Course on Innovative Processes and Practices for Wastewater Treatment and Re-use

Solar disinfection of drinking water

Dr. Pilar Fernández Ibáñez
pilar.fernandez@psa.es
CIEMAT – Plataforma Solar de Almería

Innova-Med

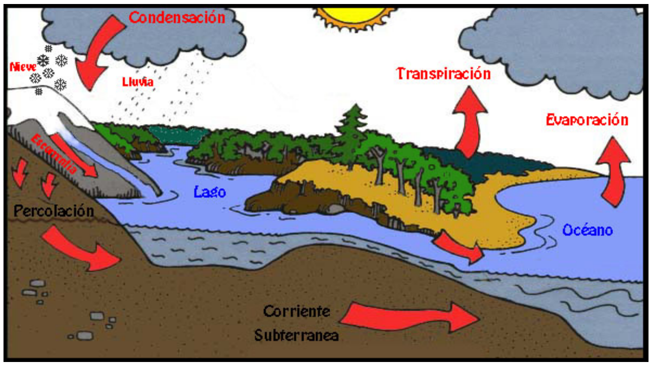
MINISTERIO DE EDUCACION Y CIENCIA
Ciemat Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas

Contents

Water availability

70% of the surface of the Earth has water

- 2,5 % freshwater
- **1 % human consumption**



-3-

Water disinfection needs

Microbial contamination of potable water due to the **lack of an appropriate treatment** of waste water is now a days a very important problem, especially in regions of developing countries.

Water is the main vehicle of distribution of many waterborne diseases. Water was responsible for big epidemics in the world like tiphus and cholera.

WHO recognised the **disinfection** as one of the most important **barriers for protection of public health**.

-4-

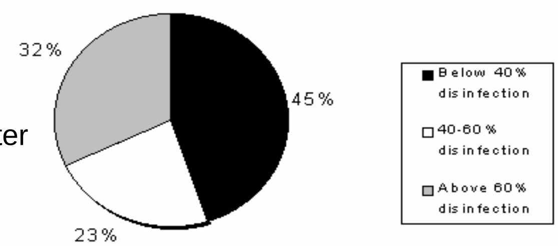
Access to water in the World in 2025

Everybody might have access to safe water to satisfying main needs of **drinking water consume**, clean, food production and **energy at a reasonable cost**. The **water suply** for these needs has to be done in a **sustainable way**.

Water disinfection issue

Causes of the problem:

- Lack of adecuated systems for water treatment and purification.
- Scarcity of rainwater.
- Restricted access to water resources due to contamination of hydric resources.
- Lack of adequated intallations for water storage.
- Lack of effective and adequate water distribution systems.
- Etc.



Percentage of disinfected water in rural areas of Latinamerica.

Contents

Disinfection of water

Desinfection: killing or inactivation of pathogenic microorganisms.

- **Indicators**: bacteria total coliforms and faecal coliforms.

- **Standard methods**:

  Chlorine
  Chloramine
  Ozone
  UV(C) light

Water Disinfection

Disinfection techniques

Physiscal removal of microorganisms

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

Microorganism inactivation (death)

- ✓*Chlorination*
  - ✓ High efficiency for virus and bacteria
  - ✓ Highly oxidative
  - ✓ Germicidal effect: 254 nm.
  - ✓ No generates toxic by-products
  - × Non-oxidative
  - × Not feasible with natural light
  - × Expensive

- ✓ **Widely used**
- × **Expensive**
- × **Do not really destroy microorganisms**

EPA (Environmental Protection Agency) Clasification , 1999

Chlorination

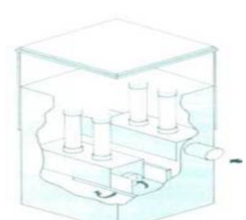
Gas chloride, sodium and calcium hypochlorite

Advantages

- Highly germicidal
- Residual effect
- Bacterial re-growth control

Disadvantages

- Generation of toxic by-products
- Bad odour and taste to water
- Dangerous reactivity with NOM



Ozonation

Ozone (from Air or Oxygen)

Advantages
- Require low doses and contact times (300-3000 faster than chlorine)
- Non-generation of THM, except for the presence of Bromide.

Disadvantages
- Non-residual effect
- Potentially toxic by-products
- *In situ* generation
- Immediately used
- Expensive O&M
- Technically complex

UV-C disinfection

UV-C lamps

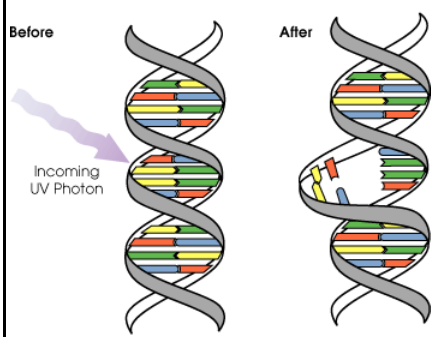
Advantages
- Easy O&M
- Non-generation of toxic by-products

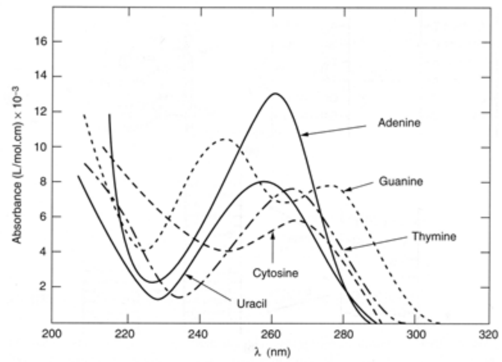
Disadvantages
- Non-residual effect
- Ueffective against **protozoan**
- Limited disinfectant effect by colour, turbidity and suspended matter
- Bacterial re-growth if genetic material is not destroyed




UV-C disinfection

Disinfection mechanism with UV-C radiation





-13-

UV-C disinfection

Microorganism	[UV-C Dose]$_{90\%}$ ($\mu W \cdot s \cdot cm^{-2}$)
Protozoa cysts	
Giardia muris	82.000
Cryptosporidium parvum	80.000
Giardia lamblia	63.000
Viruses	
Rotavirus SA 11	8.000
Poliovirus I	5.000
Hepatitis A Virus	3.700
Bacteria	
Pseudomonas aeruginosa	5.500
Escherichia coli	3.000
Salmonella Typha	2.500
Shigella dysenteriae	1.700
Legionella pneumonphila	380

More resistant

Less resistant

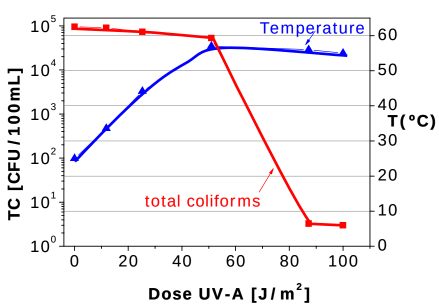
Required UV-C dose to reach a **90% of inactivation** with different microorganisms (adapted from Bitton, 2005).

-14-

Contents

Solar disinfection: SODIS

Solar radiation itself has not germicidal effect. Nevertheless, the synergistic effect of solar (UV-A) radiation and thermal heating of water under solar exposure has an important disinfectant capacity so-called SODIS or "Solar Disinfection".



*Caslake et al., Appl. Environ. Microbiol. 2004, **70**, 1145–1150*

Solar disinfection

When inactivation is done under constant irradiation conditions: Disinfection kinetics (also for disinfecting agents like chlorine, UV, etc.) obeys to a first order kinetics, **Chick Law**:

$$\frac{dN}{dt} = -kN \rightarrow N_t = N_0 e^{-kt}$$

N_t: concentration of viable microorganisms at time t.
K: constant of disinfection rate.

This relationship under solar radiation changes to:

$$\frac{dN}{dt} = -kN \rightarrow N_t = N_0 e^{-kQ_{UV}} \qquad Q_{uv,n} = Q_{uv,n-1} + \frac{\Delta t_n UV_{G,n} A}{V_T}$$

Gill & McLoughlin, Journal of Solar Energy Engineering, ASME, 2007.

