Towards industrial water footprint reduction via solar decontamination and disinfection advanced processes

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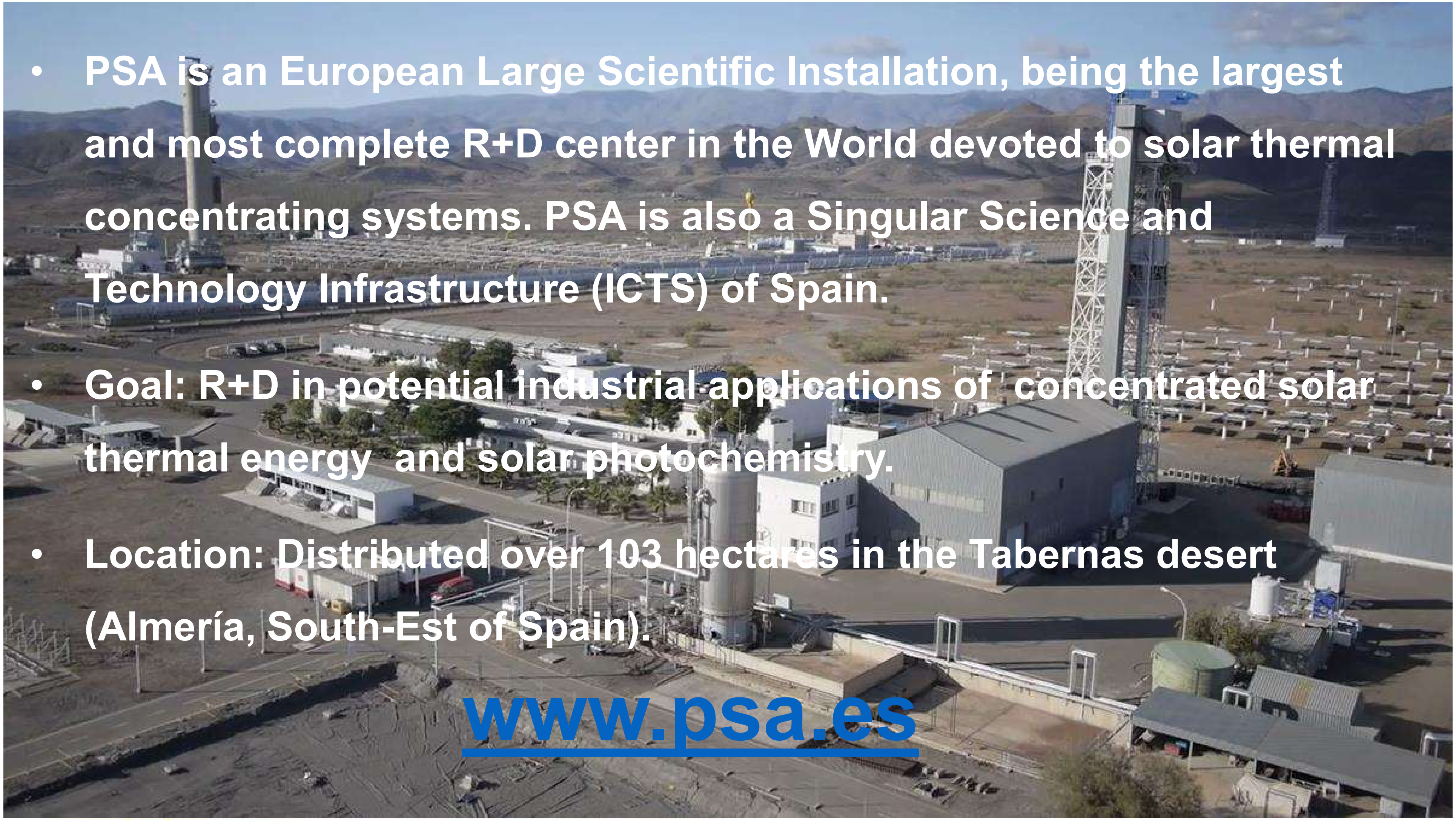
Plataforma Solar de Almería-General Information



- PSA is an European Large Scientific Installation, being the largest and most complete R+D center in the World devoted to solar thermal concentrating systems. PSA is also a Singular Science and Technology Infrastructure (ICTS) of Spain.
- Goal: R+D in potential industrial applications of concentrated solar thermal energy and solar photochemistry.
- Location: Distributed over 103 hectares in the Tabernas desert (Almería, South-Est of Spain).

www.psa.es

Plataforma Solar de Almería-General information

Solar Treatment of Water Unit

Research: water purification and other solar photochemical processes

1. **Solar photocatalytic and photochemical** processes as tertiary treatment of wastewater. Removal of pollutants and water pathogens.

2. **Integration of Solar Advanced Oxidation Processes with Advanced treatment technologies** (NF & UF, Ozone, UV-C, Bio-treatment, etc.) for remediation of industrial wastewaters with **hazardous pollutants and pathogens** with the aim of improving the **water treatment efficiency and reducing operating costs**.

3. Assessment of **photocatalytic efficiency of new materials** under real solar light conditions, and their use in solar **CPC-reactors** (pilot scale).

4. **Solar photocatalytic generation of Hydrogen** using Vis-light active materials: pilot scale solar reactor for testing.

5. Using **solar photocatalytic and photochemical processes for water disinfection**. Several types of contaminated water sources with a number of water pathogens.

6. Development, testing and assessment of **new concepts of solar photo-reactors (pilot, demo)** for either water decontamination or disinfection for different end-purposes, water reclamation & reuse (irrigation and industry), drinking water, etc.

...leading research in wastewater treatment at pilot & demo scale with solar energy

Outline

- INTRODUCTION & MOTIVATION
- PILOT PLANTS (SOLAR PHOTO-REACTORS)
- NUTRIENTS RECOVERY-DIRECT CONTACT MEMBRANE DISTILLATION
- CASE STUDIES
- KEY MESSAGES

Introduction-Motivation: Water-Energy nexus

WATER and ENERGY systems are heavily interdependent

HOW WE USE WATER FOR ENERGY

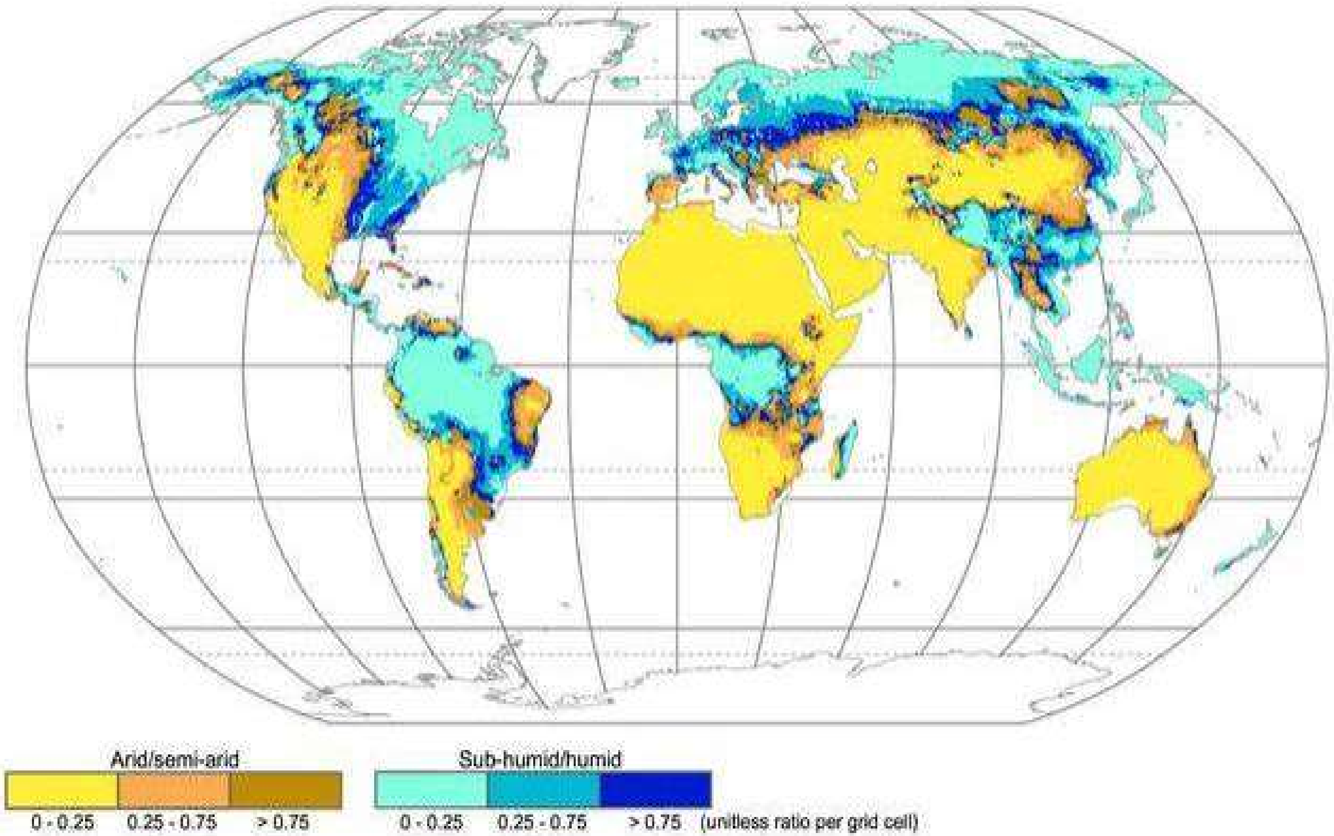
- **Electricity Generation**. Nearly half of all water withdrawn in the U.S. is used in power plants cooling.
- **Oil and Gas**. Water is used for hydraulic fracturing, enhanced oil recovery and other fossil fuel production processes.
- **Renewables**. Essential for Hydropower and also used for Concentrated Solar Power, Geothermal energy and to produce Bioenergy.

