Wastewater treatment by solar driven AOPs: design and applications

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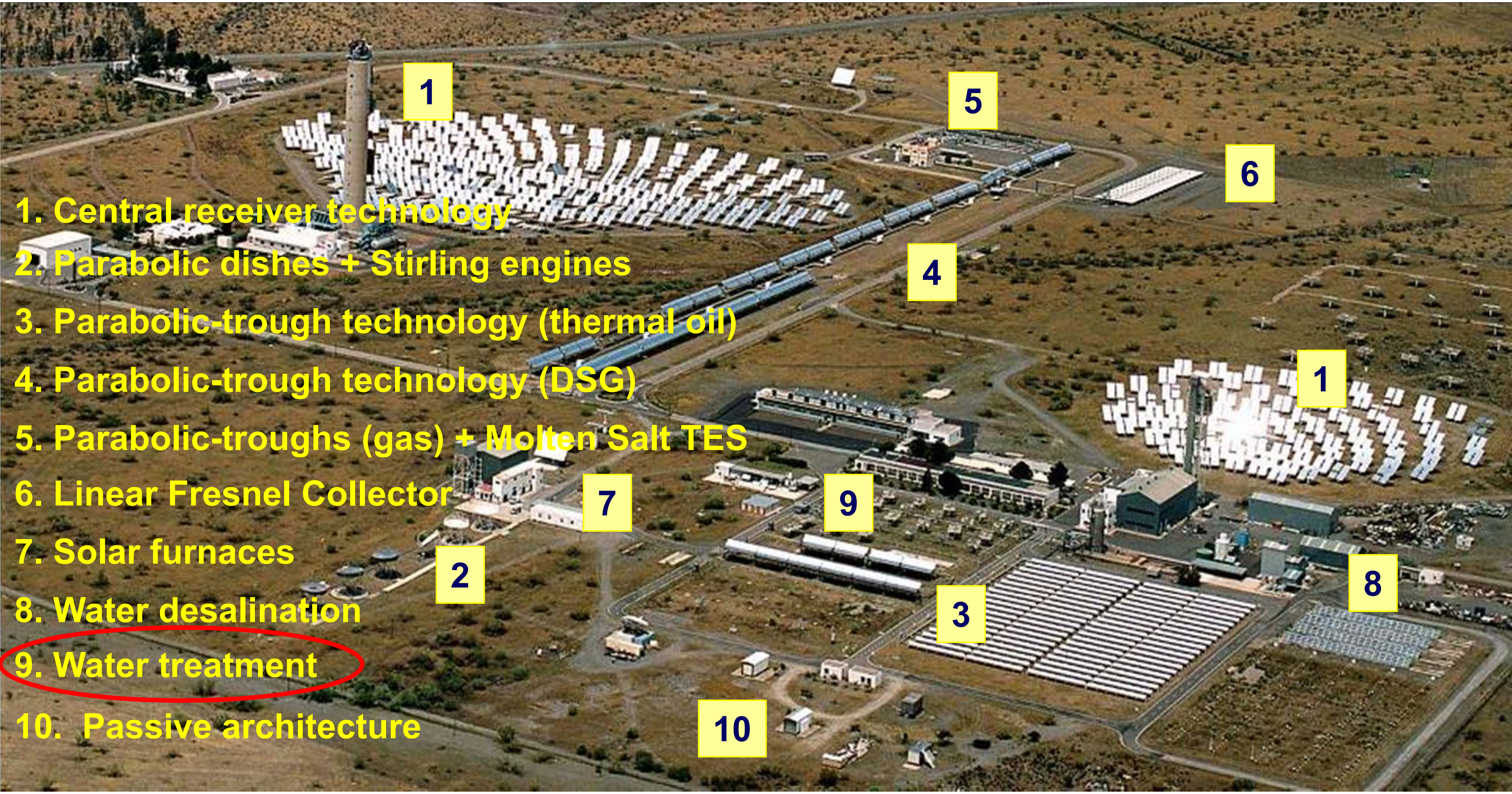


Research activities of STW Unit at PSA

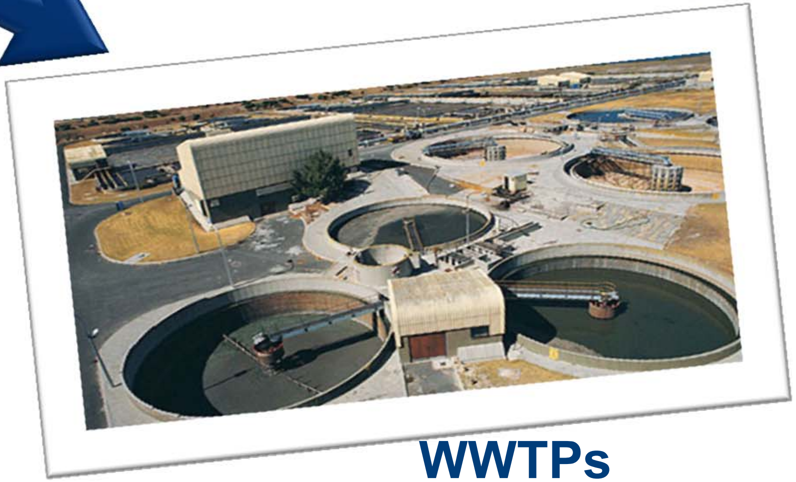
1. Using **solar photocatalytic and photochemical processes as tertiary treatment of the effluents** from secondary treatment of MWTPs, for production of clean water. For this, the removal of both **emerging pollutants** and pathogens are investigated.
2. Using **solar photocatalytic and photochemical processes for the remediation of industrial wastewaters** contaminated with several types of pollutants and water reclaim for different applications.
3. **Combining Advanced Oxidation Technologies with other water treatment techniques** such as nano- and ultra-filtration, ozonation, biological treatments, etc., for improving the water treatment efficiency and reducing operating costs.
4. Assessment of **photocatalytic efficiency of new materials** under real solar light conditions, and their use in solar CPC reactors.
5. Using **solar photocatalytic and photochemical processes for water disinfection**. Several types of contaminated water sources with a number of water pathogens are under study.
6. **Developing new solar photo-reactors** for different purposes (drinking water, water reclamation, irrigation, etc.), either water decontamination or water disinfection.

Outlook

- Introduction.
- Technical and engineering aspects of solar photo-reactors for photocatalytic applications.
- Solar photocatalysis as tertiary treatment for MWTPs effluents.
- Solar reactors for water disinfection.

Introduction

EMERGING CONTAMINANTS



WWTPs

NATURAL WATERS

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

INCOMPLETE REMOVAL

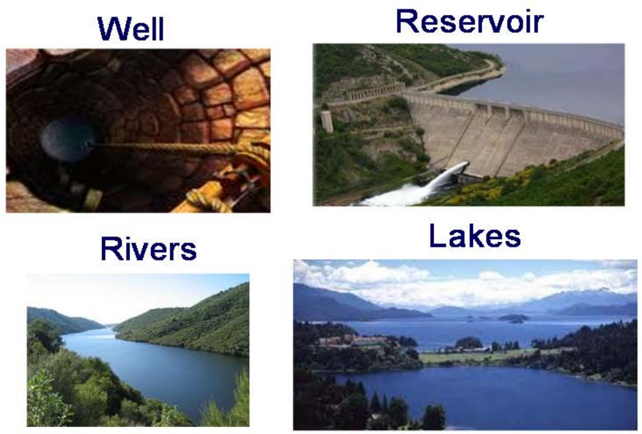
CONTINUOUS INTRODUCTION INTO THE ENVIRONMENT

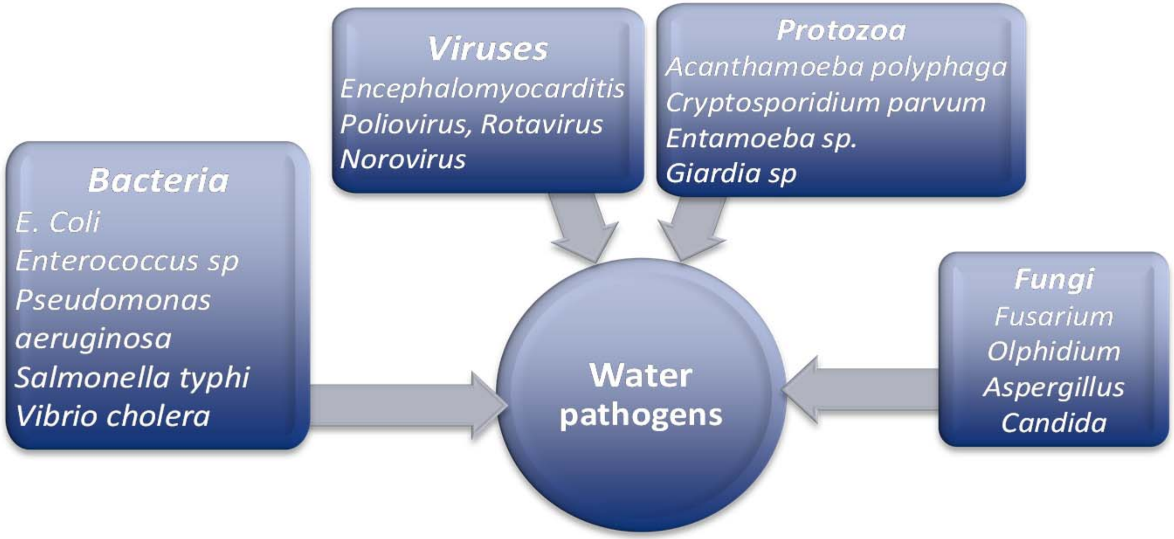
(ng-µg/L)

