Solar based AOPs as tertiary treatments for municipal wastewater recovery

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PSA

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

Solar Treatment of Water Unit

CIEMAT-Plataforma Solar de Almería

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.

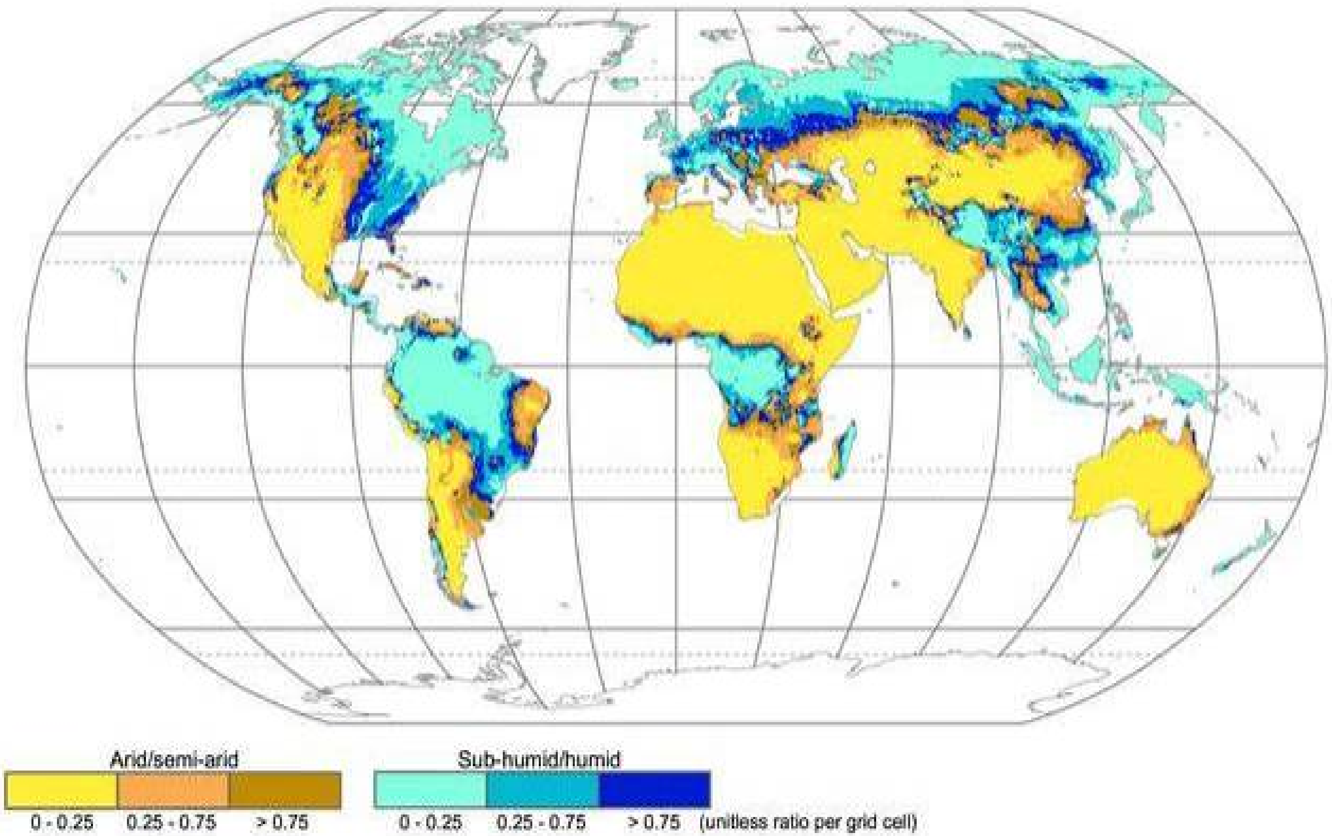
...leading research in wastewater treatment at pilot & demo scale with solar energy

Outline

- ➢ INTRODUCTION & MOTIVATION
- ➢ SOLAR PHOTO-REACTORS
- ➢ RECLAMATION OF URBAN WASTEWATER
- ➢ KEY MESSAGES

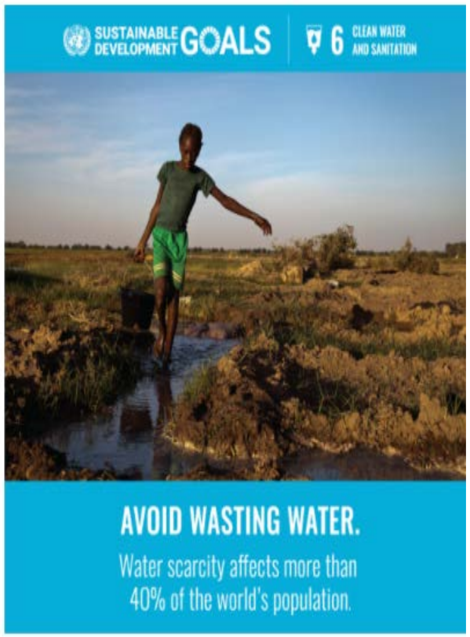
Introduction-Motivation: Solar Energy and arid zones