HOW WE USE ENERGY FOR WATER

- **Pumping**. Energy is used to pump water from aquifers for agriculture and to transport to treatment facilities and consumers.
- **Water Treatment**. Energy is needed to desalinate water and wastewater treatment before it's returned to the environment.
- **Heating & Cooling**. Energy and water work together keep building and equipment at safe & comfortable temperatures.
- **Delivery**. Energy is used to distribute and heat water for cooking, showering, cleaning and drinking

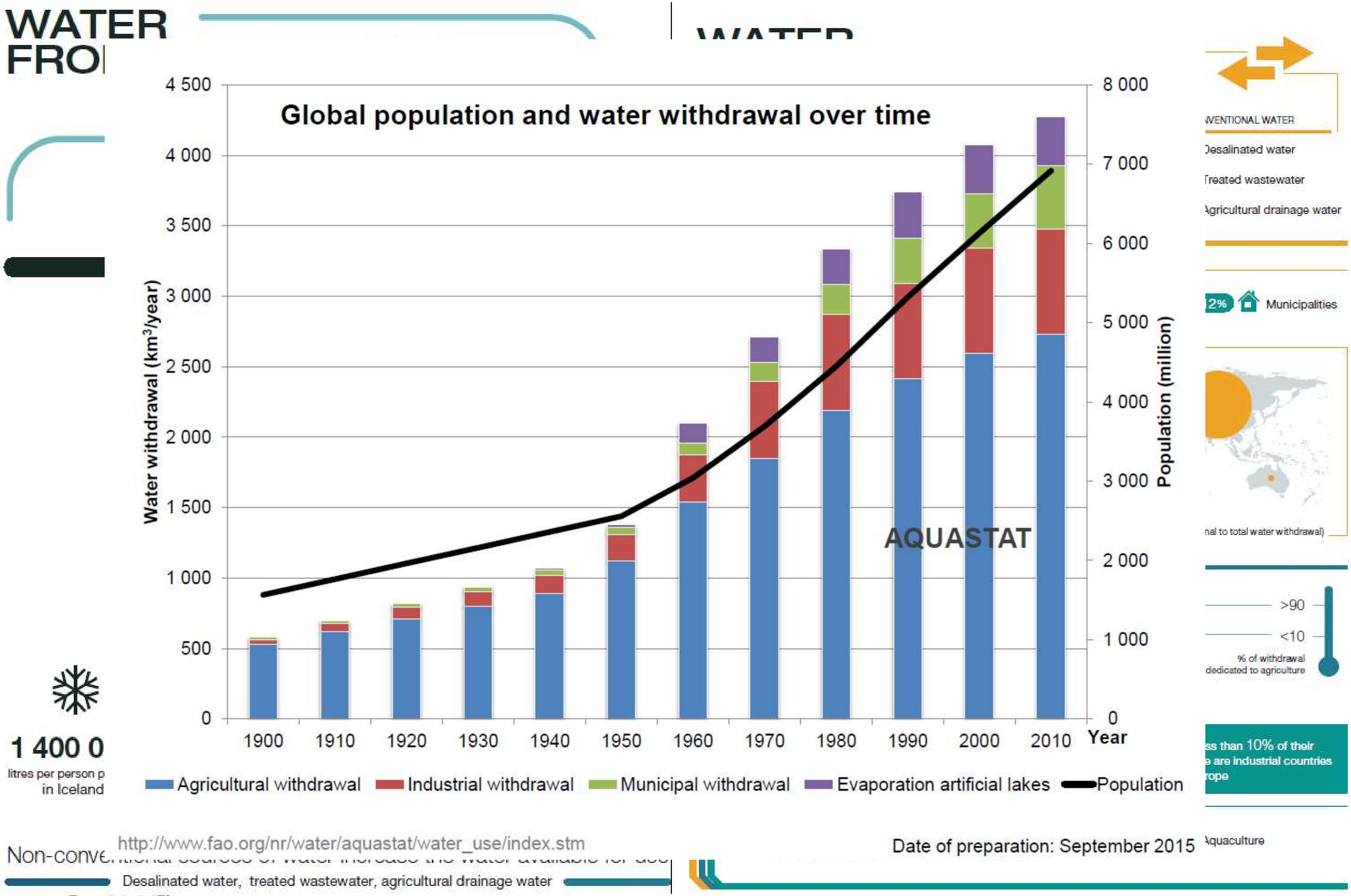
Introduction-Motivation: Solar Energy and arid zones

The binomy **WATER / ENERGY** is always present ➜ Water problems can be significantly reduced if energy is easily available. However if the energy is also a problem, the situation becomes much more complicated.



Clear coincidence in the existence of water problems (arid and semi-arid zones) and the availability of abundant solar radiation

Introduction-Motivation

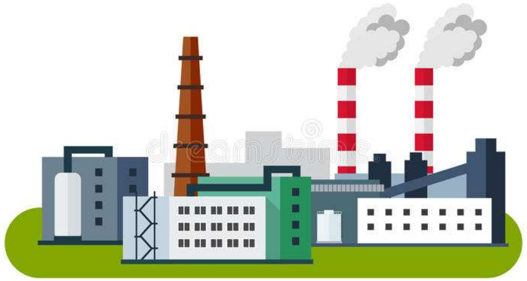


FAO, 2018

Motivation: Water-Energy-Food Nexus (WEF)

- **According to FAO, agriculture consumes 70% of fresh water used worldwide**. Approximately **75% of water withdrawal for industrial use are focused on energy production** (UNESCO, 2014)
- Food production and its worldwide supply demand around 30% of the global energy consumption (FAO, 2011). **90% of global energy generation requires an intensive consumption of water**. (UNESCO, 2014)
- In 2050 it is foreseen an increase of **55% on the global water demand,** mainly due to the increasing production demand (400%).
- In 2050 it is foreseen that more than **40% of the worldwide population would live in sever hydric stress zones** (OCDE, 2012)
- In 2035, **water withdrawal for energy production would increase in 20% and the water consumption in 85%**, powered by the change into more efficient energy plants with advance refrigeration systems. (IEA, 2012).
- **Nowadays almost 800 million of people suffer malnutrion**. In 2050 worldwide production of food will require an increase of 50% for the more than 9 million of people that will leave in our planet (FAO / FIDA / UNICEF / PMA / OMS, 2017).
- Between **3.000 - 5.000 litres of water are required to produced 1 kg of rice**, 2.000 litres for 1 kg of soya, 900 litres for 1 kg of wheat and 500 litres for 1 kg of potatoes. (WWF).

Industrial wastewater (water footprint)



Industrial processes

Direct discharge to the environment without any treatment

Wastewater Treatment Plant (WWTP)

PROBLEMS

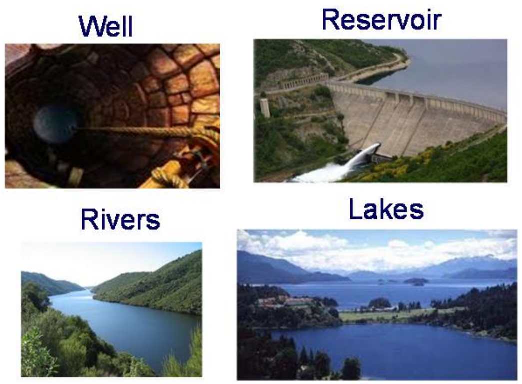
- Accumulation of persistent compounds (pesticides, pharmaceuticals….) in the activated sludge.
- Low efficiencies due to toxic and/or biorecalcitrant compounds.

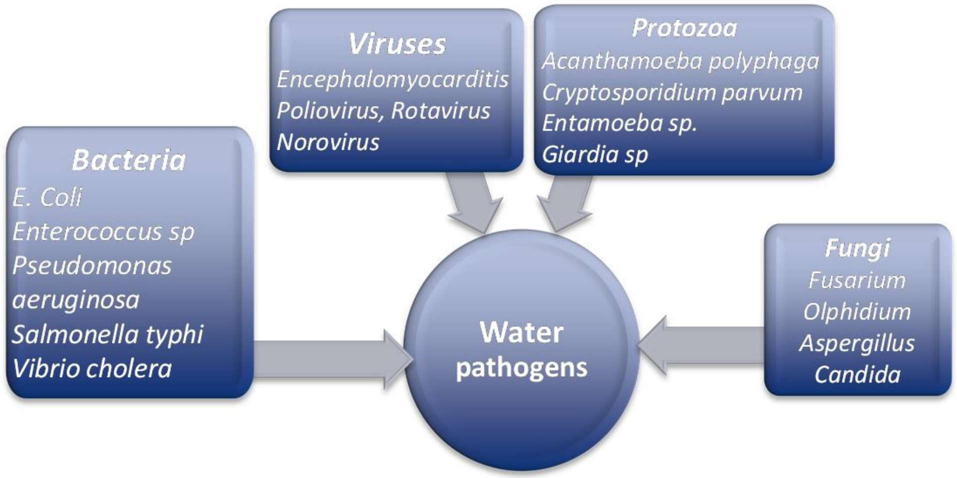
→ Control of processes

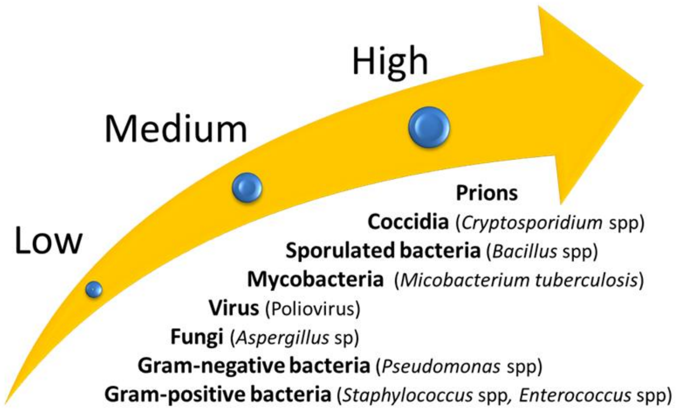
→ Alternative treatments

- ➢ Adapted/advanced biological treatments
- ➢ AOPs
- ➢ Combination BIO/AOP or AOP/BIO

Water Microbial Contamination







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/)

Solar Advanced Oxidation Processes

TiO_2/UVA (Carey et al., 1976)

$$TiO_2 \xrightarrow{h\nu} TiO_2(e^- + h^+)$$

$$h^+ + H_2O \rightarrow {}^\bullet\mathbf{OH} + H^+$$

$$e^- + O_2 \rightarrow O_2^{\bullet -}$$

Fe(III)-Fe(II)/UVA

Aquacomplexes Fe(III) + hn → •***OH***
(Mazellier et al., 1997a,b; Brand et al., 1998, 2000; Mailhot et al., 1999)
Aquacomplexes Fe(II) + hn → •***OH*** (Benkelberg and Warneck, 1995)

Fenton (J. Chem. Soc., 1894)