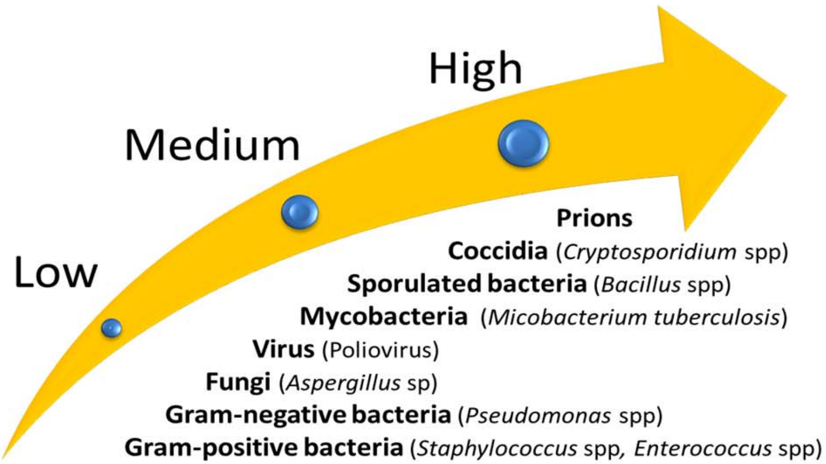
Photochemical transformations

TRANSFORMATION PRODUCTS

Water microbial contamination







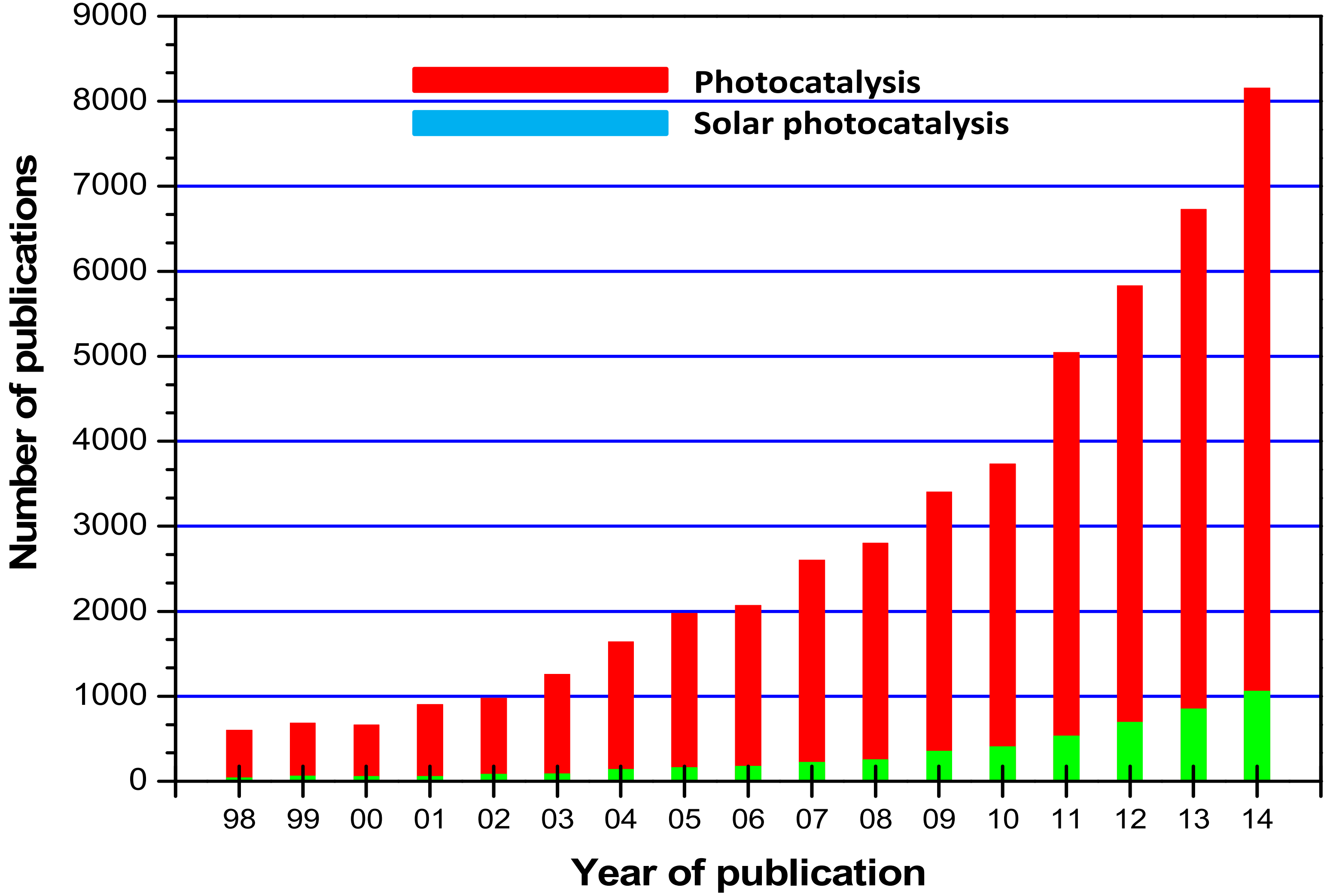
Introduction

Advanced Oxidation Processes (AOPs) are a source of hydroxyl radicals ($OH^{\bullet}$)

Nevertheless, **technical applications are still scarce**. Process costs may be considered the main obstacle to their commercial application.

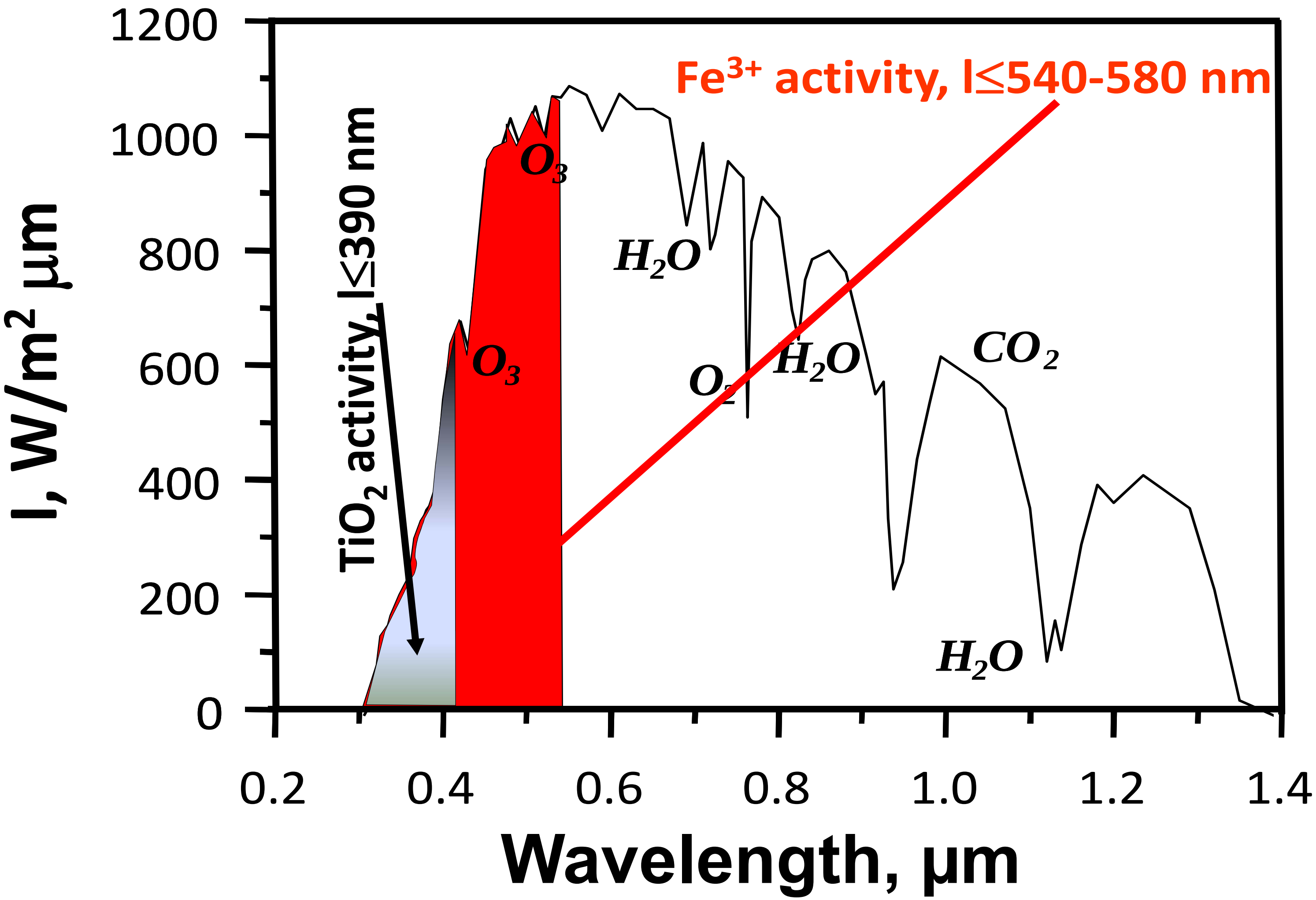
"near ambient temperature and pressure water treatment processes which involve the generation of hydroxyl radicals in sufficient quantity to effective water purification"

Introduction. Solar AOPs



source: www.scopus.com 2015

Introduction. Solar AOPs



Introduction. Solar AOPs

TiO_2/UVA (Carey et al., 1976)

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

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

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

Fenton (J. Chem. Soc., 1894)

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

Photo-Fenton (several authors, early 90s)

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

Fe(III)-Fe(II)/UVA

Aquacomplexes Fe(III) + hv → •***OH***

(Mazellier et al., 1997a,b; Brand et al., 1998, 2000; Mailhot et al., 1999)