Solar disinfection

Experimental time is used to compare results when lamps are used.
When solar radiation drives the process, we can use the following evaluation parameters:

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

$$Q_{uv,n} = Q_{uv,n-1} + \frac{\Delta t_n UV_{G,n} A}{V_T}$$

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

$$Dose_{UV} = UV_{G,n} \cdot \Delta t_n$$

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

$$Energy_{UV} = UV_{G,n} \cdot A \cdot \Delta t_n$$

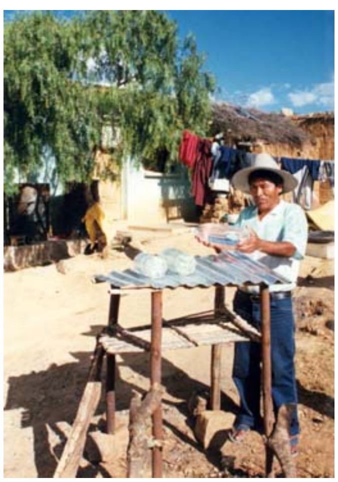
Water Disinfection

WATERBORNE PATHOGENS

VIRUS	**BACTERIA**	**PROTOZOA**	**HELMINTHS**
• Poliovirus • Hepatitis A • Parvovirus • Adenovirus • Rotavirus	• Salmonella • Shigella • Campylobacter • Vibrio • Escherichia coli	• Giardia lamblia • Entamoeba histolytica • Crystosporidium	• Taenia saginata • Ascaris lumbricoides • Schistosoma

Inactivation

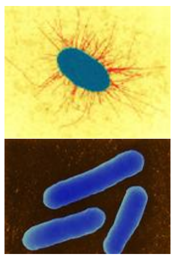
Solar disinfection: SODIS

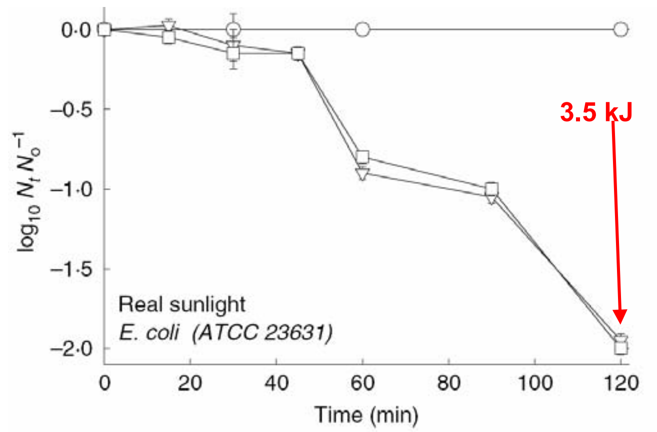


Solar disinfection of *E. coli*

Viability under Natural solar radiation at PSA

<UVA>=48 W m^{-2}
20ºC

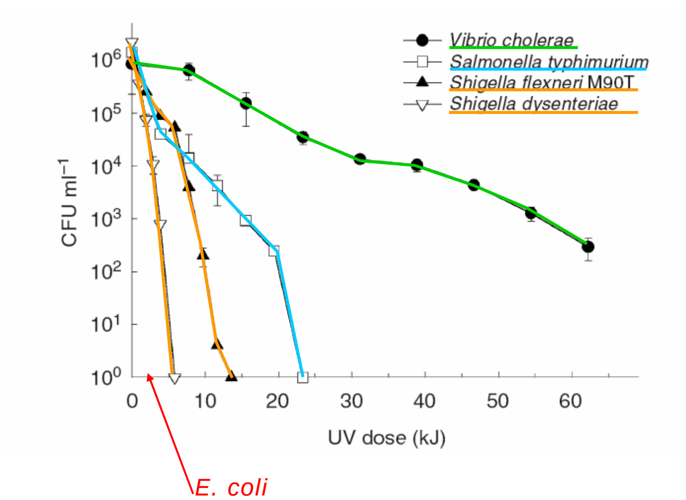


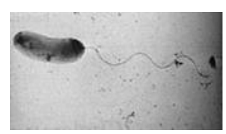


McGuigan et al., J. Applied Microbiology 2006, 101, 453-463.

-21-

Solar disinfection of pathogenic bacteria

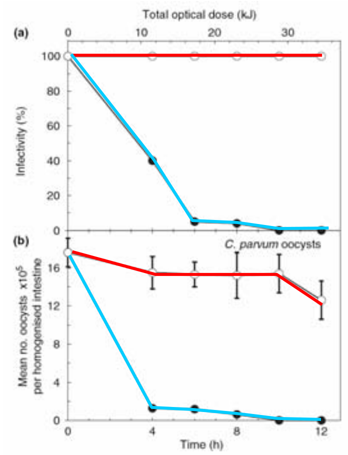




Kehoe et al., Letters in Applied Microbiology 2004, 38, 410–414.

-22-

Solar disinfection of *C. Parvum* oocysts



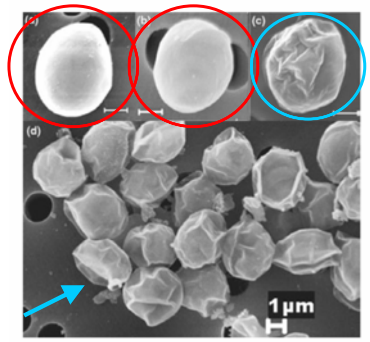
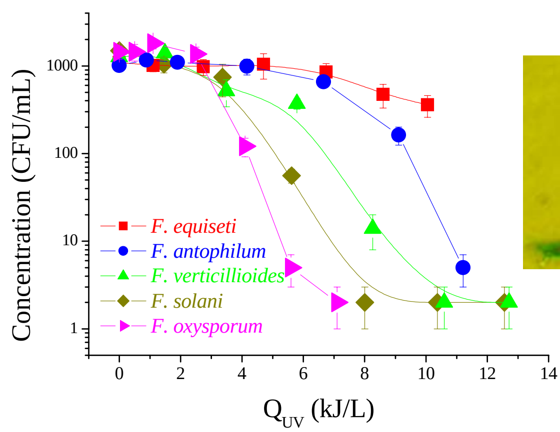


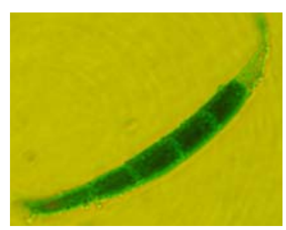
Figure 6 Scanning electron micrograph of oocysts of *Cryptosporidium parvum*. (a) *Cryptosporidium parvum* at 40°C at time = 0 h; (b) *C. parvum* at 40°C at time = 10 h; (c) *C. parvum* at 40°C + 870 W m^{-2} at time = 10 h and (d) Wide-field view of *C. parvum* at 40°C + 870 W m^{-2} at time = 10 h. Magnification is ×30 000. In each case, the scale bar represents 1 μm.

Mice Infectivity
Solar simulator: 830 W m^{-2}, 40ºC

McGuigan et al., J. Applied Microbiology 2006, **101**, 453-463.