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^\bullet OH$$

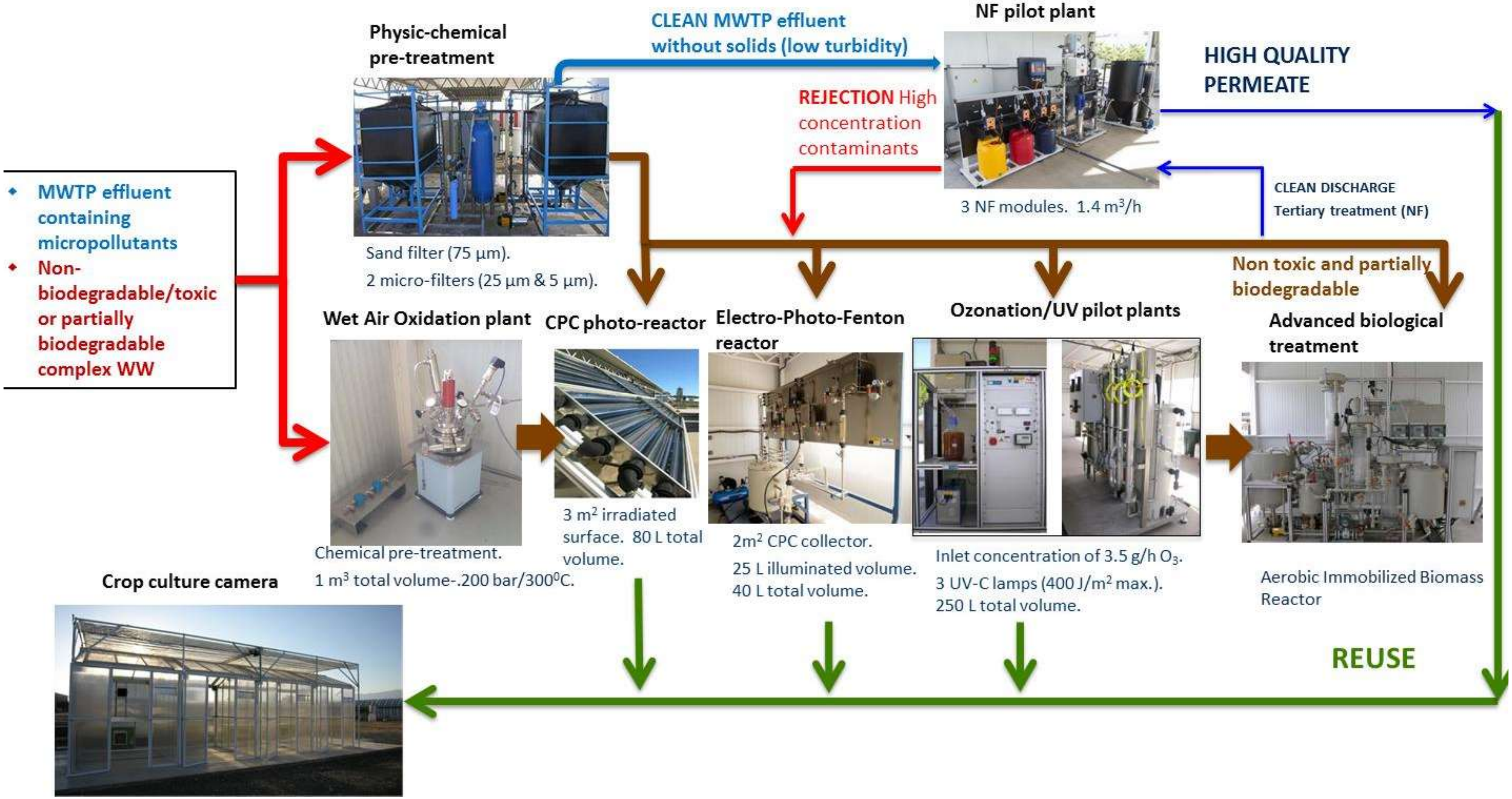
Photo-Fenton (several authors, early 90s)

$$Fe^{3+} + H_2O \xrightarrow{h\nu} Fe^{2+} + H^+ + {}^\bullet OH$$

H_2O_2/UVA

H_2O_2 + hv → 2 •***OH*** for l<280 nm
(Goldstein et al., 2007)

Water purification processes at PSA



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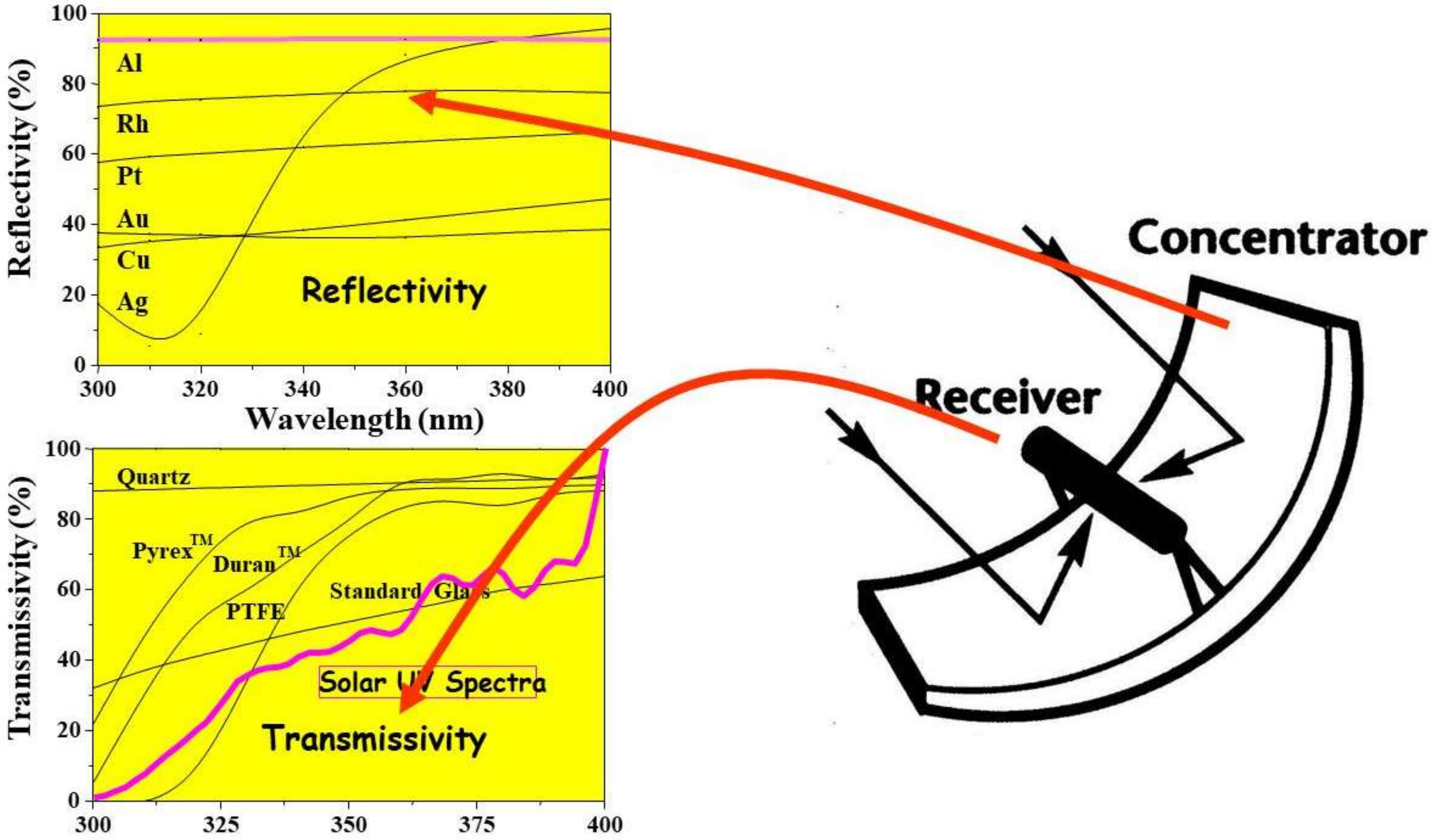
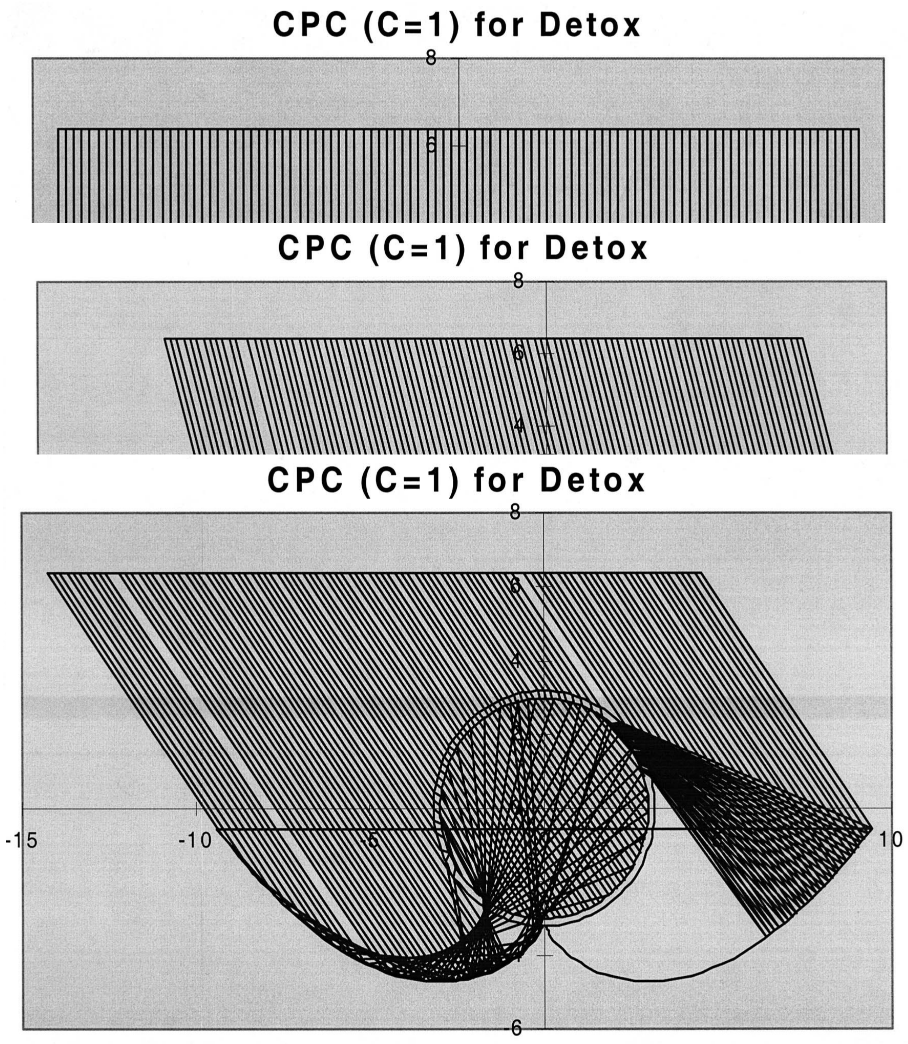
Parameters for solar reactors design

- Efficient distribution of UV radiation.
- pH resistance and chemical stability of reactor components.
- Flow guaranteed at minimal pressure.
- Maximal homogenization.
- Resistance to temperature range: 0-50ºC.
- Robust and resistant to environmental conditions.
- Easy handling, low operational cost.
- Modular systems are desirable.
- Cheap and accessible.