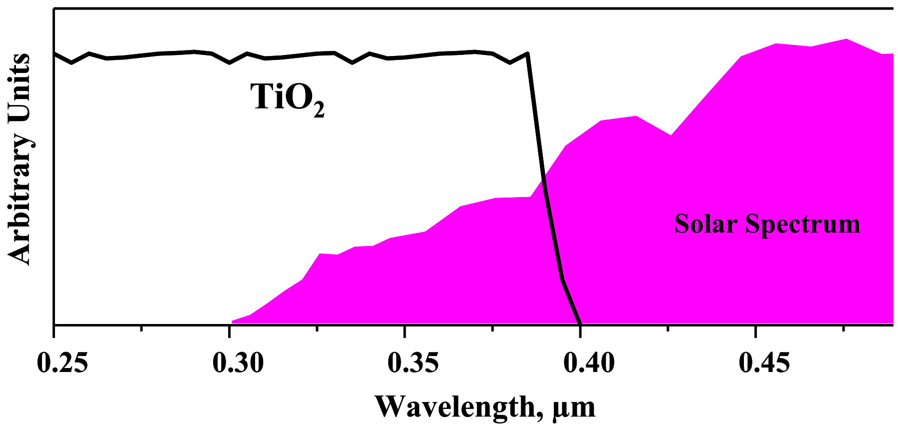
Aquacomplexes Fe(II) + h v → •***OH*** (Benkelberg and Warneck, 1995)

H_2O_2/UVA

H_2O_2 + h v → 2 •***OH*** for l<280 nm

(Goldstein et al., 2007)

Introduction. Solar photocatalysis with TiO_2



<u>Linearly dependent on the energy flux but only ~5% of the whole solar spectrum is available for TiO_2 band-gap.</u>

♦ 75% of solar collector efficiency and 1% for the catalyst means 0.04% original solar photons are efficiently used. This is a rather inefficient process.

<u>Mild catalyst working under mild conditions with mild oxidants.</u>

- ♦ As concentration of contaminants and water ionic strength increase: slow kinetics and unpredictable mechanisms need to be solved.
- ♦ TiO_2 efficiency improved with the addition of powerful oxidants or when doped (with iron, nitrogen…) to undertake practical applications.
- ♦ Pure TiO_2 can utilize only UV and new catalysts able to work with the visible component of the solar spectrum are needed.

Introduction. Solar photo-Fenton process

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

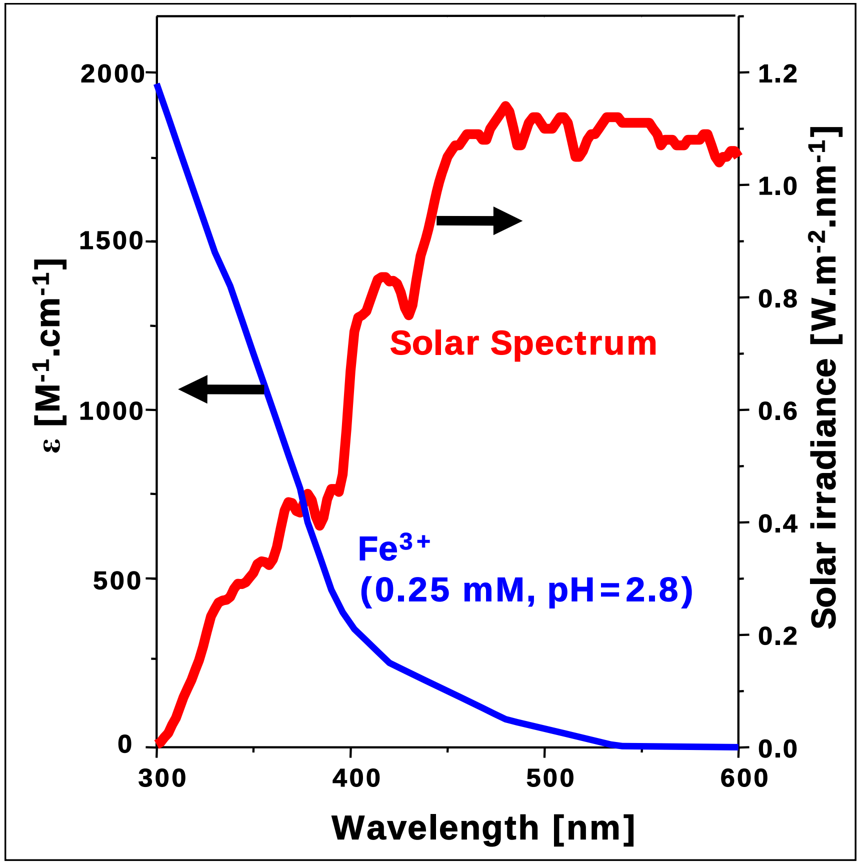
$$Fe^{2+} + OH^\bullet \rightarrow Fe^{3+} + OH^-$$

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

$$[Fe(H_2O)]^{3+} + h\nu \longrightarrow Fe^{2+} + OH^\bullet + H^+$$

$$[Fe(OH)]^{2+} + h\nu \longrightarrow Fe^{2+} + OH^\bullet$$

$$[Fe(OOC-R)]^{2+} + h\nu \rightarrow Fe^{2+} + CO_2 + R^\bullet$$



Introduction. Solar photo-Fenton process

Widely applied for wastewater treatment under different operating conditions.

Several aspects may also greatly contribute to market introduction upon achieving maturity:

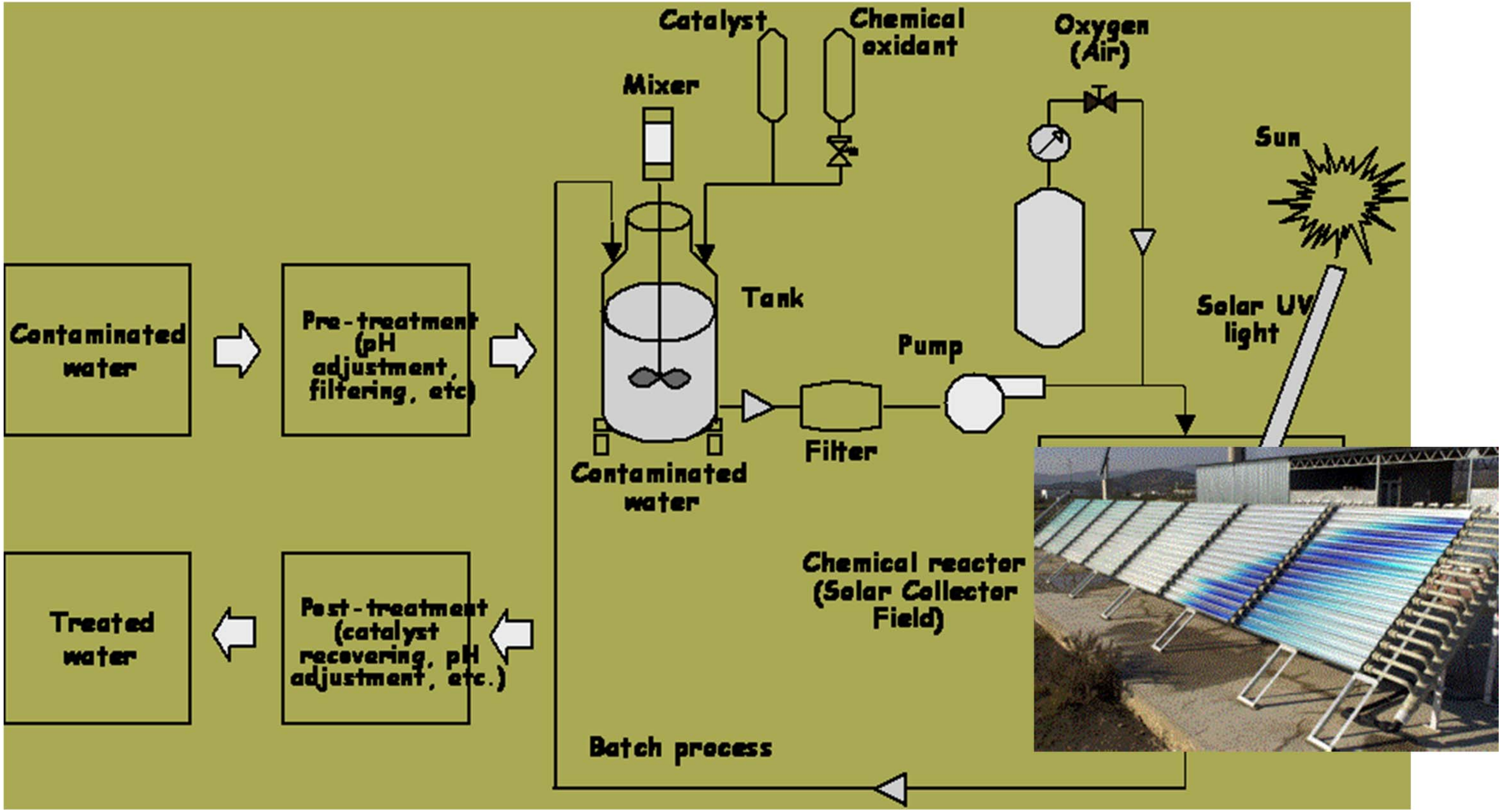
♦ Catalysts based on immobilized iron. Heterogeneous photo-Fenton for working at natural wastewaters pH.

♦ Additives which enhance the process performance, either regarding kinetics or **pH operation range.**

♦ Optimization of treatment taking into account the **wastewater specific characteristics**.

♦ Ways to minimize **hydrogen peroxide consumption**, which is the main factor regarding operating costs.