The binomial **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: Water Reclamation, a global need



Goal 6: Clean Water and Sanitation

https://www.un.org/sustainabledevelopment/water-and-sanitation/

6.1 By 2030, achieve universal and equitable access to safe and affordable drinking water for all

6.2 By 2030, achieve access to adequate and equitable sanitation and hygiene for all and end open defecation, paying special attention to the needs of women and girls and those in vulnerable situations

6.3 By 2030, improve water quality by reducing pollution, eliminating dumping and minimizing release of hazardous chemicals and materials, halving the proportion of untreated wastewater and substantially increasing recycling and safe reuse globally

6.4 By 2030, substantially increase water-use efficiency across all sectors and ensure sustainable withdrawals and supply of freshwater to address water scarcity and substantially reduce the number of people suffering from water scarcity

6.5 By 2030, implement integrated water resources management at all levels, including through transboundary cooperation as appropriate

6.6 By 2020, protect and restore water-related ecosystems, including mountains, forests, wetlands, rivers, aquifers and lakes

6.A By 2030, expand international cooperation and capacity-building support to developing countries in water- and sanitation-related activities and programs, including water harvesting, desalination, water efficiency, wastewater treatment, recycling and reuse technologies

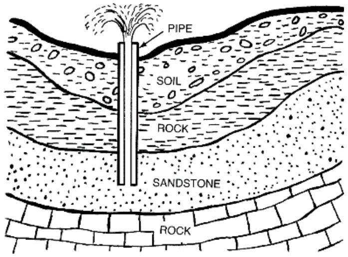
6.B Support and strengthen the participation of local communities in improving water and sanitation management

Introduction-Motivation: Water Reclamation, a global need

Benefits

- ✓ Environmental
- ✓ Social
- ✓ Economic

- It can improve the status of the environment both quantitatively, alleviating pressure by substituting abstraction, and qualitatively, relieving pressure of discharge from UWWTP to sensitive areas.



- Appropriate consideration for nutrients in treated wastewater could also reduce the use of additional fertilizers resulting in savings for the environment, farmers and wastewater treatment.

- It is considered a reliable water supply, quite independent from seasonal drought and weather variability and able to cover peaks of water demand.

- Lower investment costs and energy compared to alternative sources such as desalination or water transfer, also contributing to reduce greenhouse gas emissions.

CECs into the Environment

WWTPs

NATURAL WATERS

EMERGING CONTAMINANTS

- Until recently unknown
- Commonly use
- Emerging risks (EDCs, antibiotics)
- Unregulated

INCOMPLETE REMOVAL

CONTINUOUS INTRODUCTION INTO THE ENVIRONMENT

(ng-µg/L)