Solar photo-reactors design



Technical and engineering aspects of solar photo-reactors



1 Sun CPCs

1 Sun CPCs

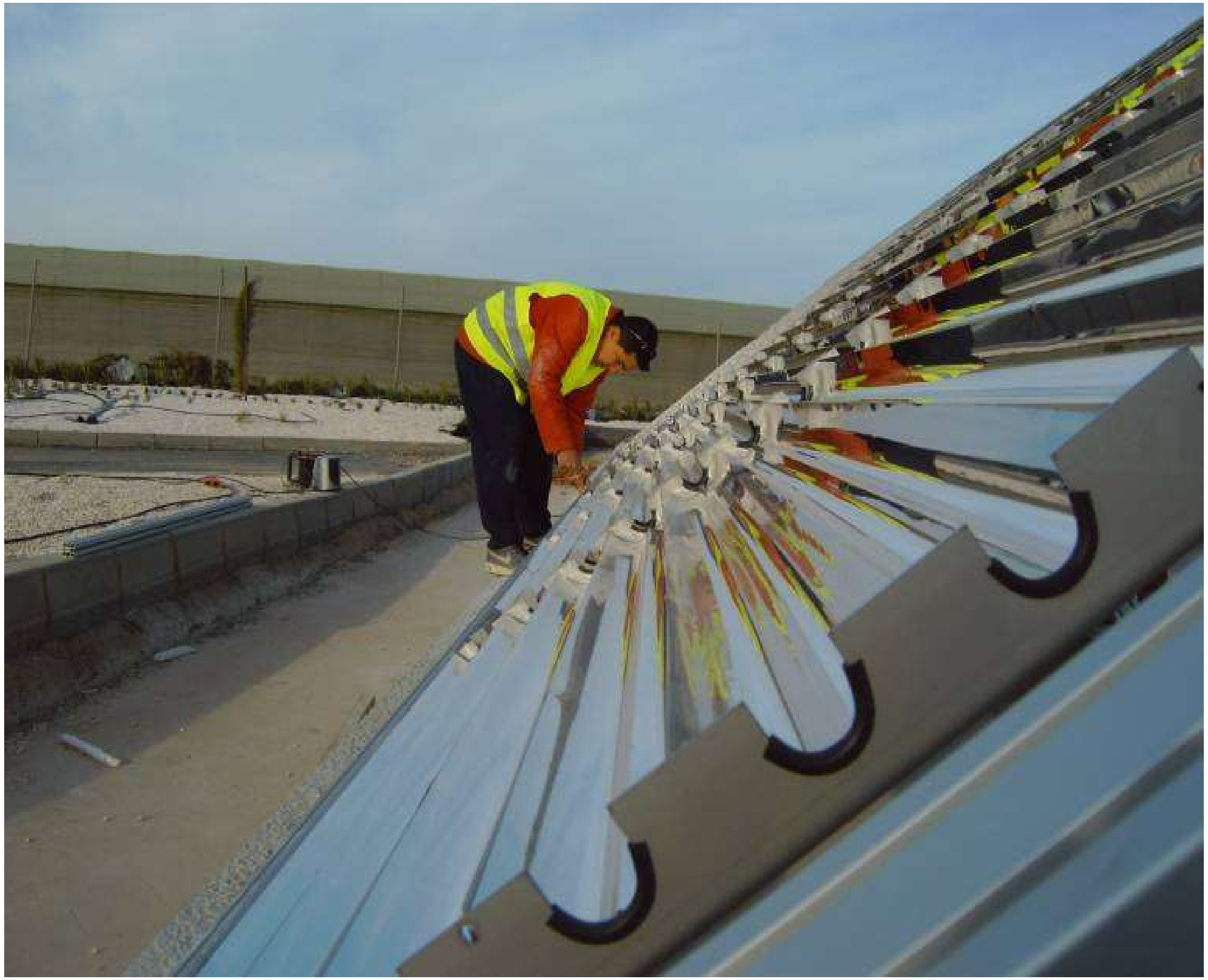
- ✓ ***Turbulent flow conditions***
- ✓ ***No vaporization of volatile compounds***
- ✓ ***No solar tracking***
- ✓ ***No overheating***
- ✓ ***Direct and Diffuse radiation***
- ✓ ***Low cost***
- ✓ ***Weatherproof (no contamination)***