Solar disinfection of *Fusarium* spores

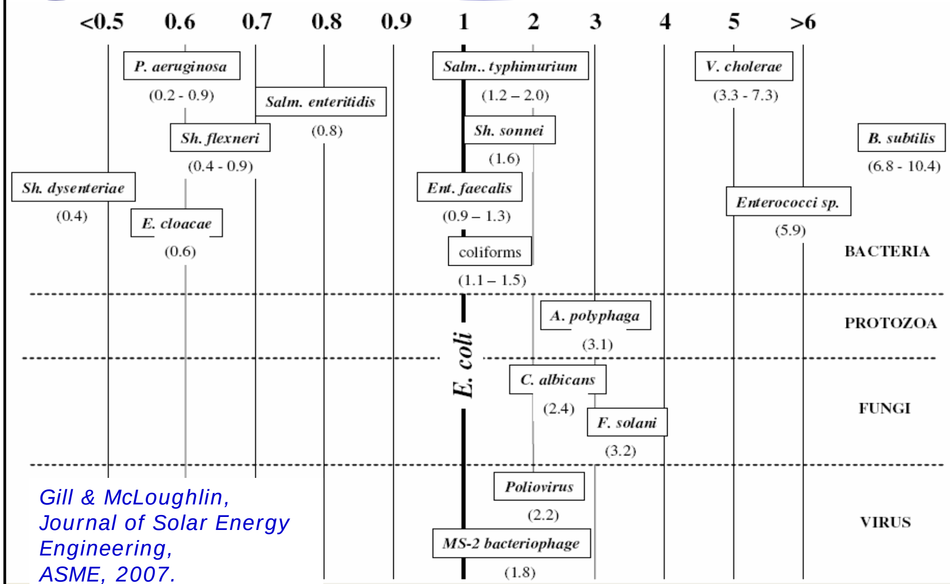




Under natural solar radiation
Wild fungal spores

C. Sichel, et al. Appl. Cat. B: Environ. 74 (2007) 152-160.

Resistance relative to the solar radiation of several microorganisms versus E. coli



Gill & McLoughlin, Journal of Solar Energy Engineering, ASME, 2007.

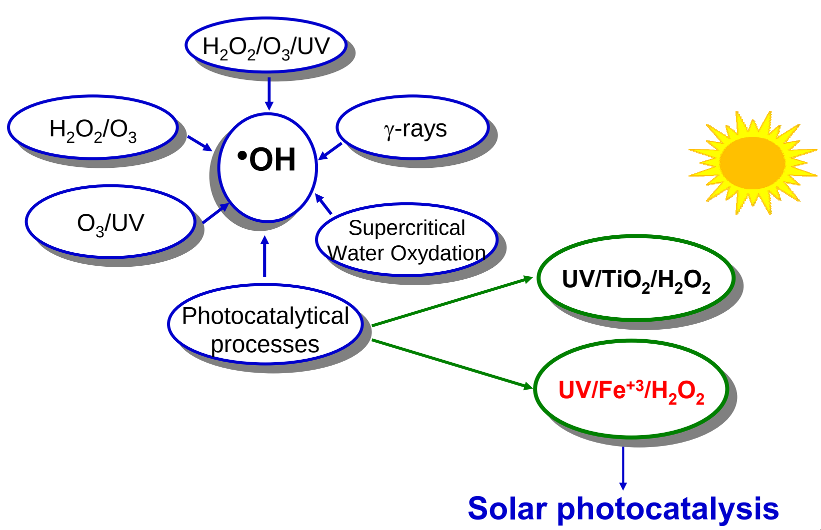
Contents

AOPs

- AOPs a … tive species.
- The AO … are the most efficient

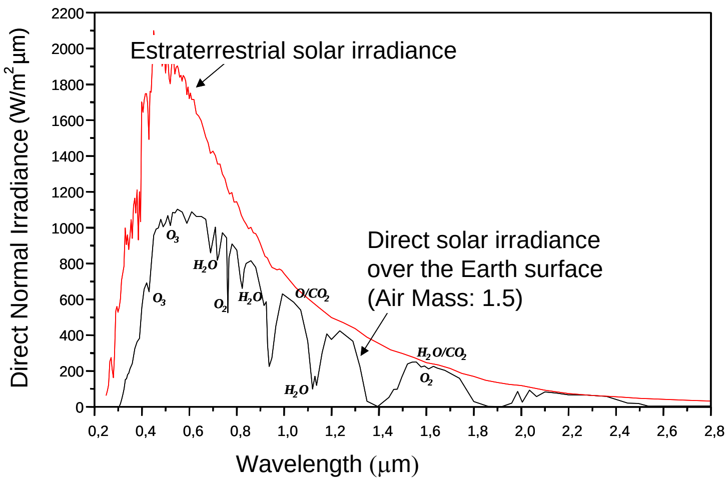
Species	*Oxidation potential ref. $HgCl_2$ (V)*
Fluorine	2.23
Hydroxyl radical	2.06
Oxygen	1.78
Hydrogen peroxide	1.31
Peroxide radical	1.25
Permanganate	1.24
Hypobromite acid	1.17
Chloride dioxide	1.15
Hypochlorite acid	1.10
Chlorine	1.00
Bromine	0.80
Iodine	0.54

AOPs - •OH



AOPs - •OH

Terrestrial and extraterrestrial solar spectrum (48.2º zenit angle)



AOPs - •OH

Several semiconductors may act as photocatalisyts

- ZnS (3.7 eV)
- ZnO (3.2 eV)
- **TiO_2 (3.05-3.25 eV)** →
- Fe_2O_3 (2.2 eV)
- CdO (2.1 eV), etc.

- ✓ High UV absorptivity
- ✓ High adsorption rate of many contaminants
- ✓ Redox potential (E_{BV}-E_{BC}) adequate for organics oxidation
- ✓ High photocatalytic activity
- ✓ Resistant to photo-corrosion
- ✓ Recyclable (re-usable)
- ✓ Inocuos
- ✓ Easy to handle
- ✓ Low cost and high production

AOPs - •OH

Heterogeneous photocatalysis using semiconductor oxides

The photoexcitation of semiconductor particles promotes an electron from the valence band to the conduction band thus leaving an electron hole in the valence band; in this way, electron/hole pairs are generated.

E_{BG} (TiO_2) = 3.05-3.25 eV

Photon: E = h·ν

h·ν > E_{BG}

λ < 300-390 nm

(5-7% Solar spectrum)

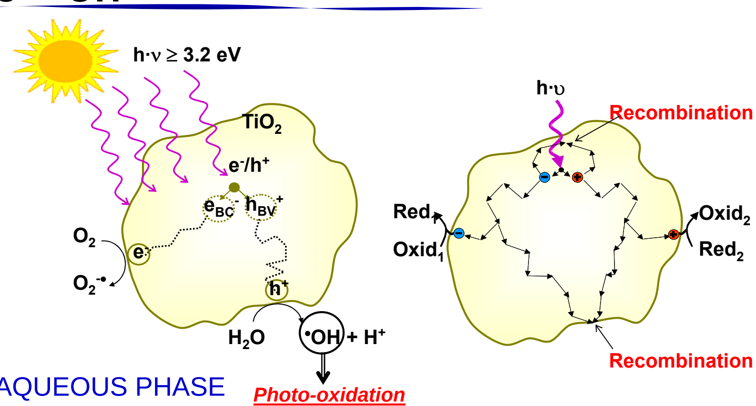
e^-/h^+ recombination ⇔ e^-/h^+ separation

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

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

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

AOPs - •OH



$$h^+ + Red_{2,ads} \rightarrow Ox_{2,ads} \qquad e^- + Ox_{1,ads} \rightarrow Red_{1,ads}$$

Before catalyst phoytoexcitation, Red_2 and Ox_1 species have to be previously adsorbed on the catalyst surface to avoid recombinations of e^-/h^+ pais.

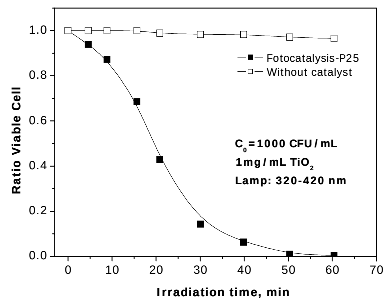
-32-

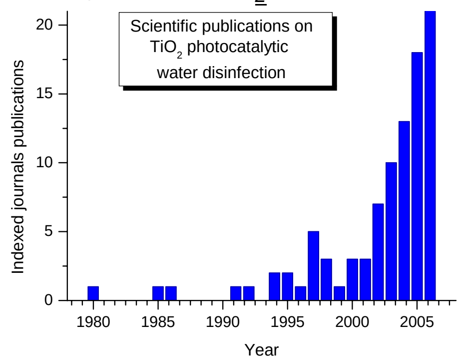
TiO_2-UV disinfection

The <u>first contribution</u> on water disinfection using TiO_2 assisted photocatalysis was done by **<u>Matsunaga in 1985</u>**.