Photochemical transformations

TRANSFORMATION PRODUCTS

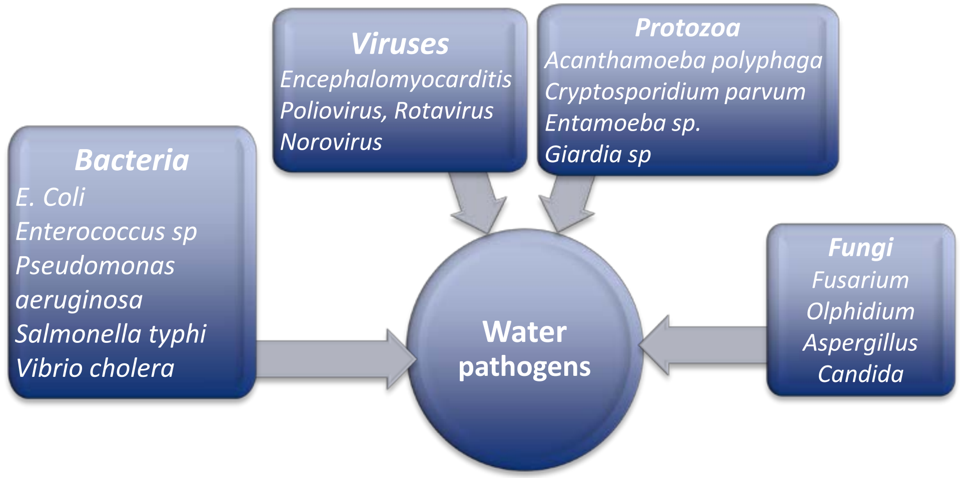
Water Microbial Contamination

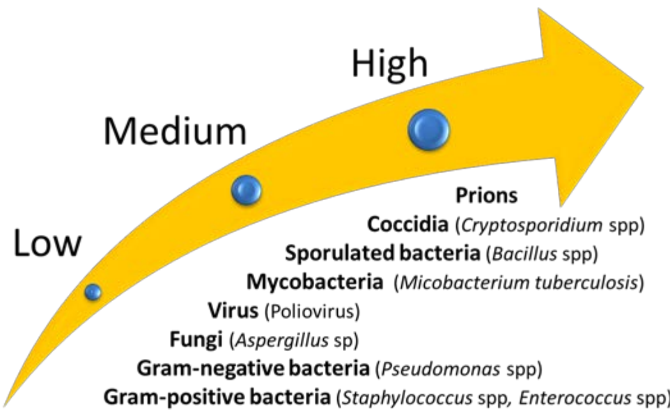
Well

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/)

Current technologies: BATs

Intensive technologies	Extensive technologies
Characterized by: -A need for large quantities of energy and minimum space. -They are accelerated artificial processes -Highly specialised operation and maintenance personnel	Characterized by: -Large amount of land (use environmental matrices and rely on natural processes), -Processes occur at almost natural rates -Energy requirement is very low. -Require low, but very important, levels of operation and maintenance.
Examples	
Physico-chemical systems (coagulation-flocculation, sand filters)	Waste stabilization ponds (maturation ponds, stabilization reservoirs, …)
Membrane technologies (Ultrafiltration, Nano filtration, reverse osmosis, membrane bioreactors…)	Constructed wetlands (vertical-flow, horizontal-flow)
Rotating biological rotators	Infiltration-percolation systems
Disinfection technologies (chlorination, Ultraviolet-C, ozonation, peracetic acid, Advanced oxidation processes…)	

Selection of the technology:

- ✓ quality of the water
- ✓ quantity of the water
- ✓ final specific use
- ✓ economic cost
- ✓ **environmental and human health impact (toxicity studies)**

Analysis of cross-contamination

Solar Advanced Oxidation Processes

TiO_2/UVA (Carey et al., 1976)

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

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

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

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)

Photo-Fenton as tertiary treatment

Advantages of organic - iron complexes

- Maintain Fe^{3+} soluble at wider pH range, enabling direct treatment at near-neutral pH values found in many natural waters
- Better absorbers in the UV-VIS region than ferric-aqua complexes
- Possible formation of additional oxidative species from Ligands via loss of electrons.

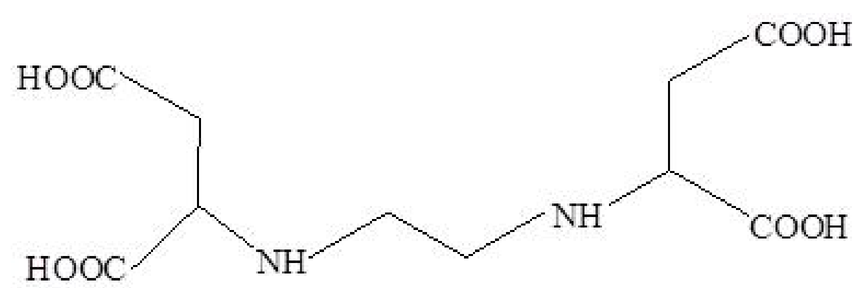
$$[Fe^{3+}L] + h\nu \rightarrow [Fe^{3+}L]^{*} \rightarrow Fe^{2+} + L^{\bullet}$$

$$L^{\bullet} + O_2 \rightarrow O_2^{\bullet-} + L'$$

$$HO_2^{\bullet} \leftrightarrow H^{+} + O_2^{\bullet-}$$

$$Fe^{3+} + O_2^{\bullet-} \rightarrow Fe^{2+} + O_2$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^{+}$$



Ethylenediamine-N,N'-disuccinic acid (EDDS)