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

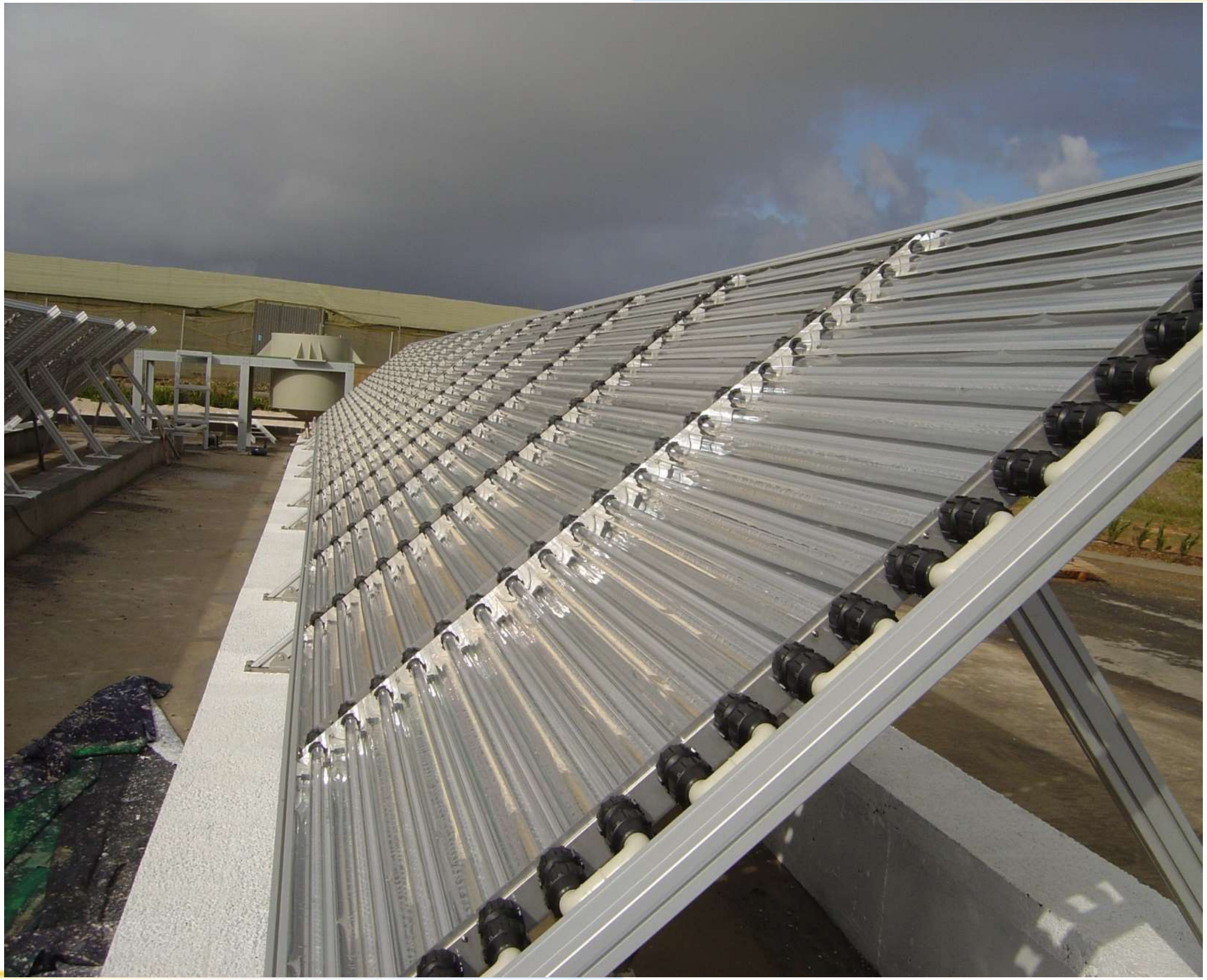
CPC photoreactors at DEMO scale

CPC photoreactors at DEMO scale

CPC photoreactors at DEMO scale

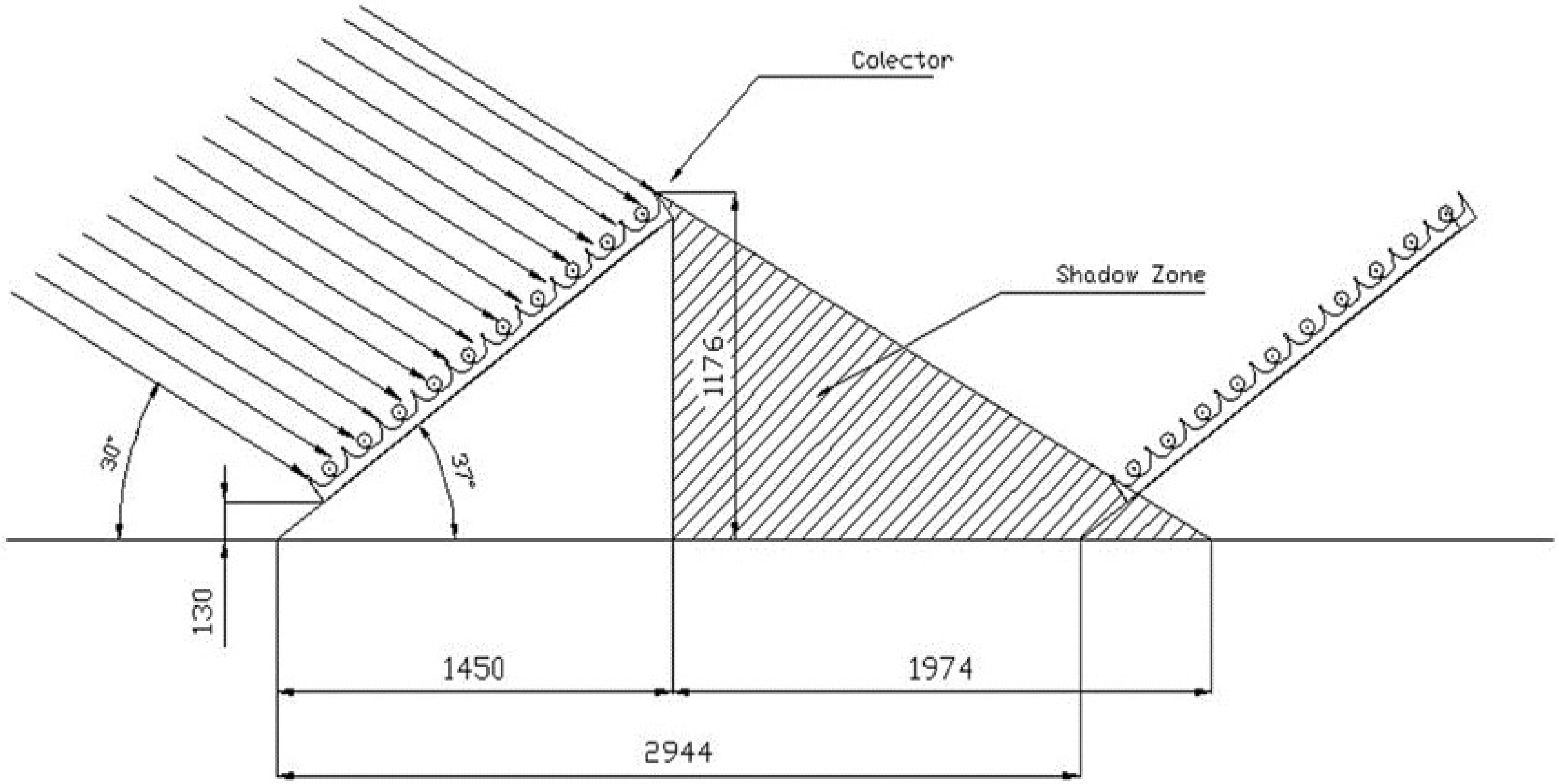


CPC photoreactors at DEMO scale



CPC photoreactors at DEMO scale

Rows separation



CPC photoreactors at DEMO scale

$$A_r = \frac{Q_{UV}\,V_t}{T_s\,\overline{\overline{UV_G}}} = \frac{12x10^3\ x1875x10^3}{3000x\,3600x\,18.6}\left[\frac{J\,L^{-1}\,L}{s\,W\,m^{-2}}\right] = 112\,m^2$$

Final selected plant dimensioning (solar collector area) was: **150 m²**

Solar field figures:

a) Individual CPC modules formed by **20 parallel tubes** (surface: **2.7** m²/module)

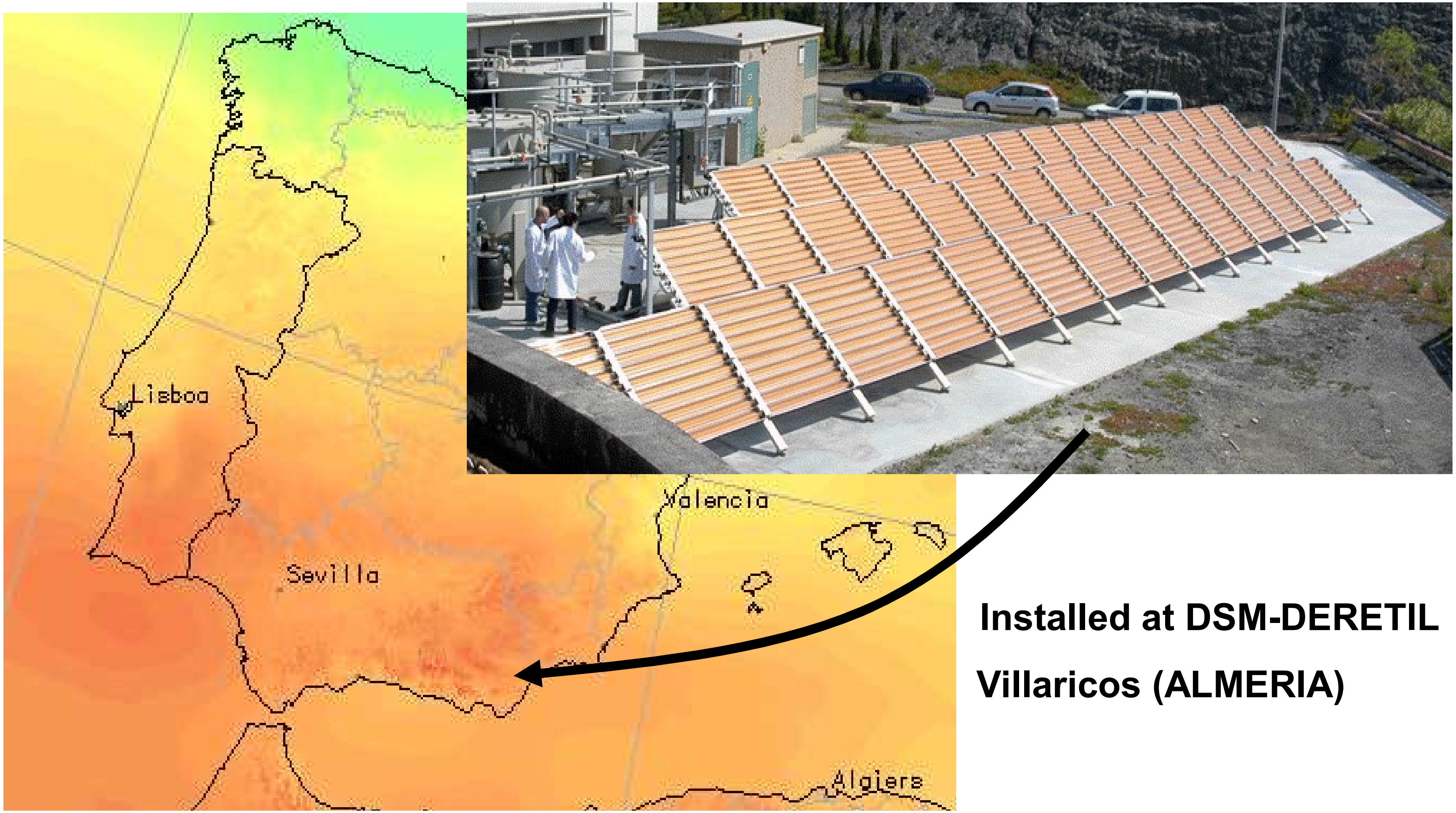
b) 4 parallel rows with **14 modules** each mounted on a 37º-tilted platform (local latitude)

c) total collectors surface: **150 m²**

d) Total photoreactor volume: **1061 L**

e) Total volume per batch: **1500** to **2000 L**

CPC photoreactors at DEMO scale



Installed at DSM-DERETIL

Villaricos (ALMERIA)

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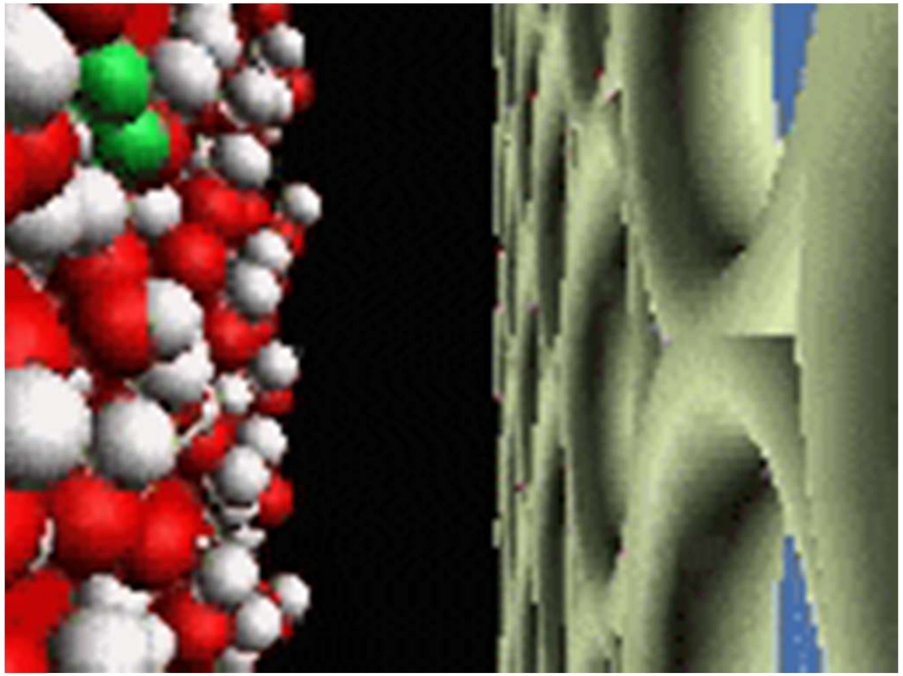
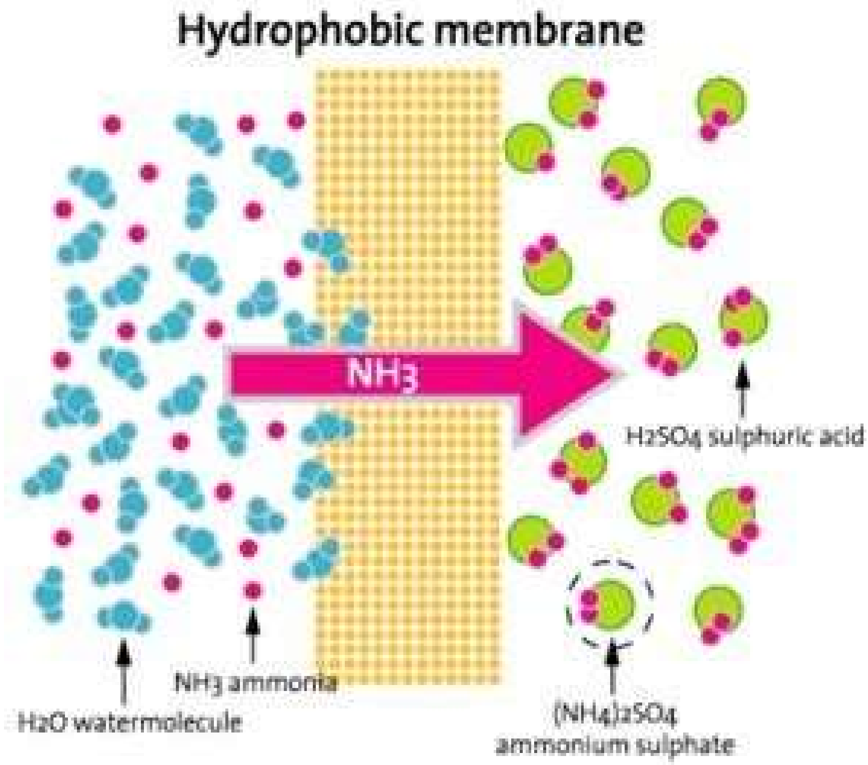
Membrane Distillation