<u>Up to now</u>:

- *Electrophotocatalyisis and <u>photocatalysis with TiO_2</u>*
- *supported and <u>slurry TiO_2</u>*
- *<u>Lamps</u> and solar radiation*

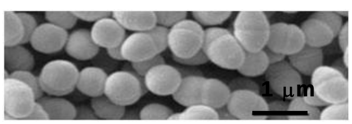


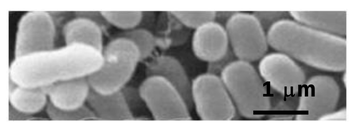


M. Bekbölet, *Water Science & Technology* **35** (1997) 95-100.

TiO_2-UV disinfection

BACTERIA: *Enterococcus faecalis (Gram+)* *Escherichia coli (Gram-)*

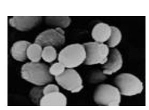




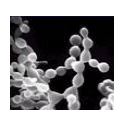
VIRUS AND BACTERIOPHAGE: *Poliovirus* 1, *Phage MS2 (RNA-bacteriophage)*

CANCER CELLS: *HeLa cells (cervical carcinoma), T24 (bladder cancer), U937 (leukemia).*

FUNGI AND YEATS:



Saccharomyces Cerevisiae



Conidia Neurospora crassa

"Advanced Oxidation Processes for Water and Wastewater Treatment" IWA Publishing, 2004.
D.M. Blake et al., *Separation and Purification Methods*, **28** (1999) 1-50.

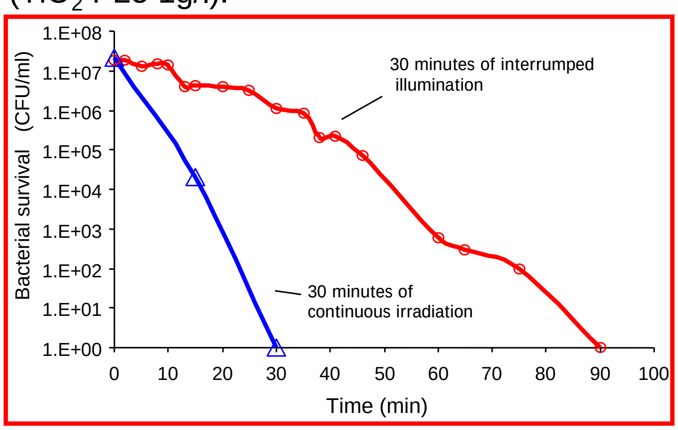
Ankara University
8-11 October 2007

Contents

Fundamental parameters

Irradiation

Continuously irradiation has a higher efficiency than intermitent exposure (TiO_2 P25 1g/l).

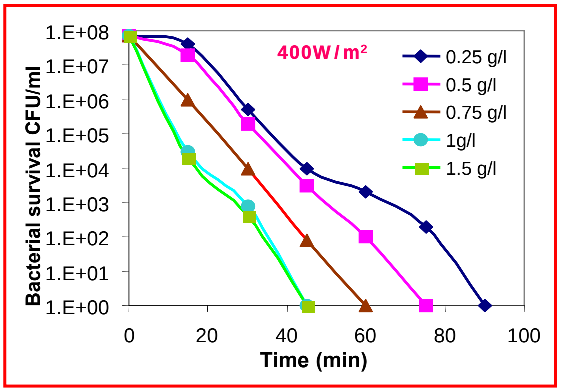


Rincón, A.G and Pulgarin C. *Appl. Catal. B: Environ.* 44 (2003), 263

Fundamental parameters

Concentration of catalyst

Initial inactivation rate increases with the catalyst concentration until it reaches a certain value, due to the light screening efect.



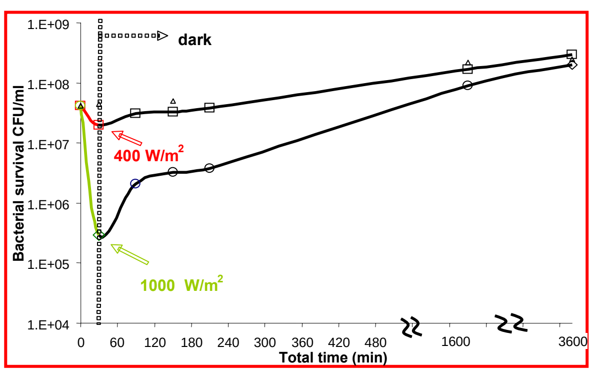
The light screening effect depends on the intensity of radiation and on the initial bacteria concentration.

Rincón, A.G and Pulgarin C. *Appl. Catal. B: Environ.* 44 (2003), 263

Fundamental parameters

Post-irradiation events

30 min. exposure to solar simulator radiation: certain inactivaton and a later bacterial regrowth in the dark was observed. The post-irradiation effect depends on light intensity.

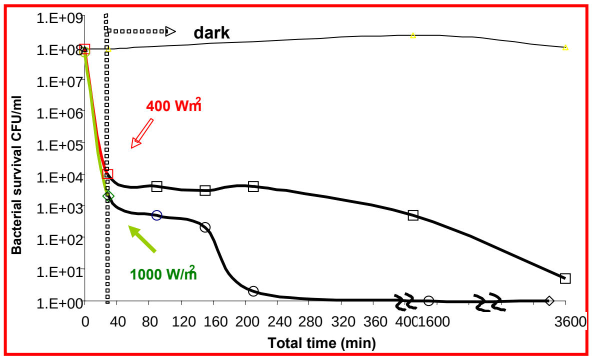


Rincón & Pulgarín, Applied Catalysis B: Environmental 49 (2004) 99–112

Fundamental parameters

Post-irradiation events

The post-radiation effect after photocatalytic treatment provokes a bacterial abatement in the dark. This effect is directly influenced by the radiation intensity.

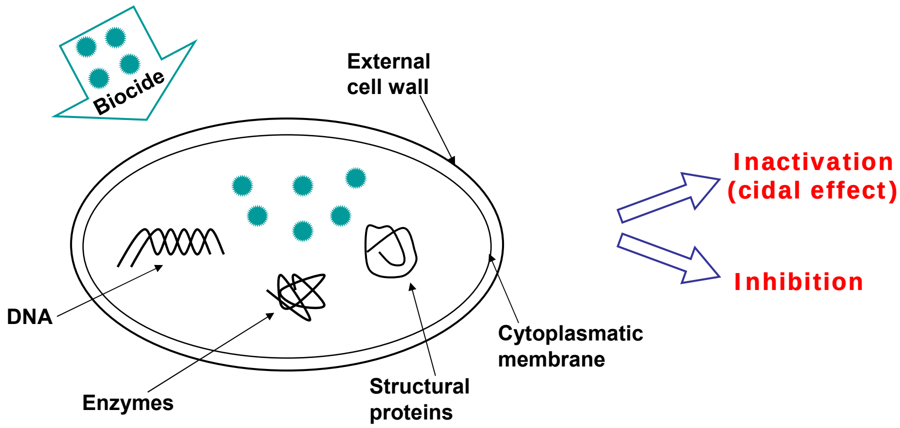


Rincón & Pulgarín, Applied Catalysis B: Environmental 49 (2004) 99–112

Contents

Disinfection mechanisms

Effects of biocidal agents on cells



"Wastewater microbiology". Gabriel Bitton, John Wiley & Sons, New Jersey, 3rd Ed., 2005.