Introduction. Solar photocatalysis pilot plant



Introduction. Evaluation and measurement of irradiance

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Q_{UV} (J l^{-1}): cumulative UV energy during exposure time per unit of volume of treated water.

$$Q_{UV,n} = Q_{UV,n-1} + \frac{A}{V_t}\int_{t_{n-1}}^{t_n} UV(t)\cdot dt$$

UV Dose (J m^{-2}): UV energy received per unit surface during exposure time.

$$Dose_{UV} = \int_{t_0}^{t_f} UV(t)\cdot dt$$

UV Energy (J): total UV energy received during exposure time.

$$Energy_{UV} = A\cdot\int_{t_0}^{t_f} UV(t)\cdot dt$$

Outlook

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- Technical and engineering aspects of solar photo-reactors for photocatalytic applications.
- Solar photocatalysis as tertiary treatment for MWTPs effluents.
- Solar reactors for water disinfection.

Technical and engineering aspects of solar photo-reactors

Concentrating or non-concentrating collectors

Sandia National Labs (Albuquerque, USA) developed in 1989 the first solar facility for water detoxification at pre-industrial level based on One-axis Parabolic Trough Collectors (PTC).

These pilot plants were the first step in the development of the solar technology.

Concentrating or non-concentrating collectors

CIEMAT, in 1990, erected the second at *Plataforma Solar de Almería* (Spain), using 2-axis PTCs.

Initially, it consisted of two-axis HELIOMAN collectors with a total collector area of 384 m^2.

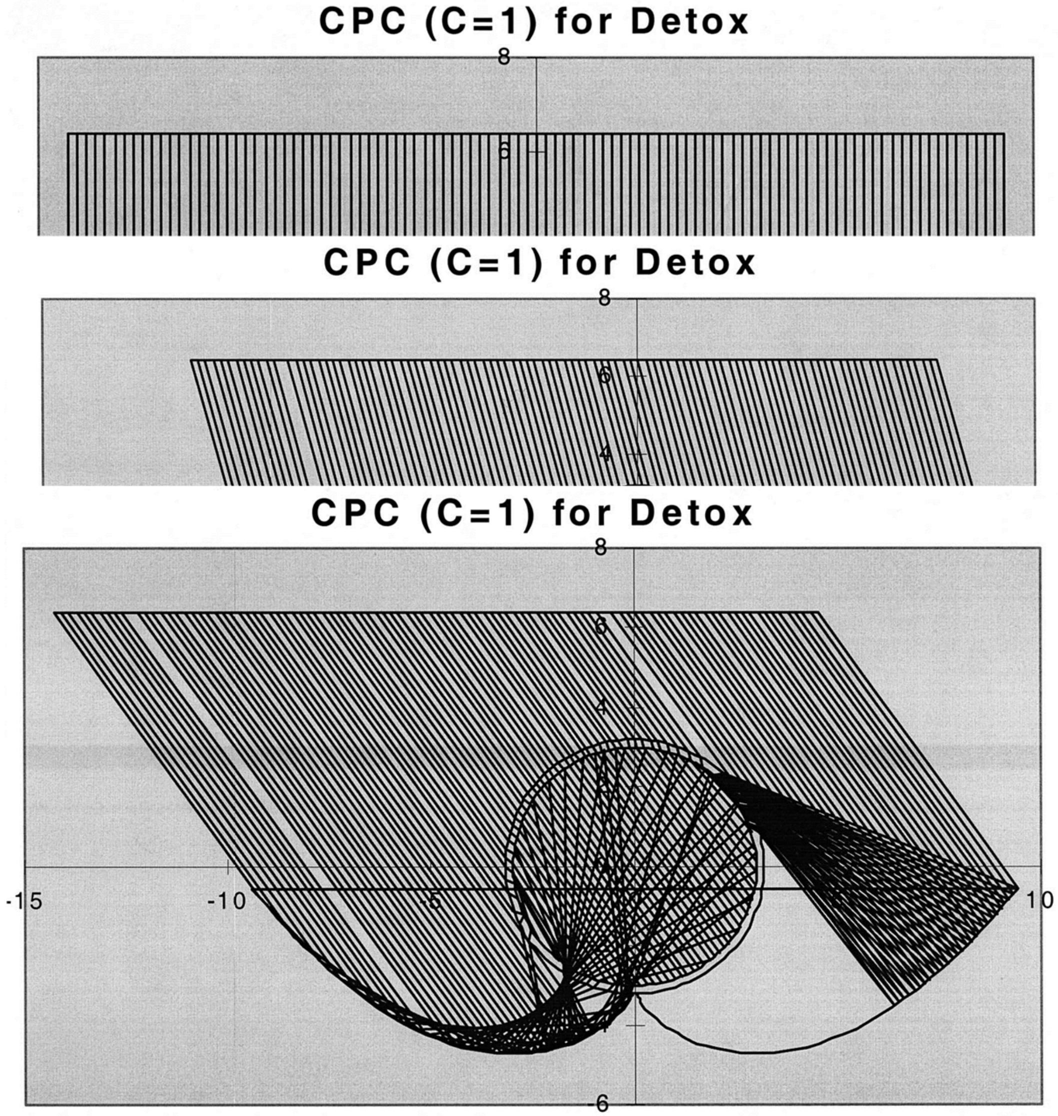
It has been widely used during the 90s by many European research groups (supported by EU) resulting in a continuous contribution of new ideas about the process and technology.

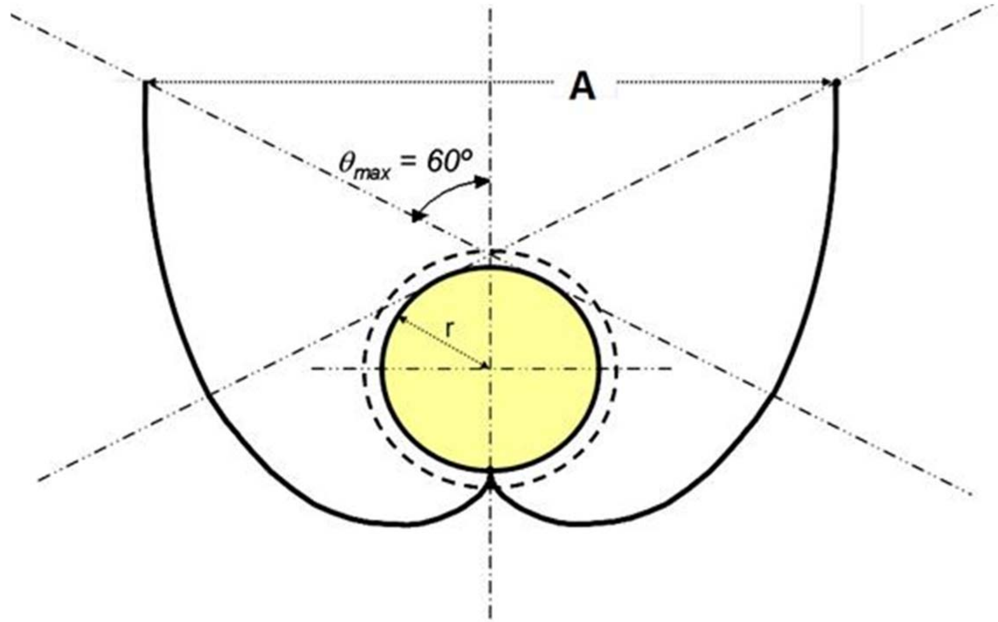
Concentrating or non-concentrating collectors

One-sun (non-concentrating) collectors are cheaper than PTCs. An extensive effort in the design of small non-tracking collectors, has resulted in the testing of several different non-concentrating solar reactors.

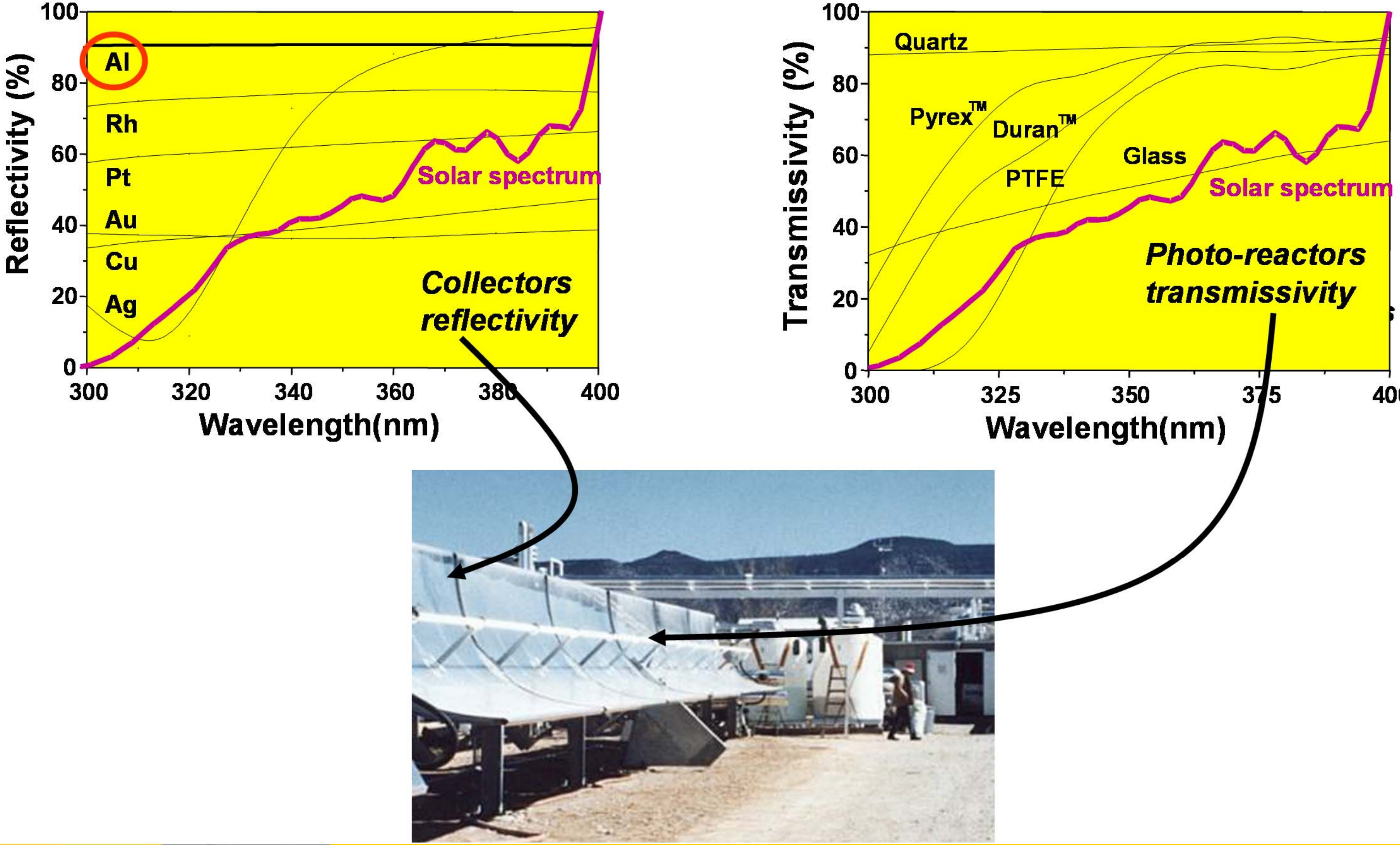
The design of a robust one-sun photoreactor is not trivial: weather-resistant, chemically inert and ultraviolet-transmissive. Also, flow in non-concentrating systems is usually laminar.