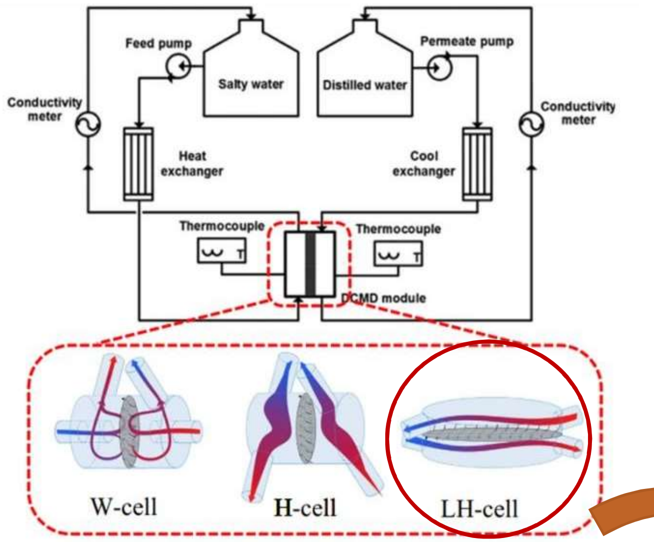


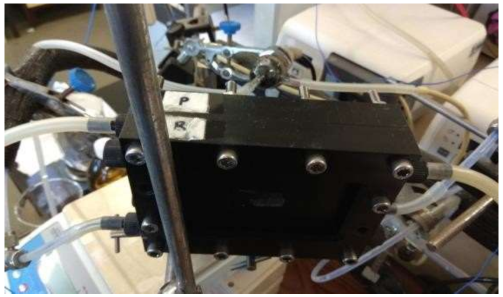


membrane.

Ammonium recovery by MD

PLANT DIAGRAM





MEMBRANE CHARACTERISTICS

Pore size (µm)	0.22
Thickness (µm)	150
S memb. (m^2)	0.007
Ref. membrane	FGLP00010

Merck Millipore Ltd.

H_2SO_4 AS A STRIPPING SOLUTION IN THE PERMEATE

Ammonium recovery by MD

Application to a secondary outlet of real water of the WWTP of Maia (Porto)

pH	Q, mL/min	$[NH_4^+]$, mg/L	$[H_2SO_4]$, M	T cell permeate, ºC	T cell retentate, ºC
12	300	200	0.01	20	80

NH_4^+ recovery, %	Interval flux, Kg/(m²·h)	V permeate, mL
54.5	25.8	600

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Combination of technologies for industrial WW treatment: Landfill leachate

Adequate remediation strategy?

- Integrated physic-chemical-biological techniques can ameliorate
- the drawbacks of individual processes and improve the overall treatment efficiency.

A **combined treatment line** for a particular landfill leachate is presented: Physic-chemical pre-treatment; Solar photo-Fenton process; Advanced biological treatment.

pH adjustment (final pH=5) H_2SO_4 (96%)

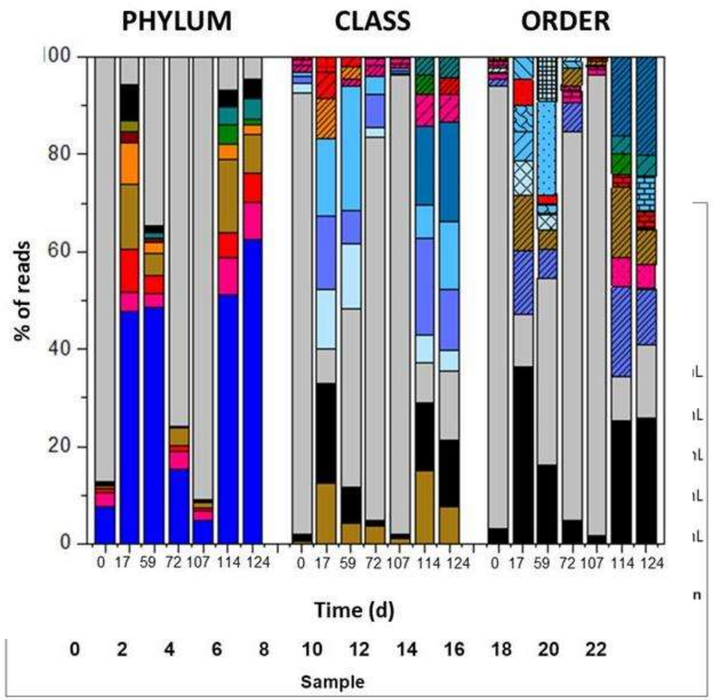
Fe^{3+} dosage ($FeCl_3 \cdot 6H_2O$) $[Fe]_{final}$=56 mg/L

Coagulation/Flocculation

Settling

pH adjustment (final pH=3) H_2SO_4 (96%)

DOC elimination (%)	H_2O_2 consumption (mg/L)	Final toxicity (%)	Final biodegradability
17.4	1800	13.8	0.44

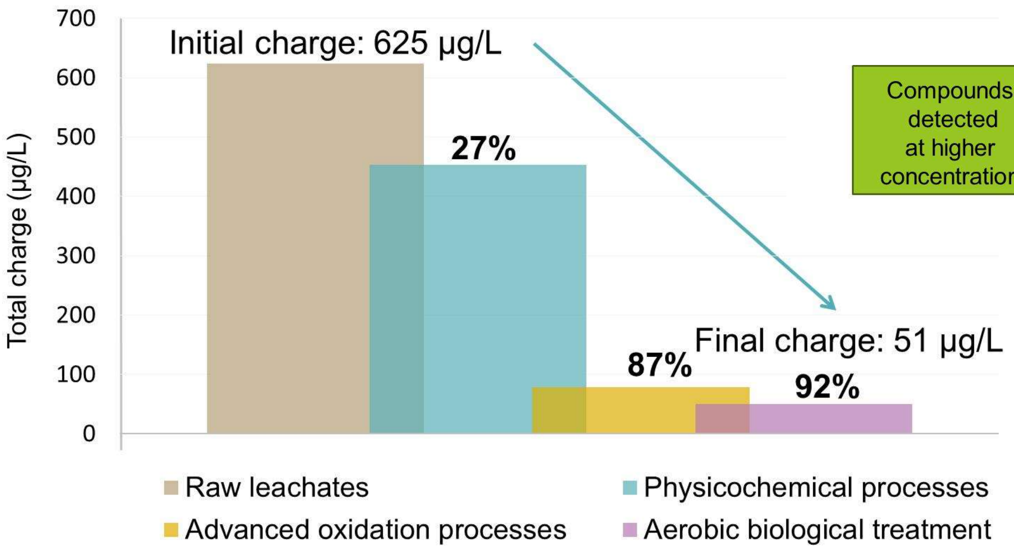


Landfill leachate treatment: Bio-treatment

ADVANCED ANALYTICAL EVALUATION

- 60 out of 115 micro-contaminants (MCs) were detected in the raw leachate
- The higher MCs removal (up to 87%) was observed after the photo-Fenton
- Over 92% of MCs were successfully degraded at the end of the treatment line

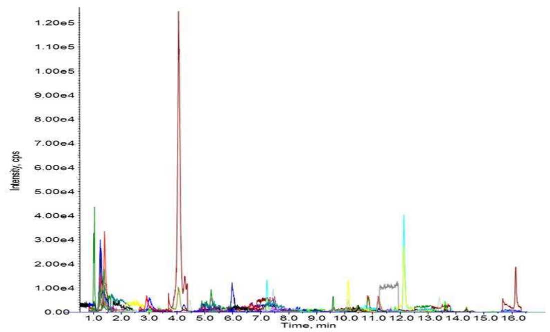
MCs REMOVAL THROUGH THE TREATMENT LINE



Compounds detected at higher concentration

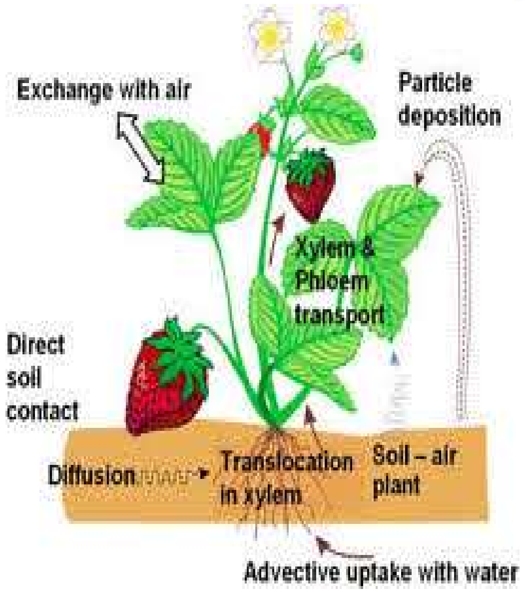
	Raw leachates (µg/L)	Treated leachates (µg/L)	% MCs REMOVAL
Ketoprofen	30	0	100
Nicotine	28	4	84
Trigonelline	37	1	97
Gabapentin	**319**	**15**	**95**
Mecropop	17	0	100
Diclofenac	25	0	100
Others	169	31	83

Compounds detected at higher concentration



Reclamation of Wastewater: CECs and OMCs

OMCs translocation to plants and detection



Pharmaceutical	Plant	Spiked concentration	Study duration (days)	Mean concentration detected in plant (μg/g)		
				Roots	Stem	Leaves
Diclofenac	*Typha latifolia*	1 mg/L	1	0.2	Not reported	0.013
Fluoxetine hydrochloride	*Brassicaceae*	280 ng/mL	12 weeks	Not detected	0.49	0.26
Carbamazepine	Cucumber	4.14 μg/L	3 months	4.5[a]	1.9[a]	39.1[a]
	Scirpus validus	0.5–2.0 mg/L	21	3.3–19.0	Not reported	0.3–0.7
Naproxen	*Scirpus validus*	0.5–2.0 mg/L	21	0.2–2.4	Not reported	0.3–0.7
Diclofenac	*Medicago sativa* L.	10 μg/L	50	162.8[a]	Not reported	Not detected
Sulfamethoxazole	*Medicago sativa* L.	10 μg/L	50	52.5[a]	Not reported	3.5[a]
Trimethoprim	*Medicago sativa* L.	10 μg/L	50	311.9[a]	Not reported	23.5[a]
17α-Ethinylestradiol	*Medicago sativa* L.	10 μg/L	50	28.9[a]	Not reported	28.3[a]

[a] Concentrations are given in μg/kg.