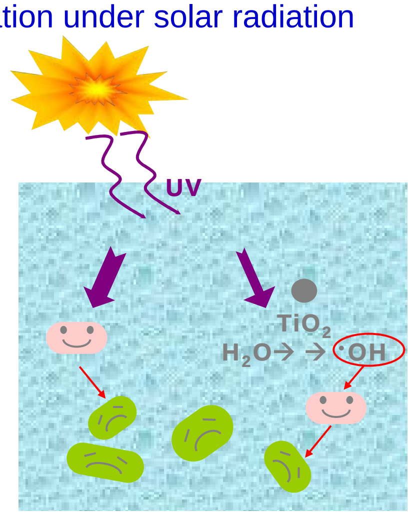
-41-

Disinfection mechanisms

Bacterial inactivation under solar radiation

Direct action

UV absorption by DNA molecules of microorganisms



Indirect action

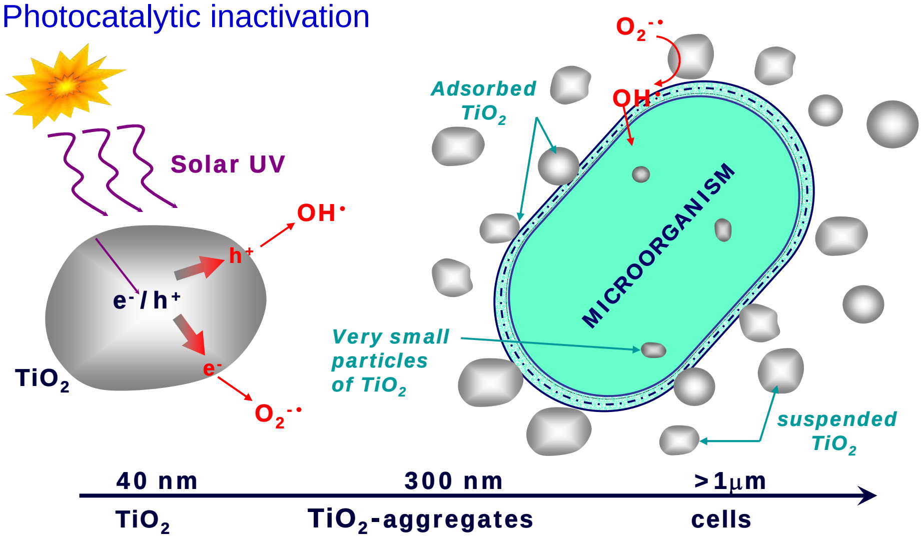
Photocatalytic effect of TiO_2 attacks the **cell membrane**.

Decrease of **Coenzyme-A** levels by photo-oxidation, which induces celular death.

-42-

Disinfection mechanisms

Photocatalytic inactivation



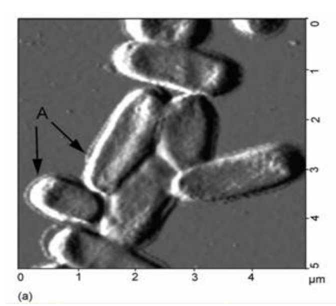
*Malato, Fernandez-Ibáñez y Blanco, J. Solar Energy Engineering **129** (2006) 1-12.*

Disinfection mechanisms

AFM image of *E. coli* cells on a TiO_2 film

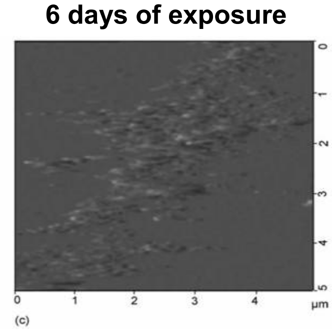
Light intensity: 1.0 mW/cm²

Without radiation



Cylindrical shape
Size ~1–2.5 μm

6 days of exposure

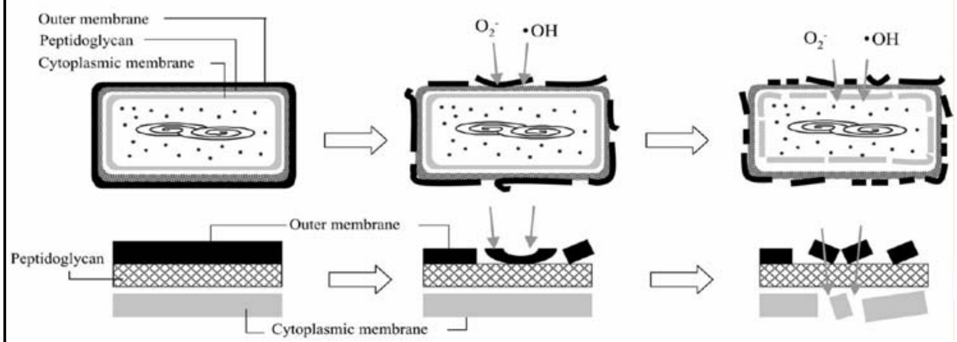


Complete cell decomposition

K. Sunada et al. J. Photochemistry and Photobiology A: Chemistry 6221 (2003) 1–7

Disinfection mechanisms

Scheme of photo-destruction (TiO_2) process



1) Partial destruction of external cell wall: partial viability lost.

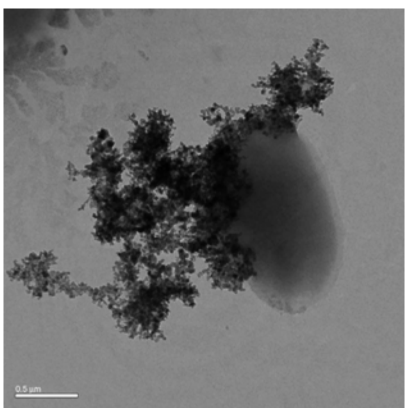
2) Reactive species reach the cytoplasmatic membrane.

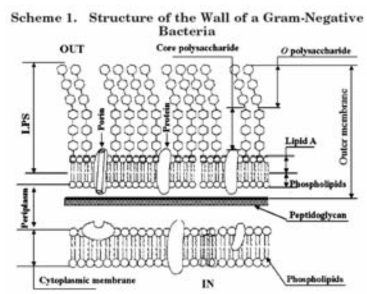
3) Reactive species attack the lipidic membrane: cell death.

K. Sunada et al. J. Photochemistry and Photobiology A: Chemistry 6221 (2003) 1–7

Adsorption of TiO_2 on *E. coli* cells

TiO_2-aggregate in contact with *E. coli*



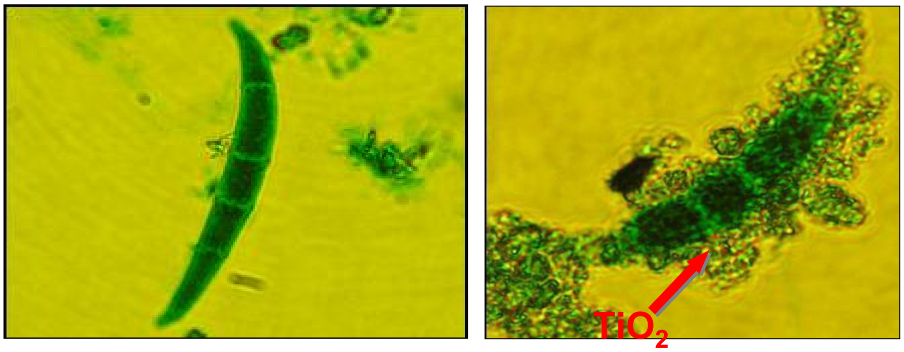


Composition of cell membrane favours contact with the catalyst.