1 Sun CPCs


CPC (C=1) for Detox
8
6
CPC (C=1) for Detox
8
6
4
CPC (C=1) for Detox
8
6
4
-15
-10
-5
10
-6

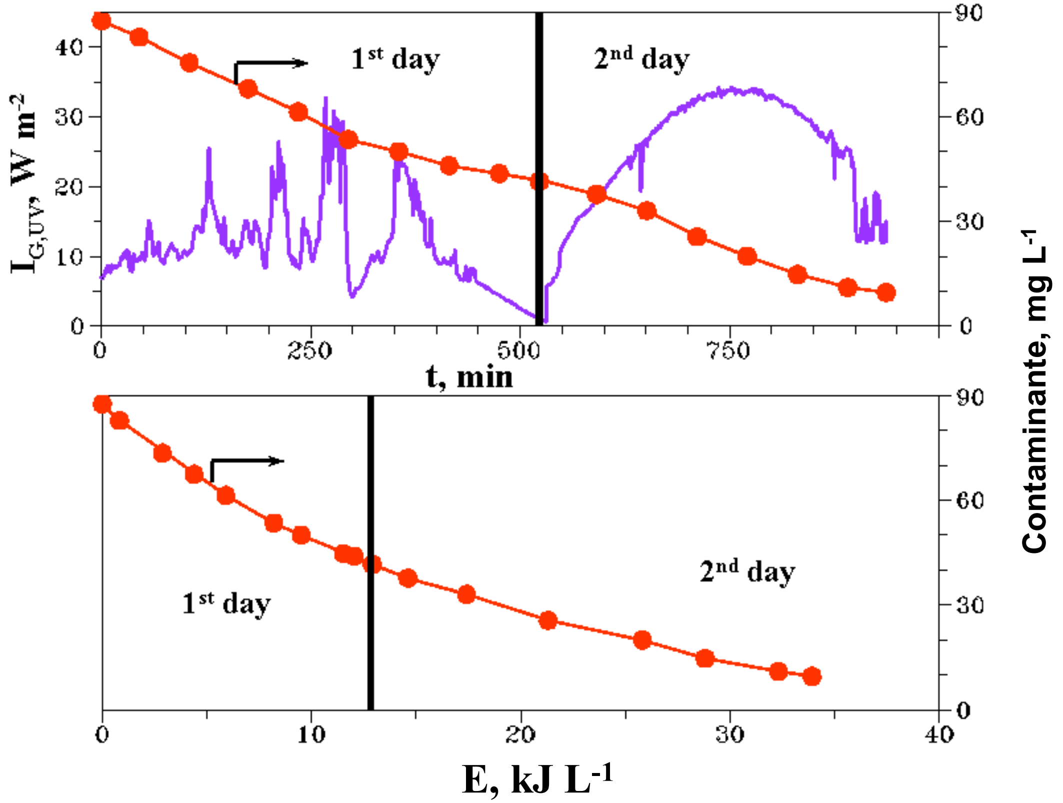

A
θ_{max} = 60º
r

Technical and engineering aspects of solar photo-reactors



Experimental results evaluation and comparison

$$E_{UV,n} = E_{UV,n-1} + \Delta t_n \, \overline{UV}_{G,n} \left(\frac{A}{V} \right) \quad ; \quad \Delta t_n = t_n - t_{n-1}$$



Concentrating or non-concentrating collectors

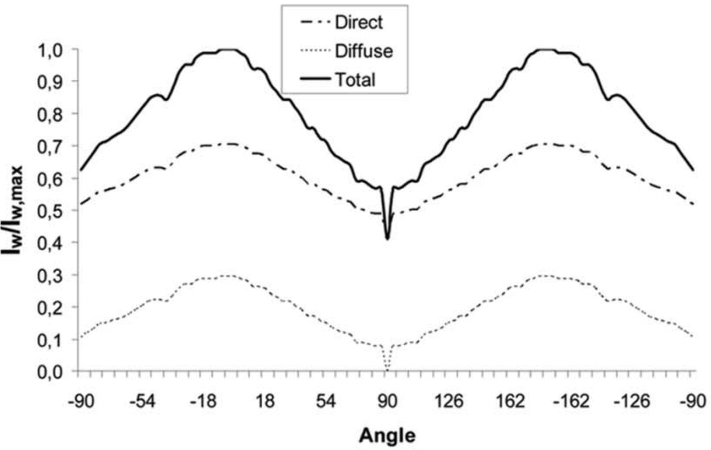
PARABOLIC CONCENTRATORS

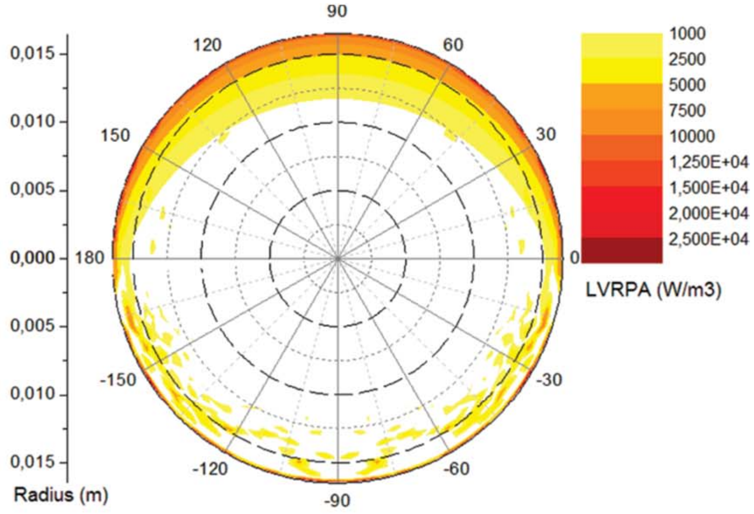
MAIN ADVANTAGES	*MAIN DISADVANTAGES*
Turbulent flow	Only Direct radiation
Vaporization of volatile compounds	High cost (Tracking)
	Low optical efficiency
	Low Quantum efficiency (with TiO_2)
	Overheating

NON CONCENTRATING PHOTOREACTORS

MAIN ADVANTAGES	*MAIN DISADVANTAGES*
Direct & Diffuse radiation	Laminar flow (low mass transfer)
No heating	Chemically inert
Low cost	
High optical efficiency	

Technical and engineering aspects of solar photo-reactors



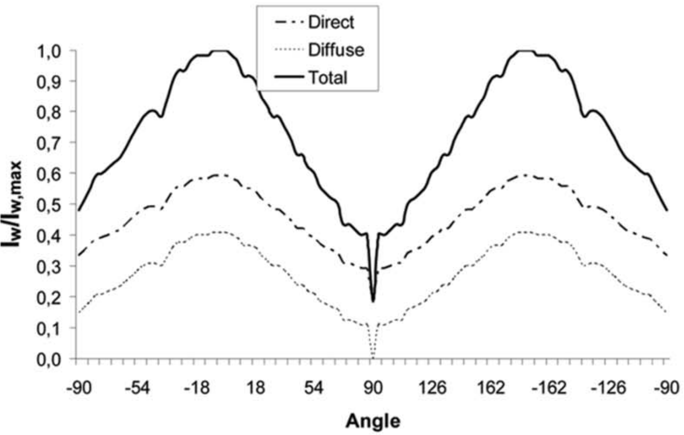


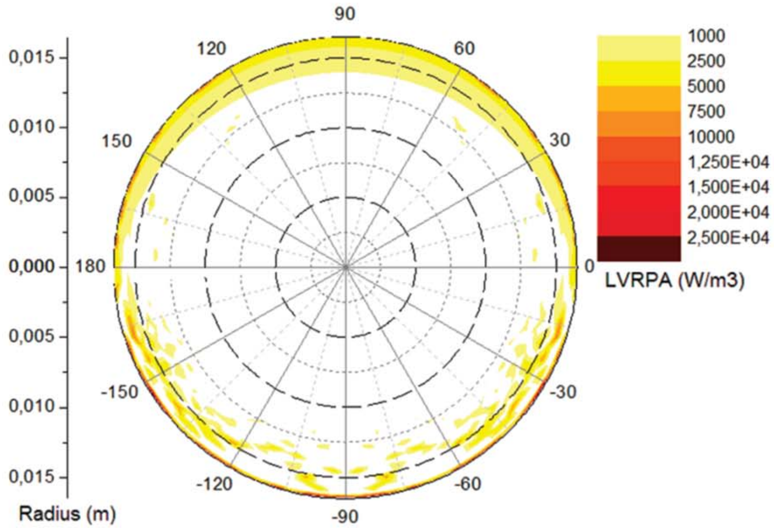
(a)

LVRPA* distribution in a CPC in sunny (a) and cloudy (b) day.