L.M. Madikizela et al. / Science of the Total Environment 636 (2018) 477–486

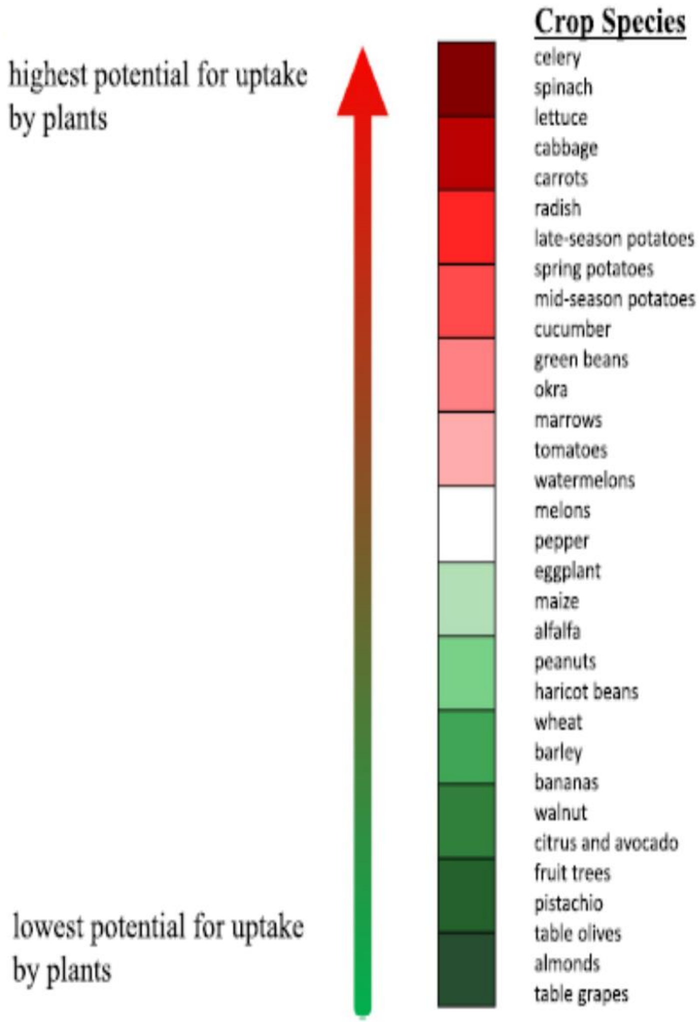
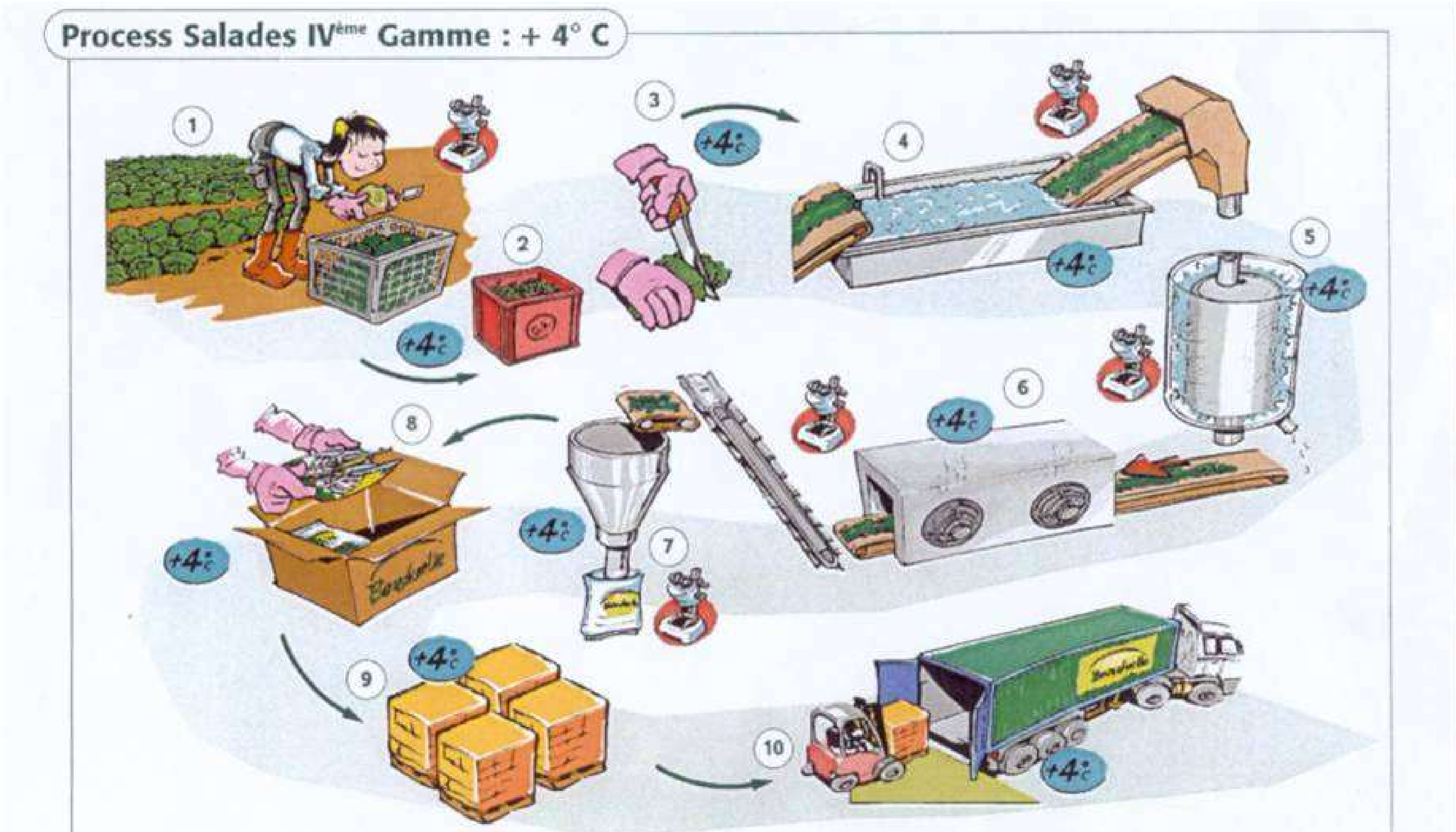


Fig. 2. Heat map showing the potential of the main crop species for CECs uptake. The highest potential for uptake is indicated with dark red; the lowest potential with dark green.

A. Christou et al. Environmental Research 170 (2019) 422–432

Fresh-cut Industry: WW reuse for crops irrigation

One of the major potable water consumers



40 m^3/t of product

Associate microbiological contamination:

E. coli O157:H7

Salmonella

ENTERIC DISEASES

Fresh-cut Industry: WW reuse for crops irrigation

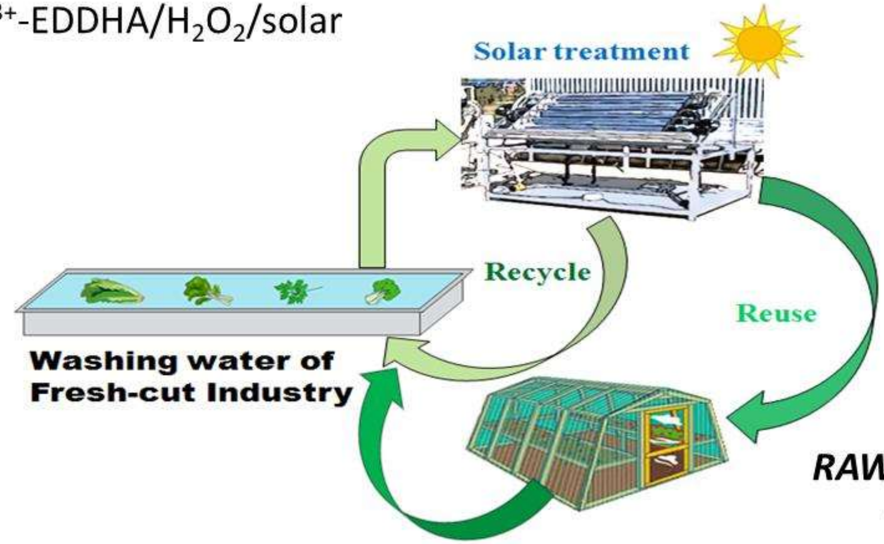
TREATMENTS:

- H_2O_2/solar
- Fe^{3+}-EDDHA/solar
- Fe^{3+}-EDDHA/H_2O_2/solar

TARGETS:

- *E. coli* O157:H7 and *Salmonella enteritidis*
- *8 OMCs*

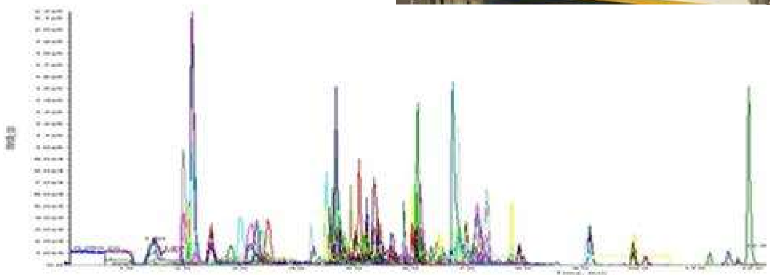
Compound	λ	t_r (min)
Thiamethoxam	250	3.0
Imidacloprid	273	3.4
Simazine	230	4.2
Atrazine	230	4.7
Azoxystrobin	214	5.4
Terbutryn	230	5.6
Procymidone	214	5.8
Buprofezin	250	6.9