- *D. Gumy et al. Appl. Cat. B: Environ., 63 (2006) 76-84.*
- *J. Kiwi and V. Nadtochenko, Langmuir 2005, 21, 4631-4641.*

Adsorption of TiO_2 on *Fusarium* spores

TiO_2-aggregates in contact with *F. equiseti*

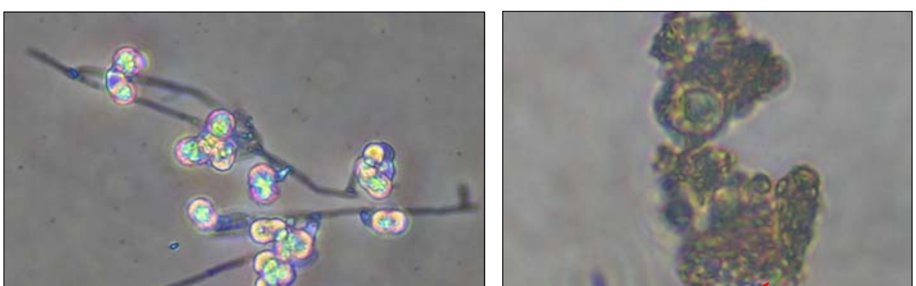


Macroconidia of *F. Equiseti* before and after the photocatalytic treatment (5h)

C. Sichel, et al. Appl. Cat. B: Environ., 74 (2007) 152-160.

Adsorption of TiO_2 on *Fusarium* spores

TiO_2-aggregates in contact with *F. solani*



TiO_2

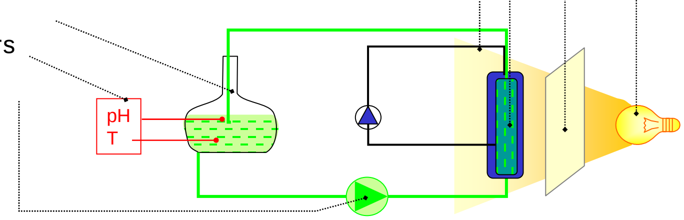
Chlamydospores de *F. solani before and after* 6h of photocatalytic treatment.

C. Sichel, Phytopathology, submitted, 2007.

Contents

Lab Photo-reactor

- Lamp (UV/VIS)
- IR filter
- Photo-reactor
- Refrigeration
- Matraz
- Sensors
- Pump



Requirements for solar photocatalytic reactors

- Chemical resistance to water, pH, without reagents changing.
- Flow guaranteed at minimal pressure and maximal homogeneisation.
- Efficient distribution of UV radiation from the solar collector to the fluid media.
- Resistance to temperatures lightly high: 40-50ºC.
- Robust and resistant to environmental condictions.
- Easy handling, low cost operation and maintenance (modular systems).
- Cheap and accesible.

Development of solar collectors

Compound Parabolic Collectors (CPC)

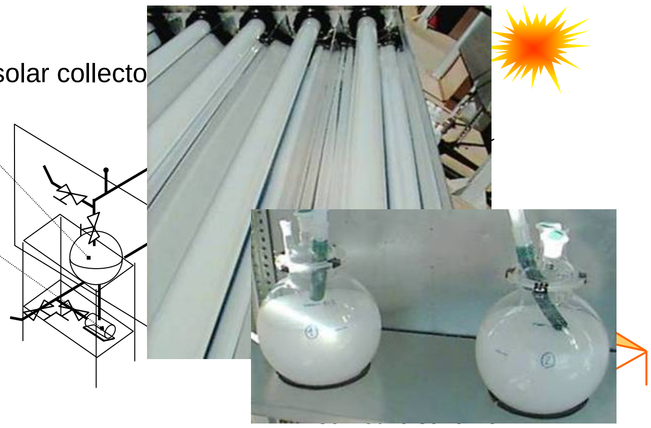
After middle 90s the "Compound Parabolic Collector" or CPC was technologically developed.

Partial view of
Solar Chemistry facilities
at PSA, Almería (CIEMAT)

Experiences at pilot plant

Prototype of solar reactor

- Solar radiation
- Photo-reactor (solar collecto
- Tank
- Air
- Sensor
- Pump
- Additives
- Catalyst

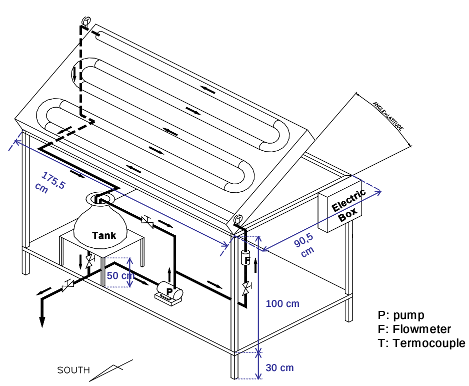


SOLARDETOX project, Brite Euram, European Commission (1997-2000)

-53-

Experiences at pilot plant

SOLWATER project, INCO Programme, European Commission (2002-2005)

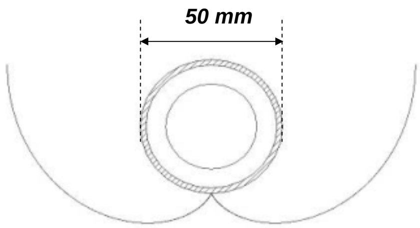


Compact module of solar photo-reactor

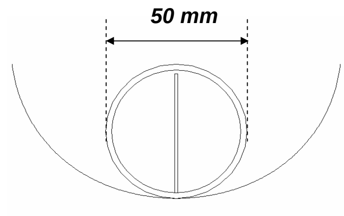
-54-

Optical development of CPC for disinfection

Application of Compound Parabolic Collectors (CPC) using new geometries for several configuration of the catalyst (AO SOL, Portugal).



Cylindrical Support in a CPC reactor (Ahlstrom paper)



Flat support with a special geometry (patent pending) solar collector

-55-

Contents

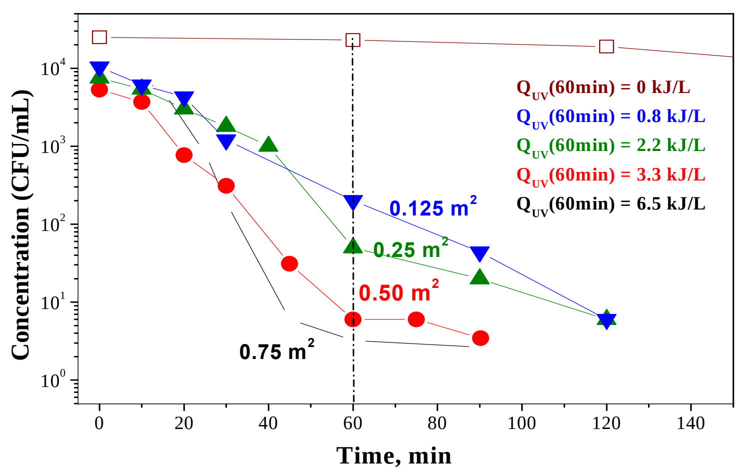
-56-

Protocol for solar experiments

1. *Catalyst preparation.*
2. *Solar collector covering.*
3. *Inoculation of culture & recirculation.*
4. *TiO_2 adding dispersed in small volume.*
5. *Remove the cover.*
6. *Experiment starting.*
7. *Average solar UV energy per unit of time and surface (**W_{UV}·m^{-2}**) incoming the photo-reactor.*

Irradiated collector surface

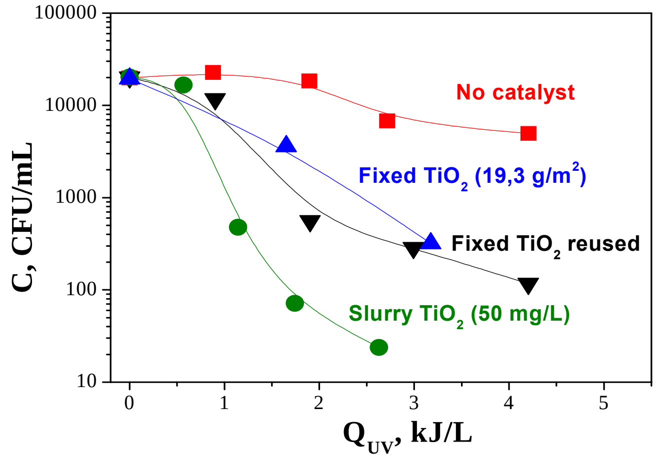
Solar Disinfection of E. coli in a CPC reactor



Fernández-Ibáñez et al. *Catalysis Today*, **101** (2005) 345-352.