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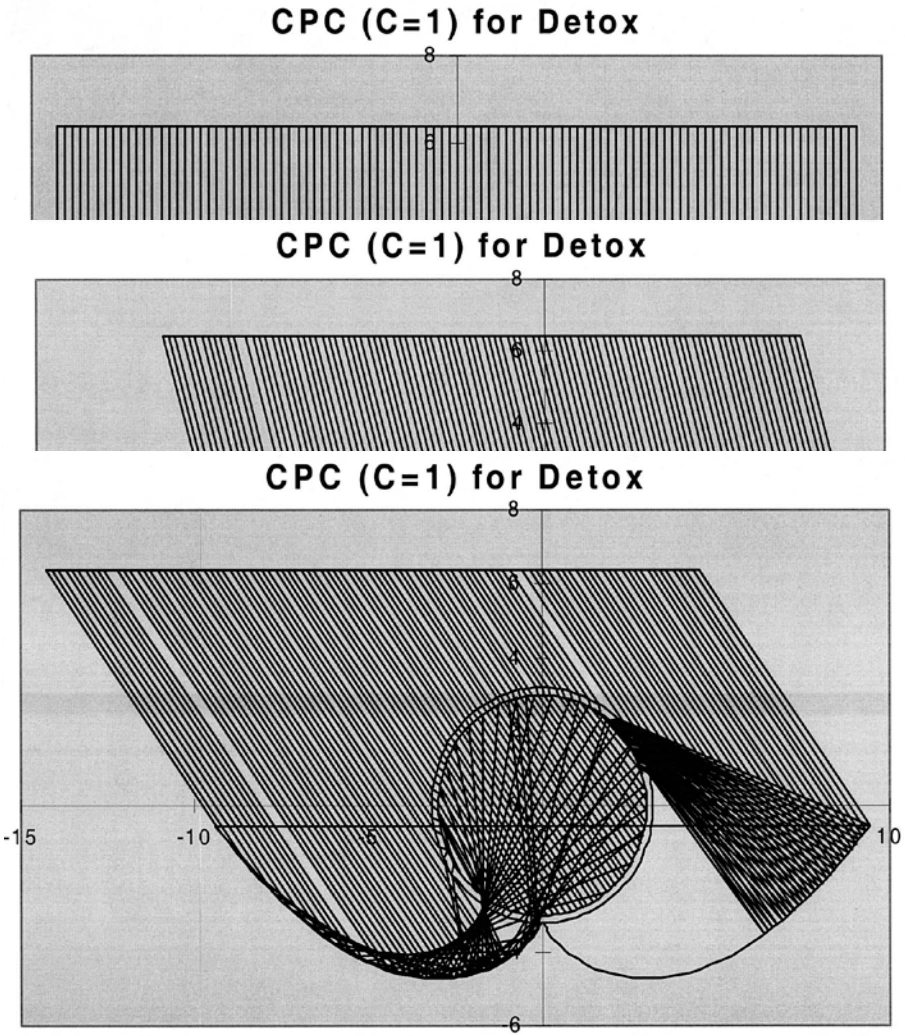
Parameters for solar reactors design

- 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.

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)***

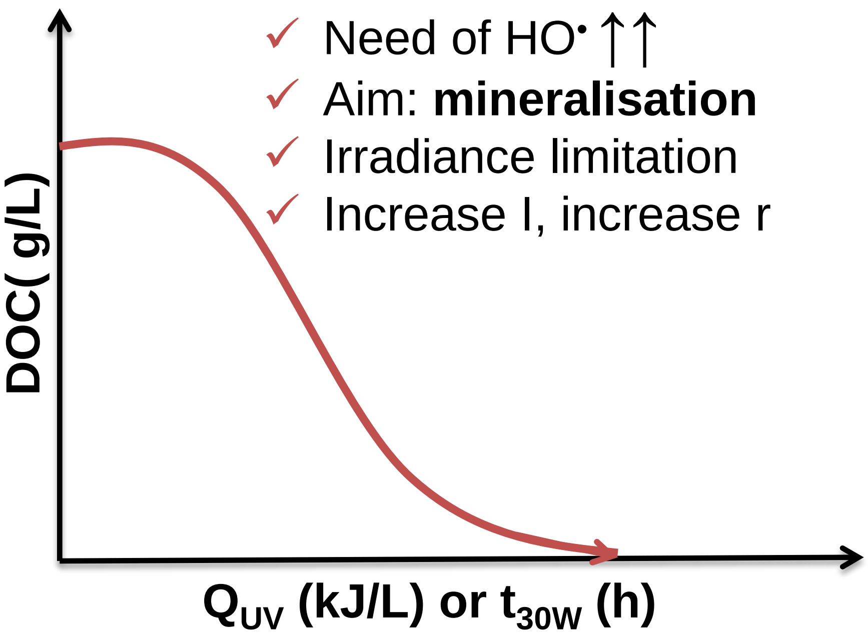
Appl. Catal. B: Environ., **37**, 1-15, 2002. Most cited paper 2002-2006.