RAW-EATEN VEGETABLES

- Lettuce
- Radish

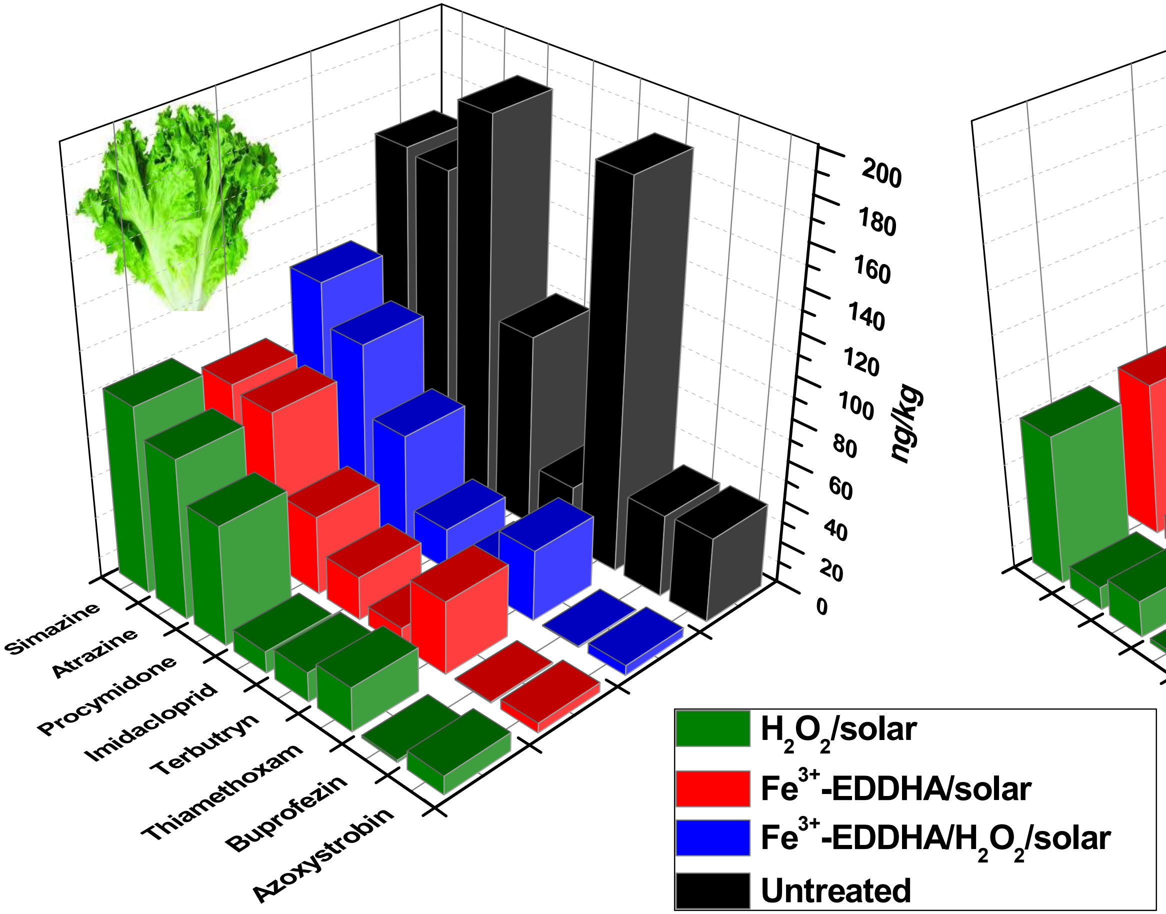
Detection of CECs

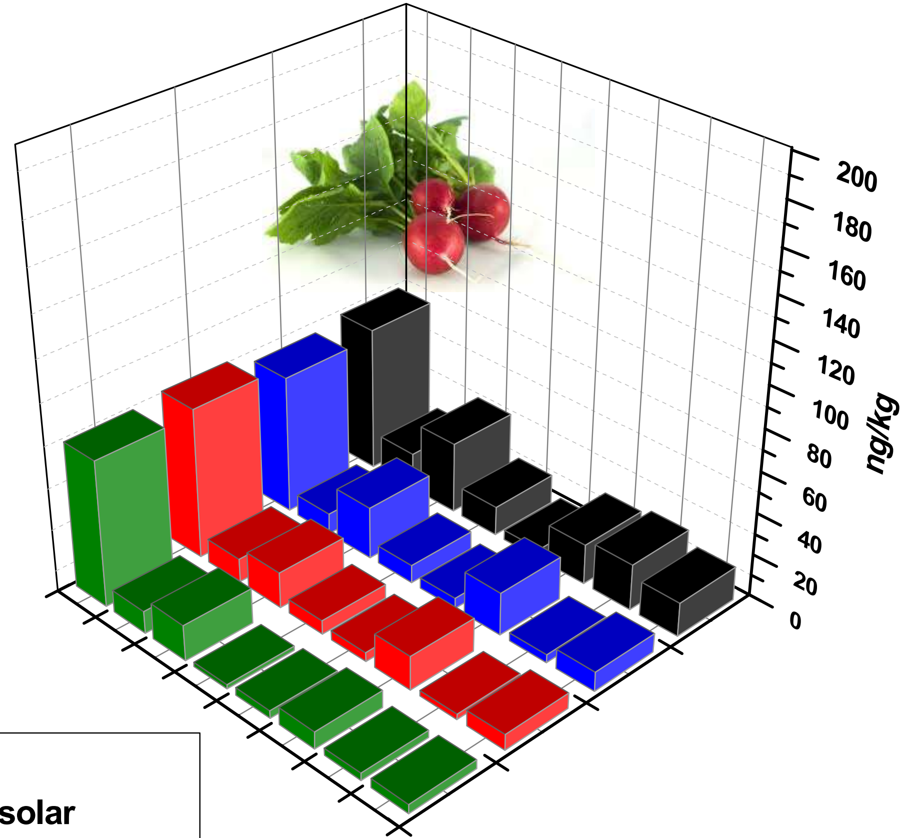


WWTP effluent irrigation

Vegetables: OMCs quantification

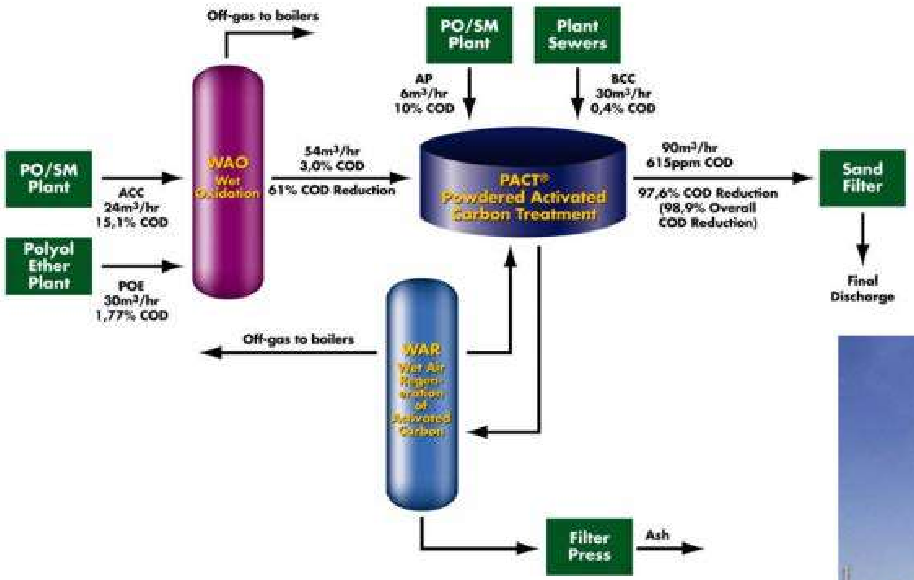
- **Lettuce**
- **Radish**

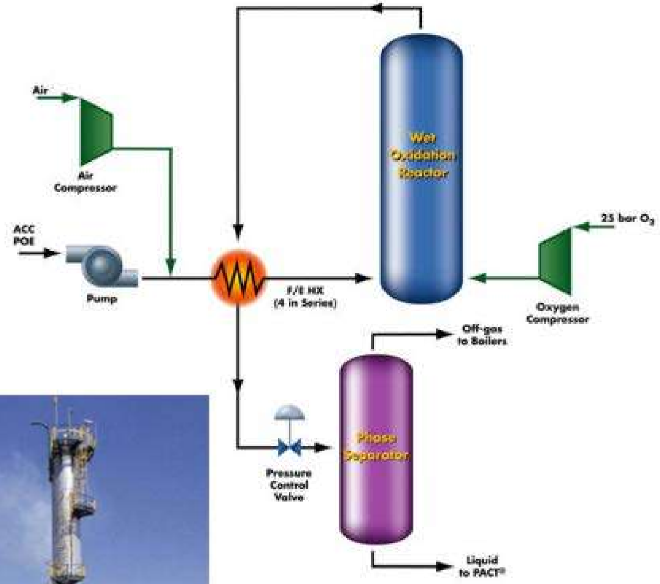




Wastewater regeneration in REPSOL

- <u>*Repsol company*</u> uses regenerated water from a municipal wastewater treatment plant (MWWTP) in some facilities. Sustainable water management is one of the challenges for 2025 by internal recycling of wastewater and the valorisation of wastes as raw material, product or energy. For example, sludge from MWWTPs used in process units or the use of waste as fertilizers.





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Key Messages

- Water scarcity and bad water quality are problems affecting all over the world, which makes it crucial to find alternative water sources, such as municipal wastewater. Municipal wastewater treatment, jointly with desalination, mean a key strategy for trying to maintain high human life quality.
- A deep evaluation on the specific problem to be solved must be done just to focus on the optimum treatment option.
- Solar based AOPs are considered a sustainable and actual viable option for reducing contaminant impact on the Environment.
- Advanced microbiological and analytical tools applied to the evaluation of industrial wastewater treatment allows the design and performance estimation of new integrated bio-chemical oxidation technologies.
- Water quality parameters monitoring as well as contaminant transfer to crops must be carried out for ensuring a "safe reuse".

Solar Treatment of Water Unit (PSA)

1 Professor; 5 PhD (2 senior, 3 Post-Doc), 3 technicians, PhD students 5 ± 2 and 15-20 visitors/year!!!

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GOBIERNO DE ESPAÑA
MINISTERIO DE CIENCIA E INNOVACIÓN
Ciemat
Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas

Thank you very much for your attention!

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