Considerations:

- **I Constant = 30 W/m^2**
- **Direct/diffuse = Constant**
- **75% UV trasmittance by clouds**





(b)

***LVRPA= local volumetric rate of photon absorption, W/m^3**

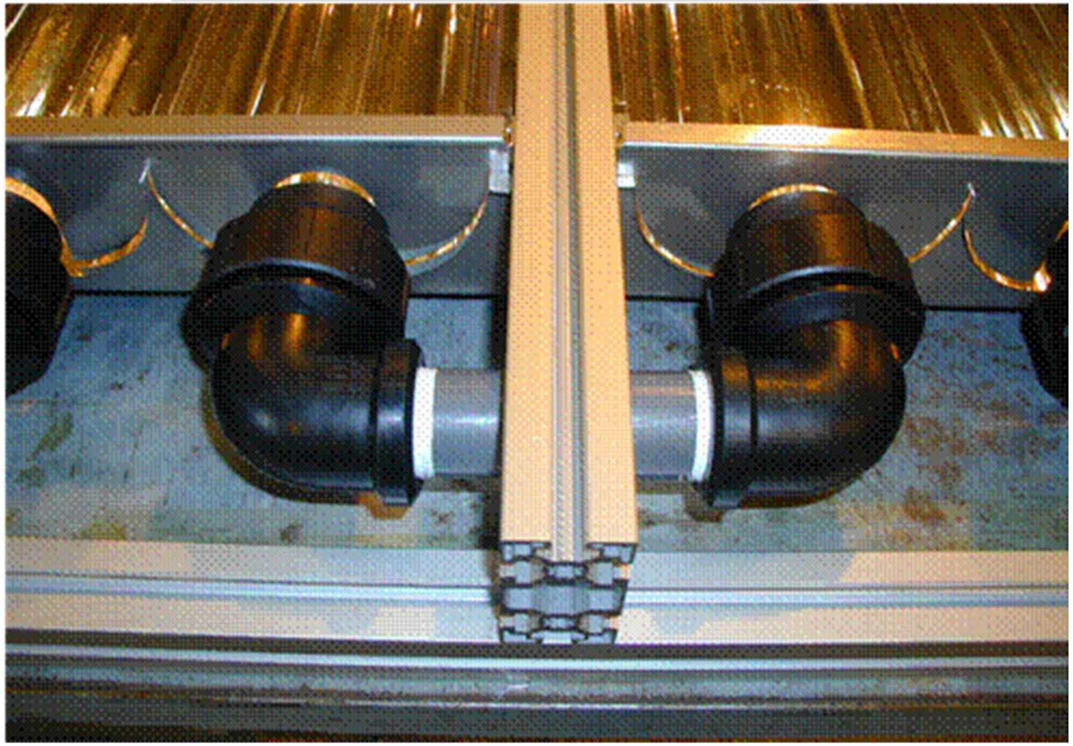
Colina-Márquez , Machuca-Martínez , Li Puma. Env. Sci. Technol., 43, 2009

Compound Parabolic Collectors (CPC)

Compound Parabolic Collectors (CPC)

Connections

(elbow joints)



Solar photocatalysis demonstration plants

Outlook

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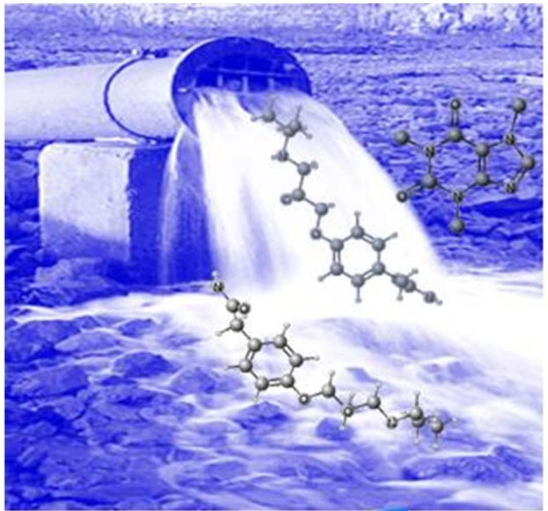
AOPs for tertiary treatment. ECs



contaminant	average [ng L-1]	min [ng L-1]	max [ng L-1]	detected [-]
Caffeine*	18527.9	331	66379	10
4-AAA*	13732.0	1976	36727	10
Paraxanthine*	6816.9	124	16140	10
4-FAA*	6741.7	2236	9831	10
Nicotine*	6524.6	136	43103	8
Cotinine*	6039.4	16	18393	10
Ibuprofen	5295.0	181	12859	5
Gemfibrozil*	3652.2	1291	7161	6
Furosemide*	2206.8	181	7667	9
4-MAA*	2090.3	93	5684	10
Hydrochlorothiazide*	2046.5	314	3783	8
4-AA	1492.5	611	2542	8
Naproxen*	1385.8	142	5272	9
Diclofenac*	1326.9	110	3577	9
Ofloxacin*	1081.5	566	2299	10
Atenolol*	921.5	280	1361	10
Ranitidine*	916.6	100	2675	9
Codeine	889.4	43	1603	8
Sulfamethoxazole*	843.6	219	1879	10
Antipyrine*	829.1	49	3503	9
Isoproturon	715.0	54	1376	2
Ciprofloxacin*	705.4	192	1510	10
Acetaminophen	610.5	49	1172	2
Diuron*	539.5	103	2379	6
Ketoprofen*	451.6	254	735	10
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	-

LC-QLIT-MS/MS

CHARACTERIZATION

29/62 Compounds with higher contribution in MWTP Effluent

AOPs for tertiary treatment. ECs

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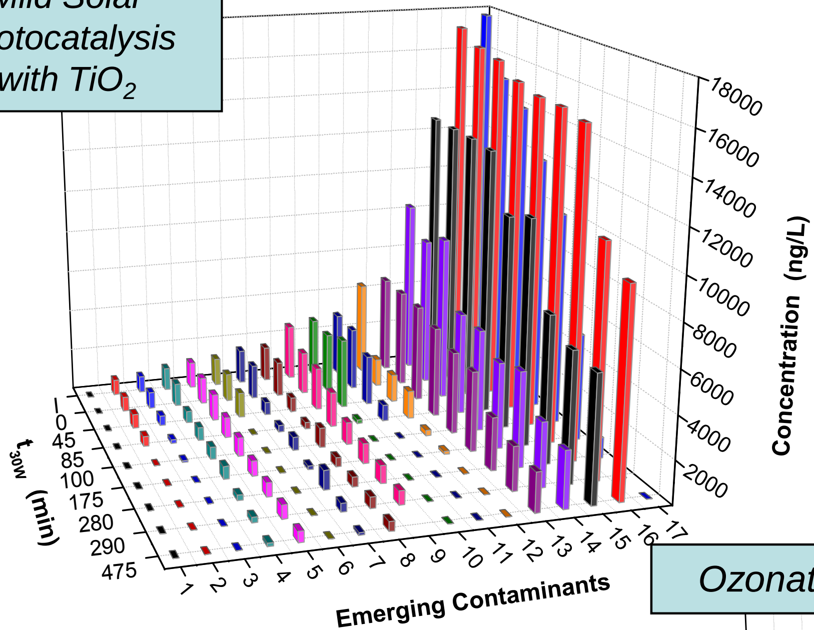
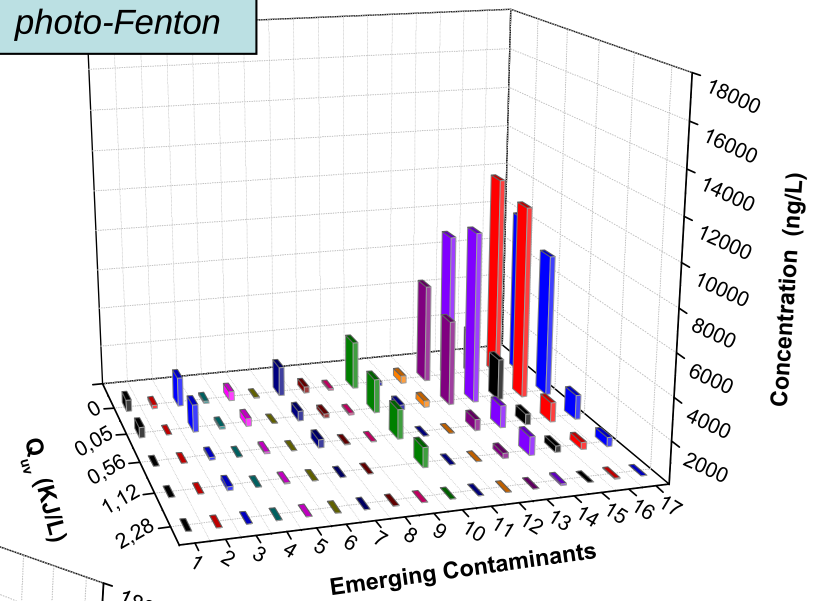
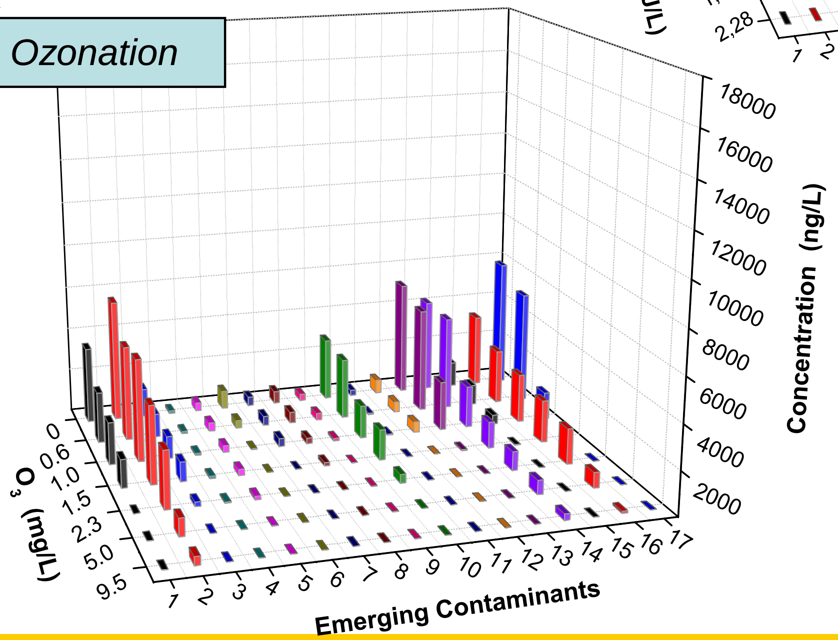
Mild Solar photocatalysis with TiO_2