Catalyst disposal

Disinfection with TiO_2 of E. coli in a solar CPC reactor

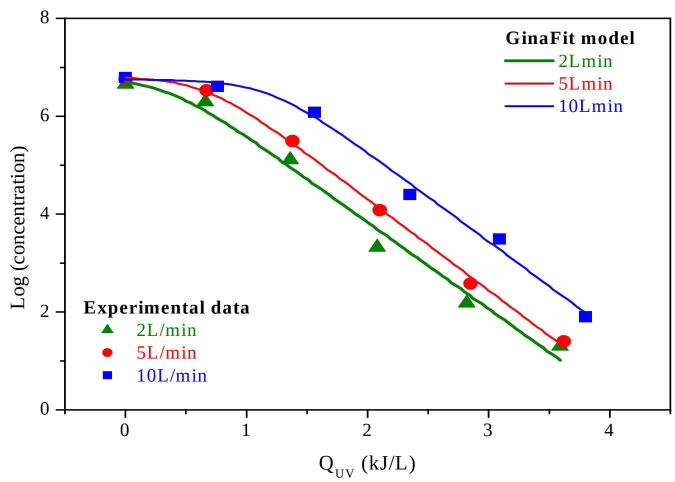


Fernández-Ibáñez et al. *Catalysis Today*, **101** (2005) 345-352.

-59-

Reactor flow rate

Disinfection of E. coli with immobilised TiO_2 in a CPC reactor

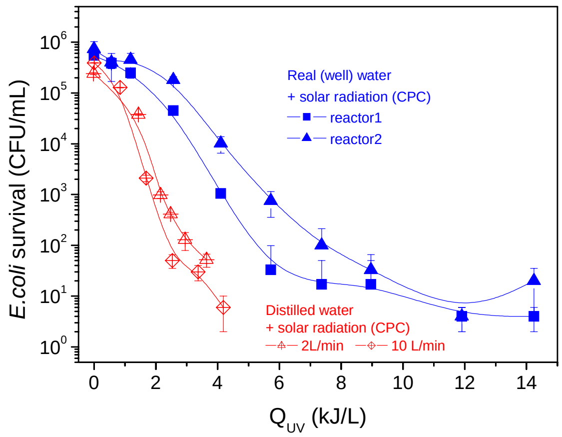


C. Sichel, et al. *J. Photochem. Photobiol. A, 189 (2007) 239-246.*

-60-

Matrix of the water

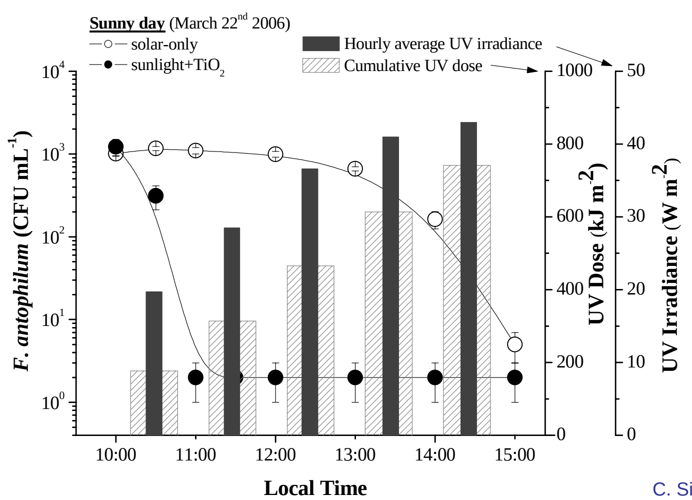
Solar disinfection of E. coli in a CPC reactor



Solar disinfection for real water is slower and less efficient than for distilled water. This graph shows the "tailing effect" attributed to resistant colonies of bacteria.

Weather conditions

Solar disinfection of F. antophilum with slurry TiO_2



SUNNY DAY

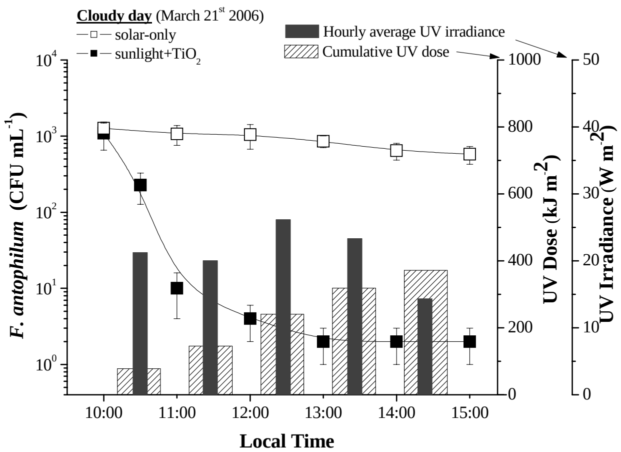
Max. UV Irradiance: 42 Wm^{-2}

Max. UV Dose: 750 kJm^{-2}

C. Sichel, et al. *Catalysis Today* 2007, in press.

Weather conditions

Solar disinfection of F. antophilum with slurry TiO_2



CLOUDY DAY

Max. UV Irradiance: 25 Wm^{-2}

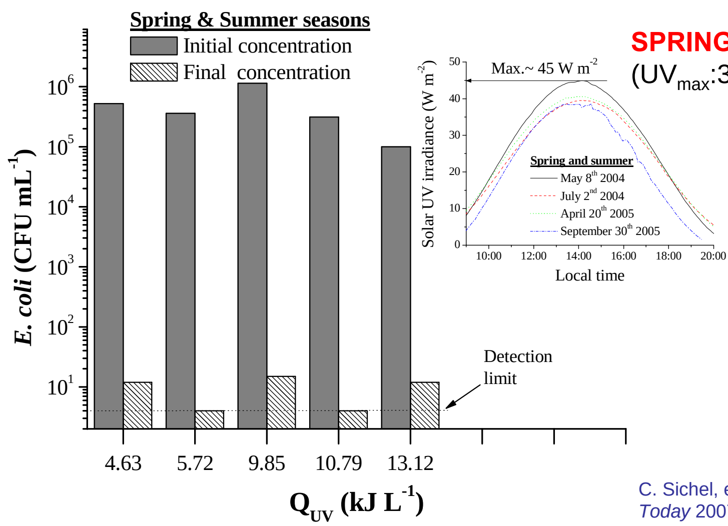
Max. UV Dose: 380 kJm^{-2}

Similar photocatalytic kinetics for both cases.
Solar disinfection yields very different results.

C. Sichel, et al. *Catalysis Today* 2007, in press.

Weather conditions

Disinfection of E. coli with immobilised TiO_2

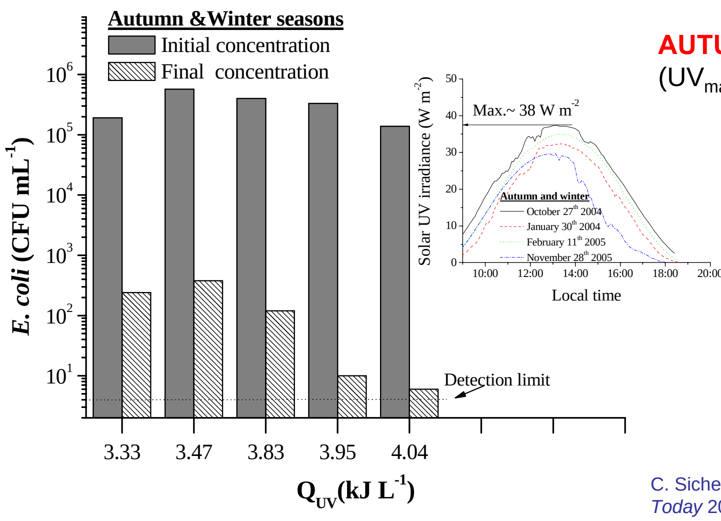


SPRING AND SUMMER (UV_{max}:38-45wm^{-2}).

C. Sichel, et al. *Catalysis Today* 2007, in press.

Weather conditions

Disinfection of E. coli with immobilised TiO_2



AUTUM AND WINTER
(UV_{max}: 28-38Wm^{-2}).

C. Sichel, et al. *Catalysis Today* 2007, in press.

-65-

Role of solar radiation

Comparison of experiments in different seasons, early and later in the day, and under cloudy and sunny conditions, leads us to conclude that solar photocatalytic disinfection does not depend proportionally on solar UV irradiance (solar UV intensity) as long as enough photons have been received for disinfection.