CPC photoreactors at DEMO scale

Photosaturation in CPC. Alternative Photoreactors

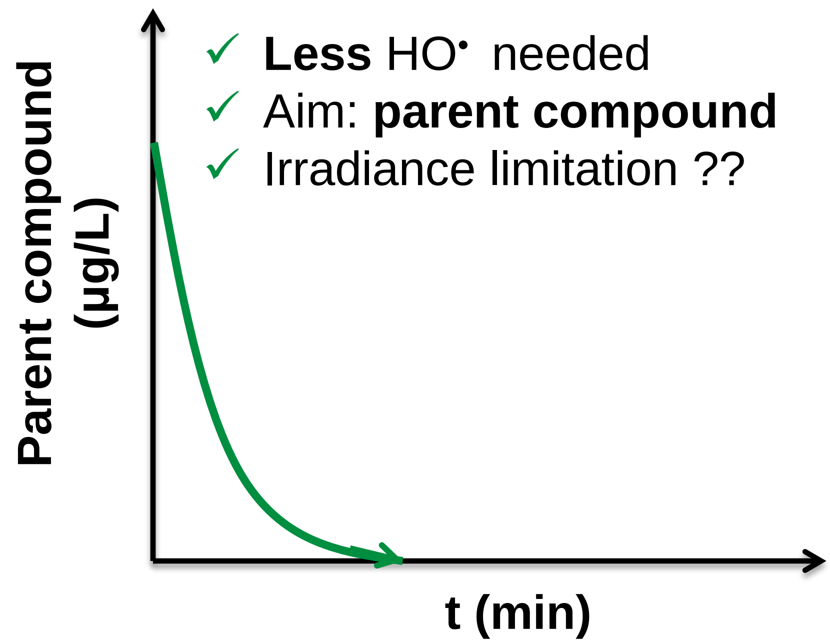
Highly polluted effluents (g/L or mg/L)

- ✓ Need of $HO^{\bullet}$ ↑↑
- ✓ Aim: **mineralisation**
- ✓ Irradiance limitation
- ✓ Increase I, increase r



Effluents containing micropollutants (µg/L)

- ✓ **Less** $HO^{\bullet}$ needed
- ✓ Aim: **parent compound**
- ✓ Irradiance limitation ??



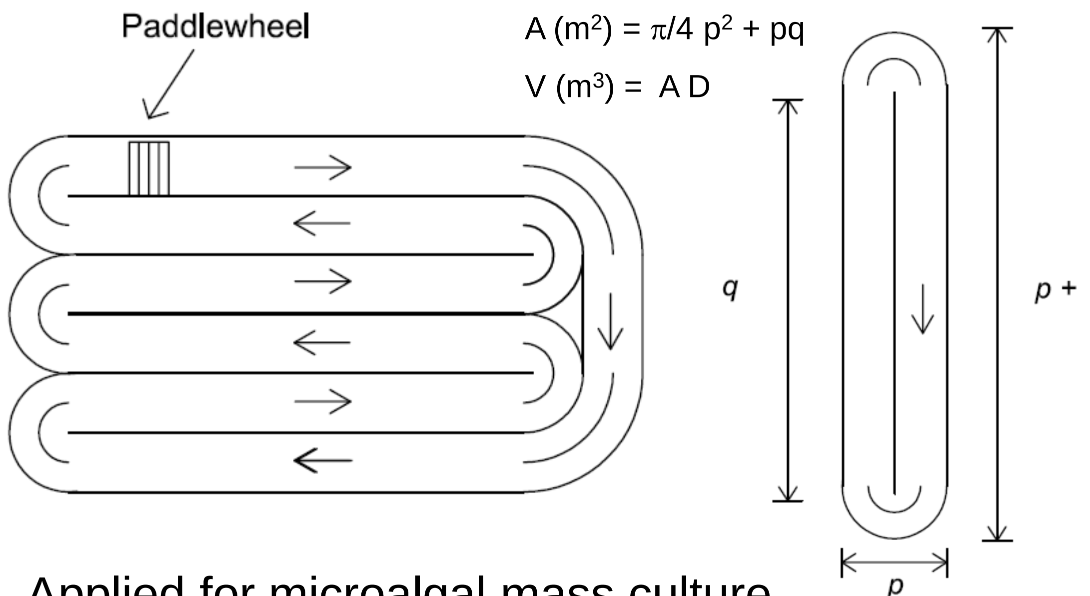
For micropollutant removal, **there is photosaturation,** so the process can be operated in photoreactors with wider optical lengths. **NOT possible with CPCs !!!**

J. Hazar. Mat., **279**, 322-329, 2014.
Appl. Catal. B: Environ., **178**, 210-217, 2015.

Alternative photoreactor: Raceway Pond Reactors

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

Microalgal cultures in RPR and TPBR. Almería.



Applied for microalgal mass culture

Low cost materials, mainly plastic liners. Construction cost **~ 10 €/m²**

Production costs in RPR are markedly lower than in tubular photobioreactors for microalgal applications

Alternative photoreactor: Raceway Pond Reactors

Por cortesía, **Prof. Gabriel Acien** (Univ. Almería)
http://www.eu-sabana.eu/

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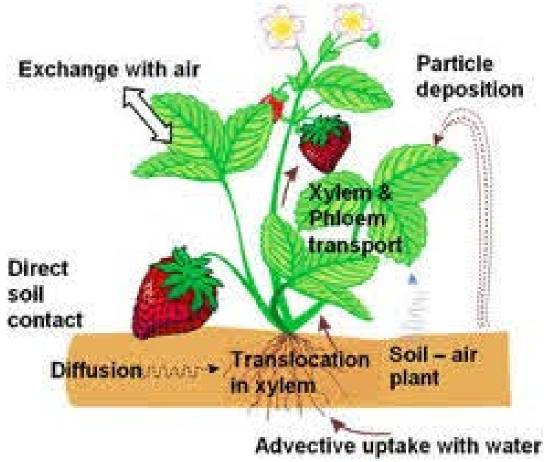
Reclamation of Wastewater: CECs and OMCs