Mild Solar photo-Fenton



Ozonation

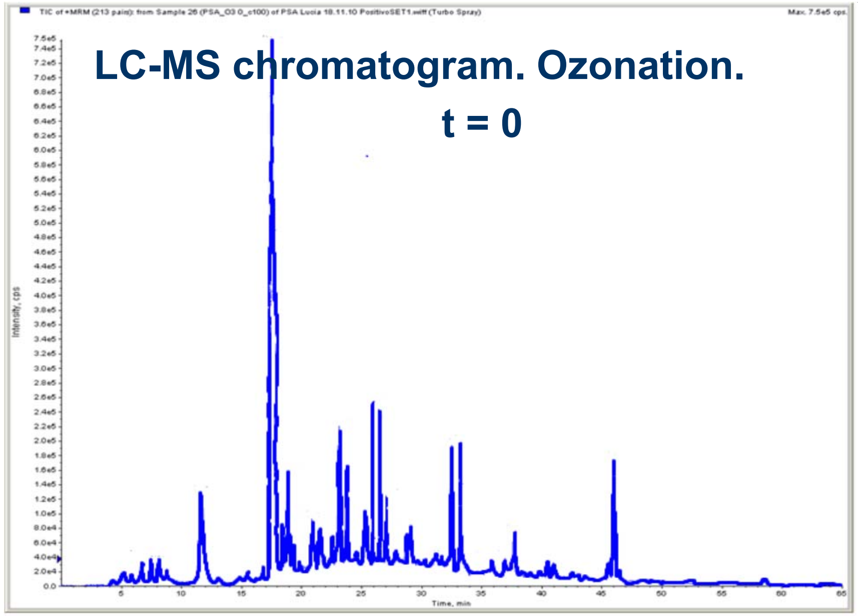


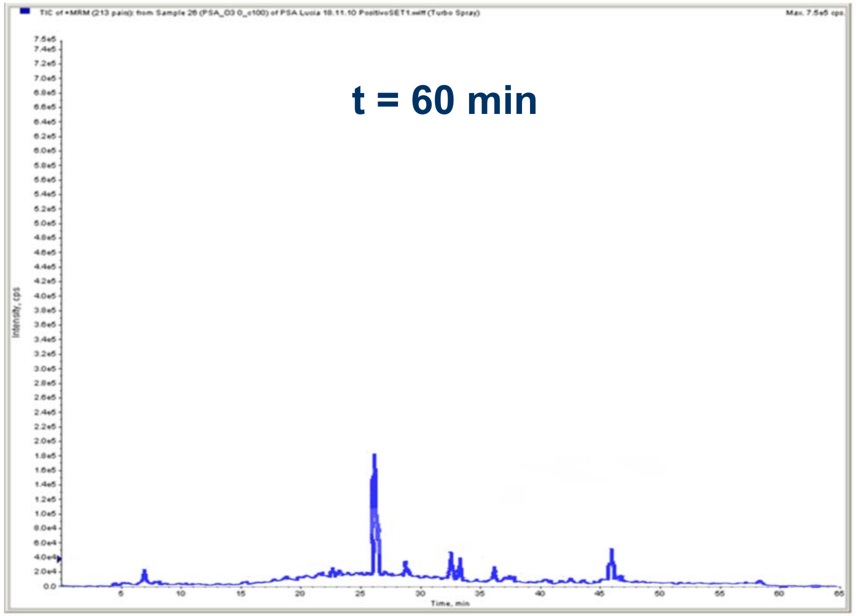
- Bisphenol A
- Ibuprofeno
- Hidrochlorothiazide
- Diuron
- Atenolol
- 4-AA
- Diclofenac
- Ofloxacin
- Trimethoprim
- Gemfibrozil
- 4-MAA
- Naproxen
- 4-FAA
- ΣEC <1000ng/L
- 4-AAA
- Caffeine
- Paraxanthine

Water characteristics and Micro-contaminants concentration change depending on the day that were taken.

AOPs for tertiary treatment. ECs

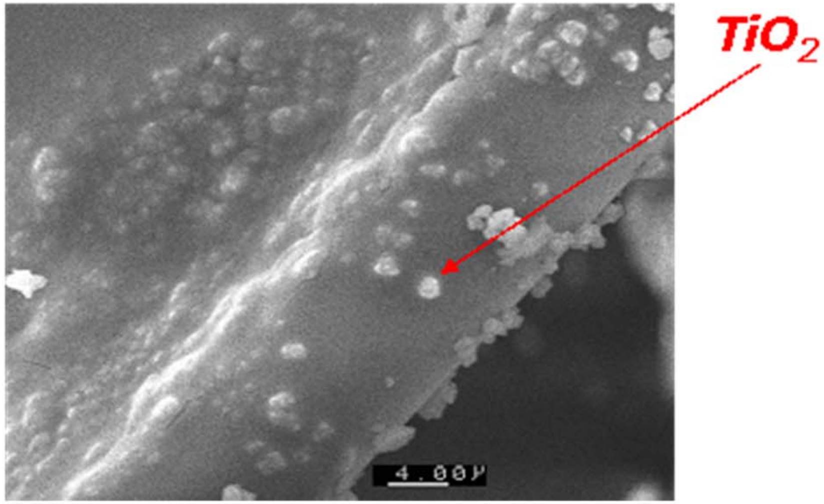
	Solar TiO_2	Solar photo-Fenton		Ozonation
Treatment time, min	475	20		60
Accumulated solar Energy, kJ L^{-1}	212	2.3		-
Reagent Consumption	- -	H_2O_2 54 mg L^{-1}	Fe(II) 5 mg L^{-1}	O_3 9.5 mg L^{-1}

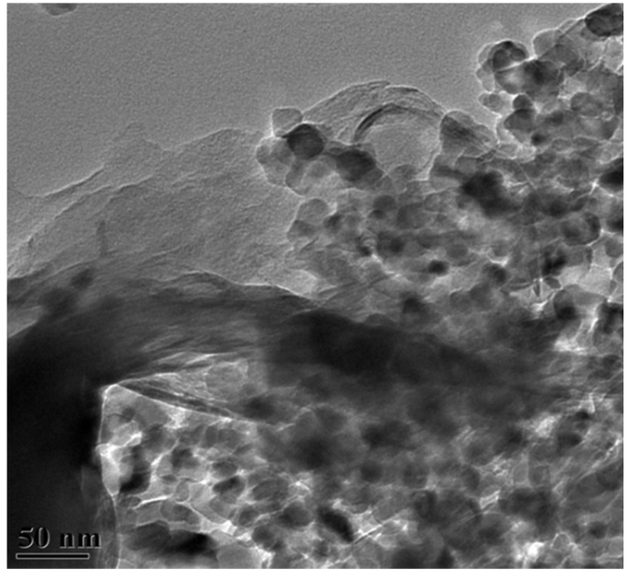


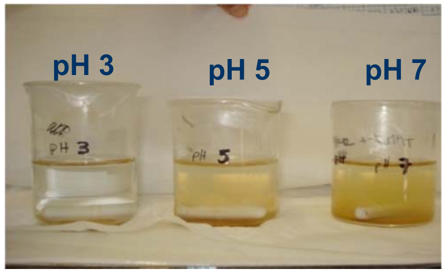


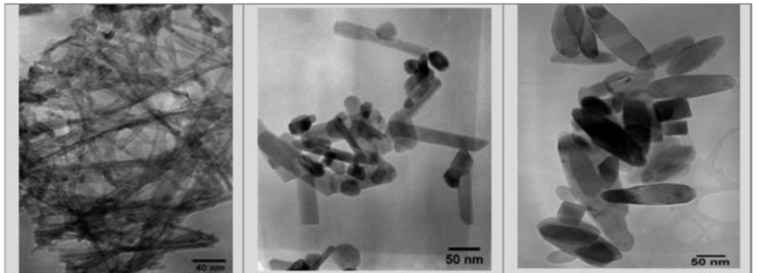
New materials for solar photocatalysis applications

TiO_2 based materials (immobilised, modified with graphene, several morphologies) and iron based materials like clays etc.









a- TiO_2 nanotubes (NT) | b- TiO_2 nanoplates and nanoparticles (NPL) | c- TiO_2 nanorods (NR)

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Solar reactors for water disinfection

