illuminated surface: 12.5 m^2

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