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

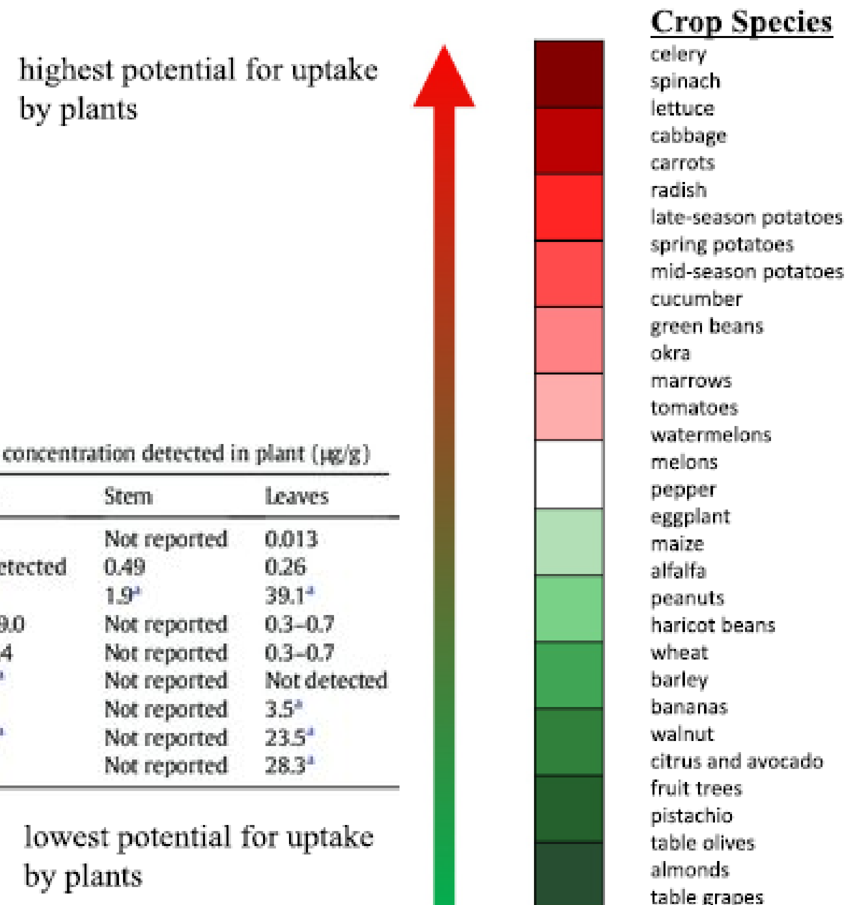
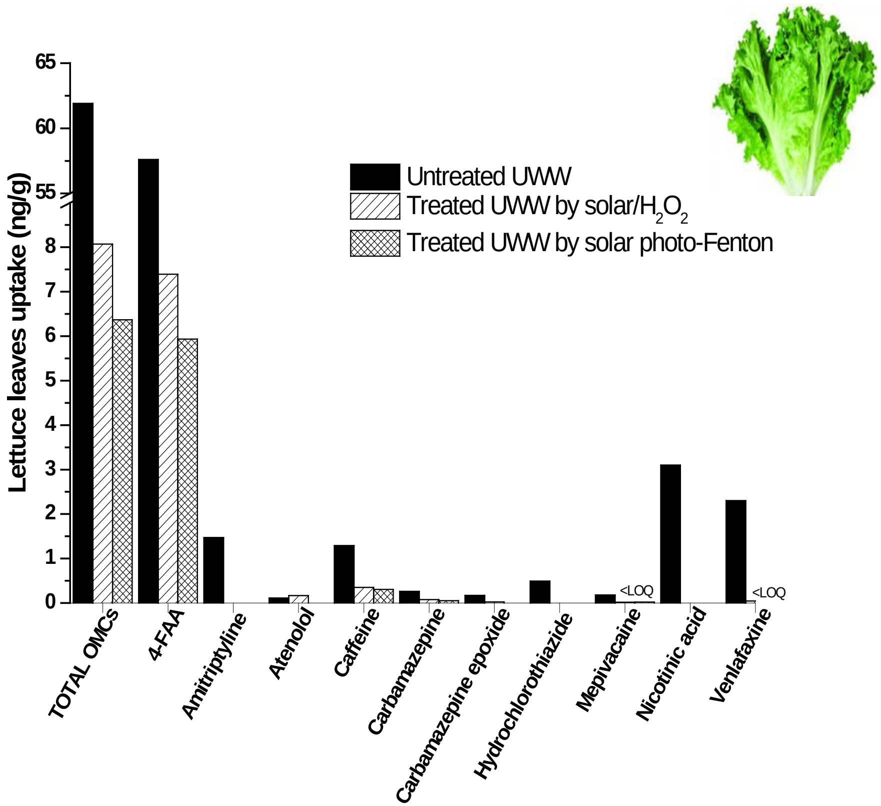