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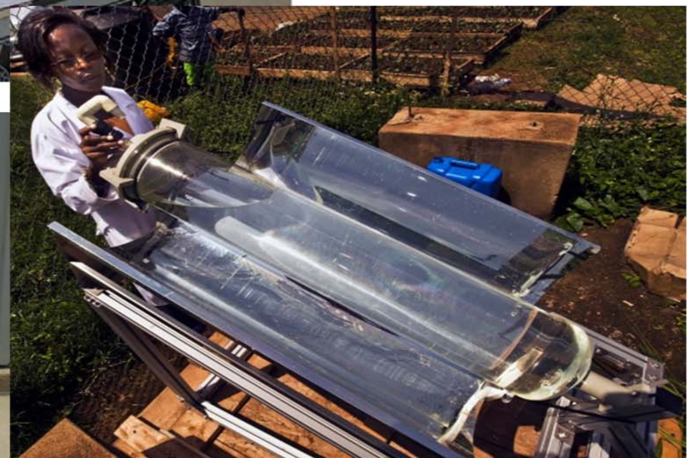
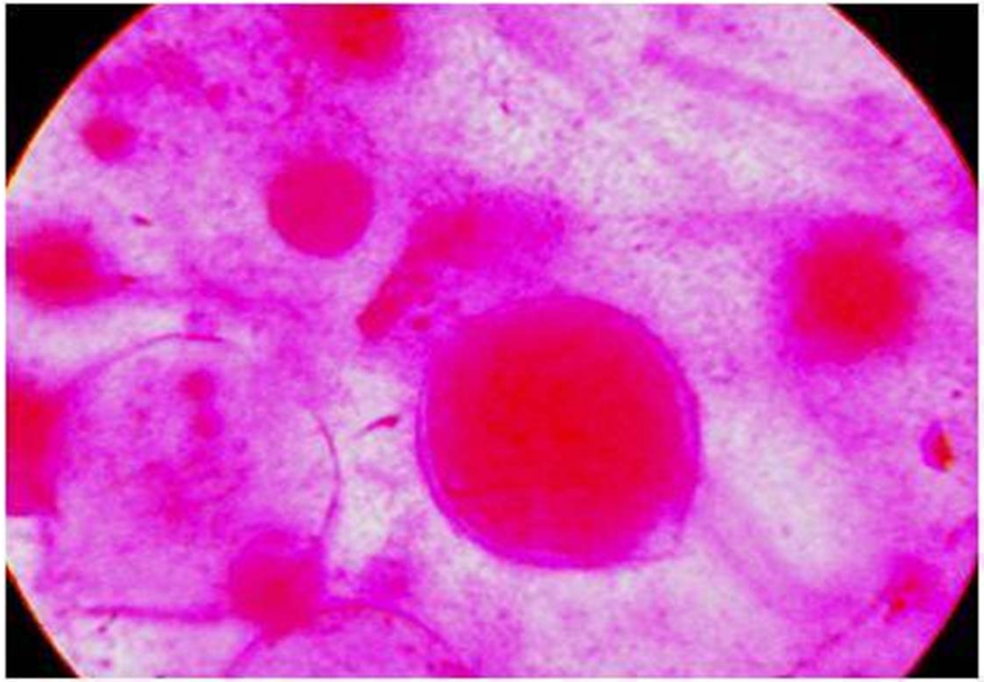
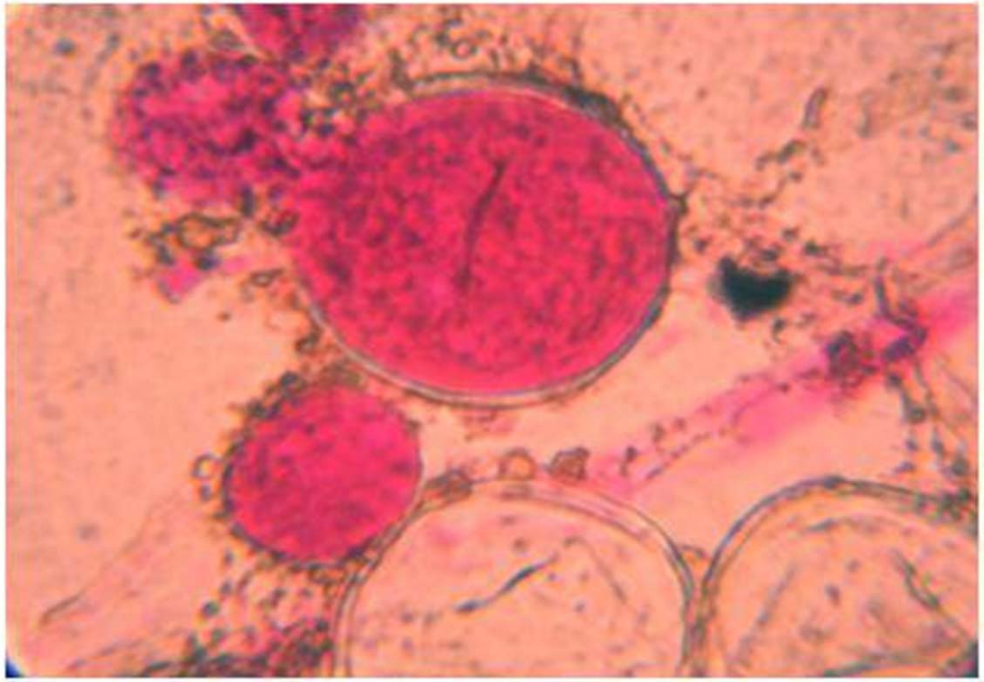


Makerere University, Uganda

Solar photocatalytic disinfection

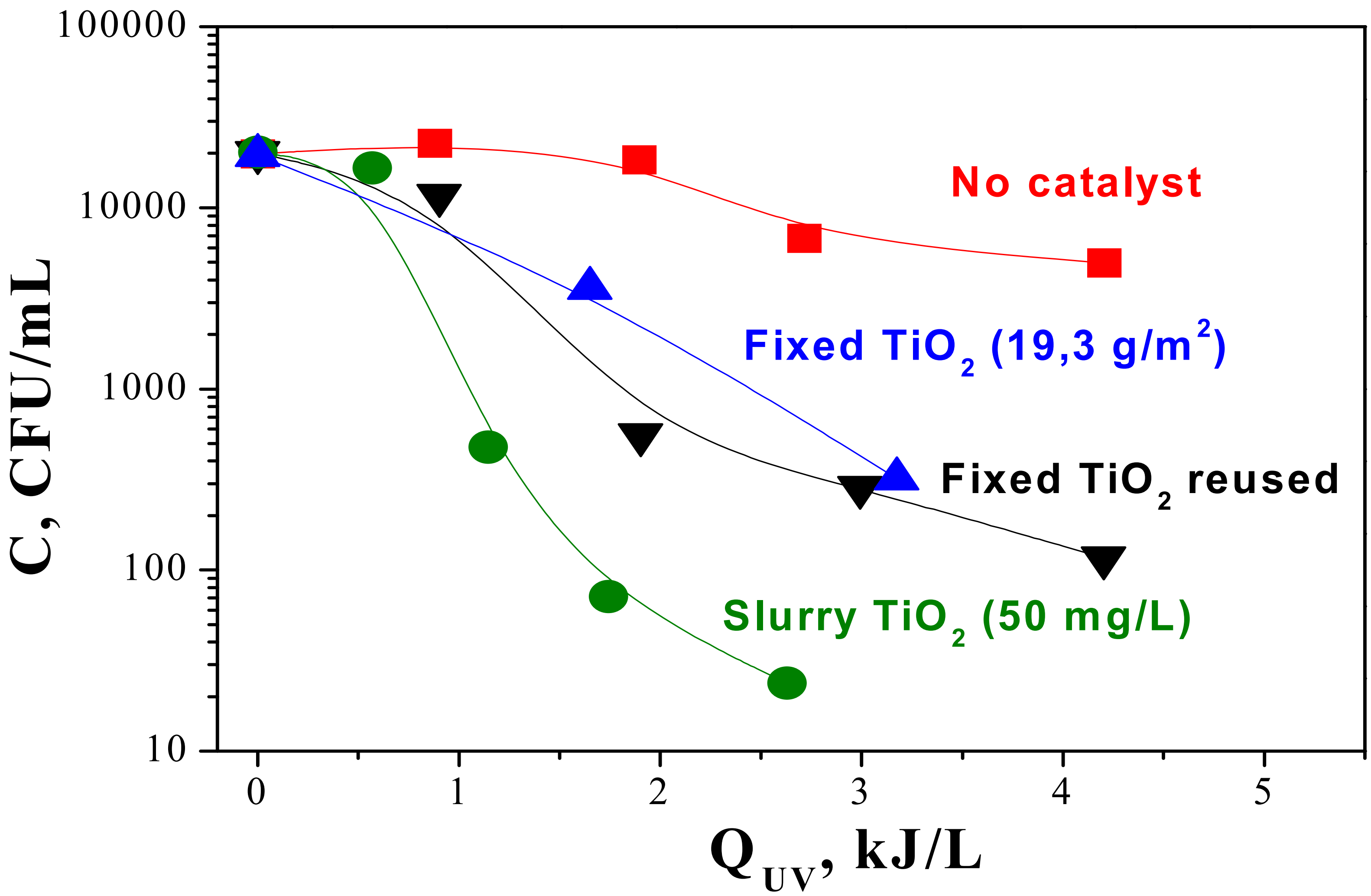


Phytophtora after 5 h of solar exposure ***without TiO_2.***



Phytophtera after 5 h of solar exposure ***with TiO_2.***

Solar photocatalytic disinfection



Solar photocatalytic disinfection

Acknowledgments

Unidad de Tratamientos Solares de Agua (*Solar Treatment of Water Research Group*).

Plataforma Solar de Almería (CIEMAT).

http://www.psa.es/webeng/areas/tsa/index.php