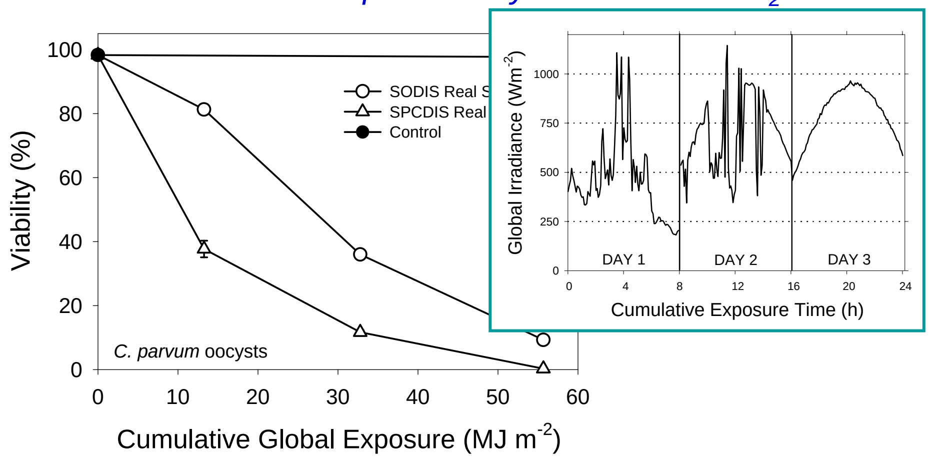
The minimum UV energy necessary to reach a certain disinfection depends on the microorganism and the reactor configuration.

Solar-only disinfection requires higher minimum solar UV irradiance and higher minimum UV dose for disinfection than solar photocatalytic disinfection.

-66-

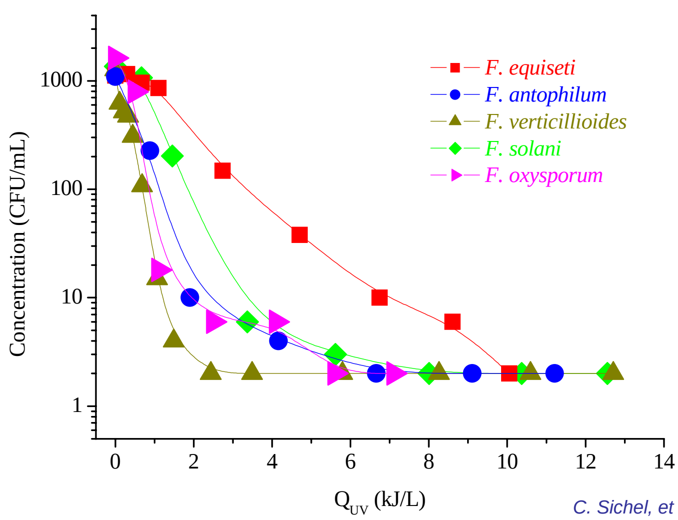
Inactivation of *C. parvum*

Sodis and solar photocatalysis with fixed TiO_2



F. Mendez-Hermida, et al. *J. Photochem. Photobiol. A, 88 (2007) 105-111.* -67-

Photocatalytic inactivation *Fusarium*



C. Sichel, et al. Appl. Cat. B: Environ., 74 (2007) 152-160.

-68-

Applications

The **AQUACAT** and **SOLWATER projects** were financed by EU under the INCO-DEV program during (2003-2006)

MAIN OBJECTIVE: development of a completely **autonomous solar system chemical-free for drinking water disinfection** and, additionally, elimination of potential organic pollutants at trace level.

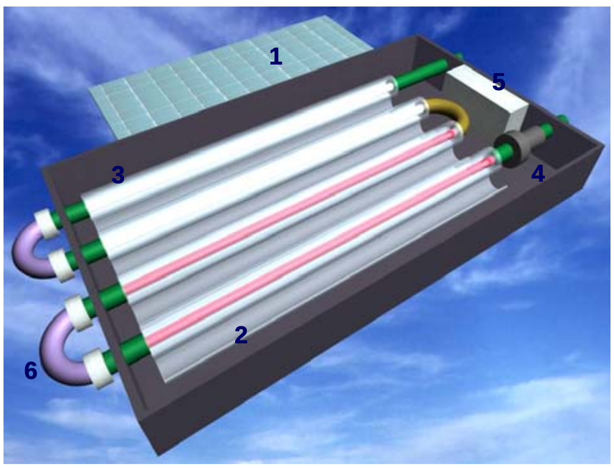
Fixed catalyst Ahlstrom patent, 1999 France

SOLWATER prototype at PSA

-69-

Applications

Design of the final system for disinfection of drinking water



1. PV panel
2. & 3. Solar Photo-reactor
4. Pump
5. Electric box
6. Connections

S. Malato et al., Review, Catalysis Today 122 (2007) 137-149.

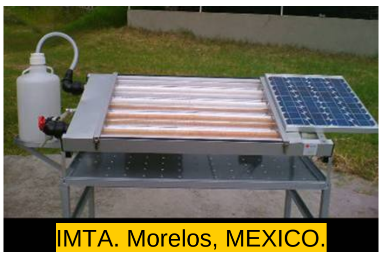
-70-

Applications

Final reactor systems in South-America and North-Africa


ESTF. Fez, MOROCCO


Photo Energy Center. Cairo, EGYPT


IMTA. Morelos, MEXICO.


CNEA. Tucumán, ARGENTINA

Applications

SODISWATER project

Solar Disinfection of Drinking Water for Use in Developing Countries or in Emergency Situations

Partners:

1. RCSI (IRELAND)
2. UU (UK)
3. CSIR (SOUTH AFRICA)
4. EAWAG (SWITZERLAND)
5. IWSD (ZIMBABWE)
6. CIEMAT (SPAIN)
7. UL (UK)
8. ICROSS (KENYA)
9. USC (SPAIN)

Objetive:
The objective of this project is the development of an **implementation strategy for the adoption of solar disinfection of drinking water as an appropriate, effective and acceptable intervention against waterborne disease** for vulnerable communities in developing countries without reliable access to safe water, or in the immediate aftermath of natural or man-made disasters.

The main activity of PSA within this project is the development of a solar reactor to enhance the disinfection results of "batch" SODIS processes.

Applications

FITOSOL project

Elimination of phytopathogens in water through photocatalytic processes: application for the water disinfection and reuse in recirculation hydroponic cultures

Main objetives:

- Study at laboratory scale of solar photocatalytic elimination of model phytopathogenic microorganisms in recirculation liquid nutrient solutions in soil-less cultures.
- Design and construction of a pilot solar reactor for disinfection of water containing the mentioned phytopathogenic organisms to reuse in recirculation hydroponic cultures.
- Demonstration of the photocatalytic process ability to disinfect water from nutrient solutions of hydroponic cultures.

Future

1. Low-cost solutions for drinking water suply at house-hold level.
2. Use of AOPs (different to TiO_2) for water disinfection.
3. Improve the knowledge on the disinfection mechanisms at microbiological level.
4. Investigate the effects of the disinfection treatment using infectifivity tests for pathogenic microorganisms.
5. Field trials of solar disinfection to better Health Impact Assessment of the technology.

Acknowledgements

This work has been financed by:

European Commission under the **SOLWATER** project ICA4-CT-2002-10001.

ıropean Commission under the **AQUACAT** CO project, ICA3-CT2002-10016.

ɔpean Commission under the **SODISWATER** ɜct, contract FP6-2004-INCO-DEV-3-301650.

Spanish Ministerio de Educación y Ciencia under the **FITOSOL** project, AGL2006-12791-C02.

-75-

Ankara University
8-11 October 2007

THANKS

Dr. Pilar Fernández Ibáñez
pilar.fernandez@psa.es

Plataforma Solar de Almería –CIEMAT
Ministerio de Educación y Ciencia
www.psa.es

-76-

Ankara University
8-11 October 2007