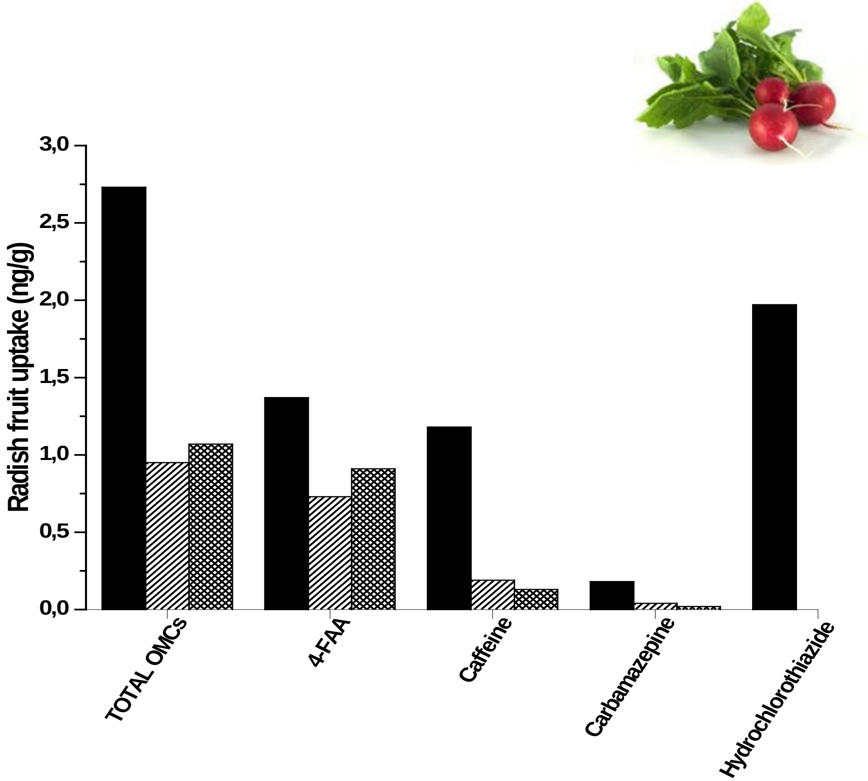
Fig. 2. Heat map showing the potential of the main crop species for CECs uptake. The highest potential for uptake is indicated with dark red; the lowest potential with dark green.

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

Reclamation of Wastewater: OMCs

Concentration (ng/g) of target analytes found in lettuces and radish fruit irrigated with untreated and treated UWW with solar processes, solar/H_2O_2 and solar photo-Fenton.





Aguas et al., Environ. Sci. Technol. 53, 9705−9714, 2017

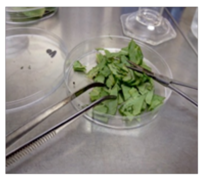
Reclamation of Wastewater: Pathogens

Microbial analysis

Detection of pathogens on lettuce and radish crop irrigated with untreated and treated UWW (Aguas et al., 2019)

3 g of leaves
Unit of fruit

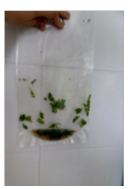
Cut in small pieces & add isotonic water

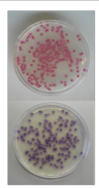


5 min stomachar
360 rpm

Plate the leaves extract

Counting colonies after incubation





Crop sample	UWW sample	Total coliforms*	*E. coli**	*Salmonella spp**	*Enterococcus spp**
Lettuce					
	Untreated	15/15 (400)	5/15 (200)	15/15 (200)	9/15 (200)
Leaves	Treated (H_2O_2/solar)	3/15 (200)	0/15 (<LOD)	0/15 (<LOD)	0/15 (<LOD)
	Treated (PhotoFenton)	3/15 (200)	0/15 (<LOD)	0/15 (<LOD)	0/15 (<LOD)
	Untreated	15/15 (15500)	15/15 (1200)	15/15 (200)	0/15 (<LOD)
Soil	Treated (H_2O_2/solar)	11/15 (900)	0/15 (<LOD)	0/15 (<LOD)	0/15 (<LOD)
	Treated (Photo-Fenton)	0/15(<LOD)	0/15 (<LOD)	0/15 (<LOD)	0/15 (<LOD)
Radish					
	Untreated	0/15 (<LOD)	0/15 (<LOD)	0/15 (<LOD)	0/15 (<LOD)
Leaves	Treated (H_2O_2/solar)	0/15 (<LOD)	0/15 (<LOD)	0/15 (<LOD)	0/15 (<LOD)
	Treated (PhotoFenton)	0/15 (<LOD)	0/15 (<LOD)	0/15 (<LOD)	0/15(<LOD)
Fruits	Untreated	10/15 (4400)	10/15 (3900)	15/15 (200)	15/15 (23300)
	Treated (H_2O_2/solar)	1/15 (1800)	0/15 (<LOD)	0/15 (<LOD)	0/15 (<LOD)
	Treated (Photo-Fenton)	0/15 (<LOD)	0/15 (<LOD)	0/15 (<LOD)	0/15 (<LOD)
Soil	Untreated	12/15 (6300)	12/15 (400)	15/15 (200)	0/15 (<LOD)
	Treated (H_2O_2/solar)	10/15(400)	0/15(<LOD)	0/15 (<LOD)	0/15 (<LOD)
	Treated (Photo-Fenton)	1/15 (100)	0/15 (<LOD)	0/15 (<LOD)	0/15 (<LOD)

* Number of positive detected samples / Total samples analized, i.e., 15 (maximum concentration in CFU/mL detected)
(< LOD): below limit of detection: 20 CFU/100mL

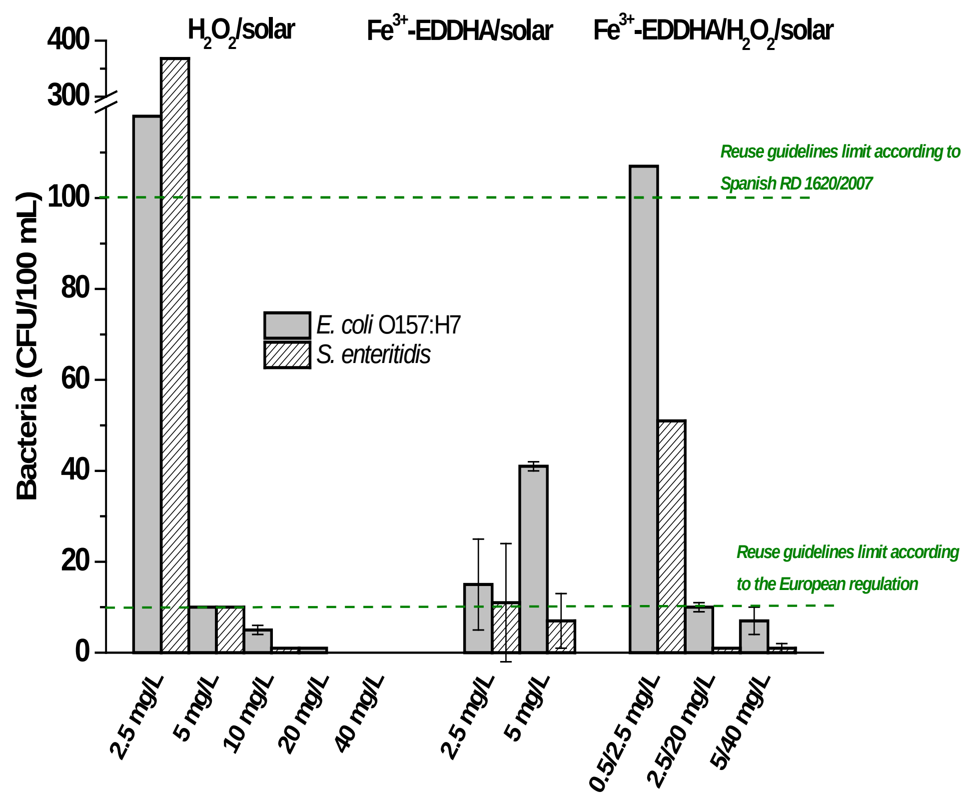
Reclamation of Wastewater: Pathogens

Regrowth during storage

Analysis of bacteria concentration in treated UWW after 24 h of storage.

INACTIVATION
OR
INHIBITION

?



S. Nahim-Granados, et al. Applied Catalysis B: Environmental 278 (2020) 119334

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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.
- Normally, different AOPs based technologies show highly efficiency as tertiary treatment for CECs & ARB elimination, but economic, health and life cycle assessments must support the final selection.
- Solar based AOPs are considered a sustainable and actual viable option for reducing contaminant impact on the Environment.
- 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; 6 PhD (2 senior, 4 Post-Doc), 3 technicians, 3 PhD students and 15-20 visitors/year!!!

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PSA

Thank you very much for your attention!

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