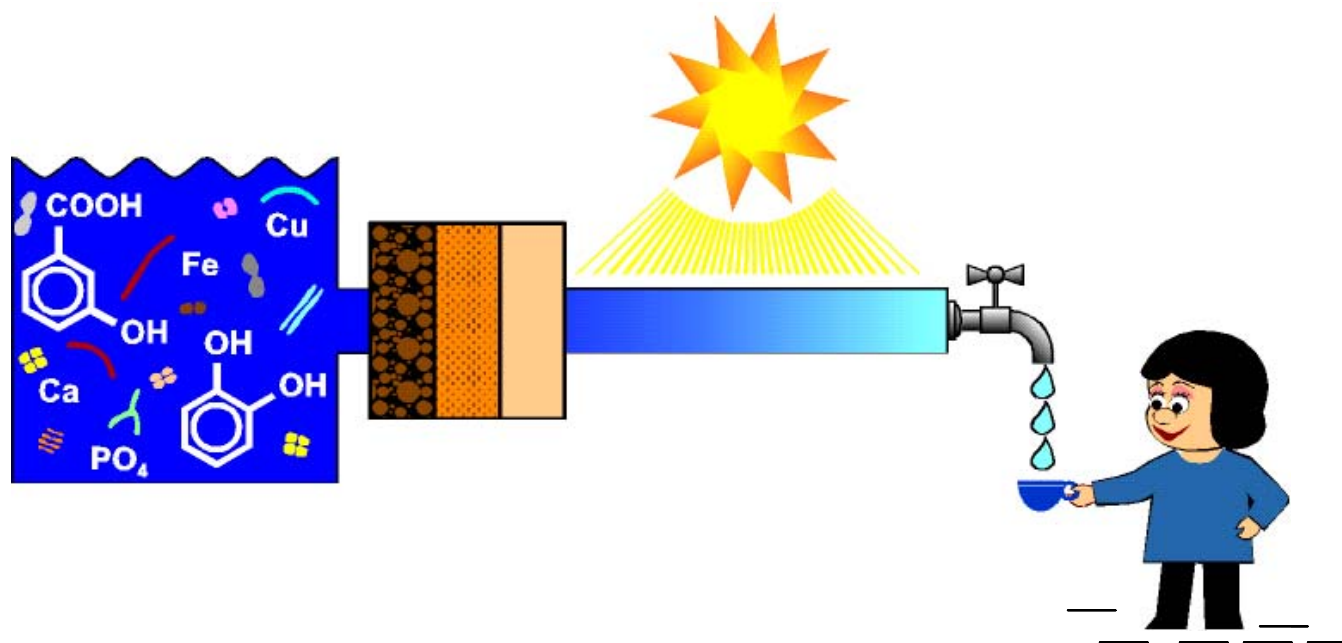


Desinfección de agua por fotocatálisis.

Aspectos básicos



Angela-Guiovana Rincón B. y Cesar Pulgarin.
Curso « Posibilidades para la provisión de agua segura usando nuevas tecnologías ». Iguazu-Argentina, 14-10.2005.

Solar Disinfection of Water by Photocatalytic Processes.

Physico-Chemical and Biological Aspects

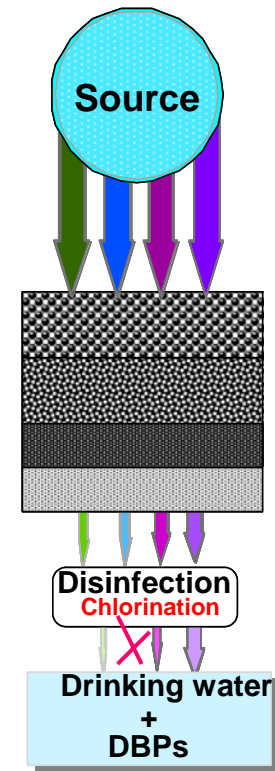


Angela-Guiovana Rincón B. and Cesar Pulgarin

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Swiss Federal Institute of Technology, CHB Ecublens CH 1015

Water disinfection

Chlorination is a widely used technique for the disinfection of water. Its bacterial inactivation effect has been proven but a great concern is that chemical risks could be enhanced due to by-products formed during the chlorination process.



Therefore, the necessity to find low cost, environmental friendly and sustainable alternatives to chlorination.



Disinfectants and disinfection-by products (DBPs)

apparition of chemical risk to human

- ✓ chlorine
- ✓ chlorine dioxide
- ✓ chloramine

- ✓ ozone

- ✓ hydrogen peroxide

- UV

THMs: CHCl_3 , CHCl_2Br , CHClBr_2 , CHBr_3
haloacetates, haloacetonitriles, haloacetaldehydes,
haloketones, halofuranones, chloropicrin, chlorate
aldehydes, carboxylic acids

Halogenated compounds, chlorite, chlorate
cyanogen, chloride and others generally thought to be
the same DBPs as chlorine, but lower concentration

Bromate, hydrogen peroxide
bromomethanes, bromoacetates,
bromoaldehydes, bromoketones, iodinated
Analogs, aldehydes, carboxylic acids

Carboxylic acids

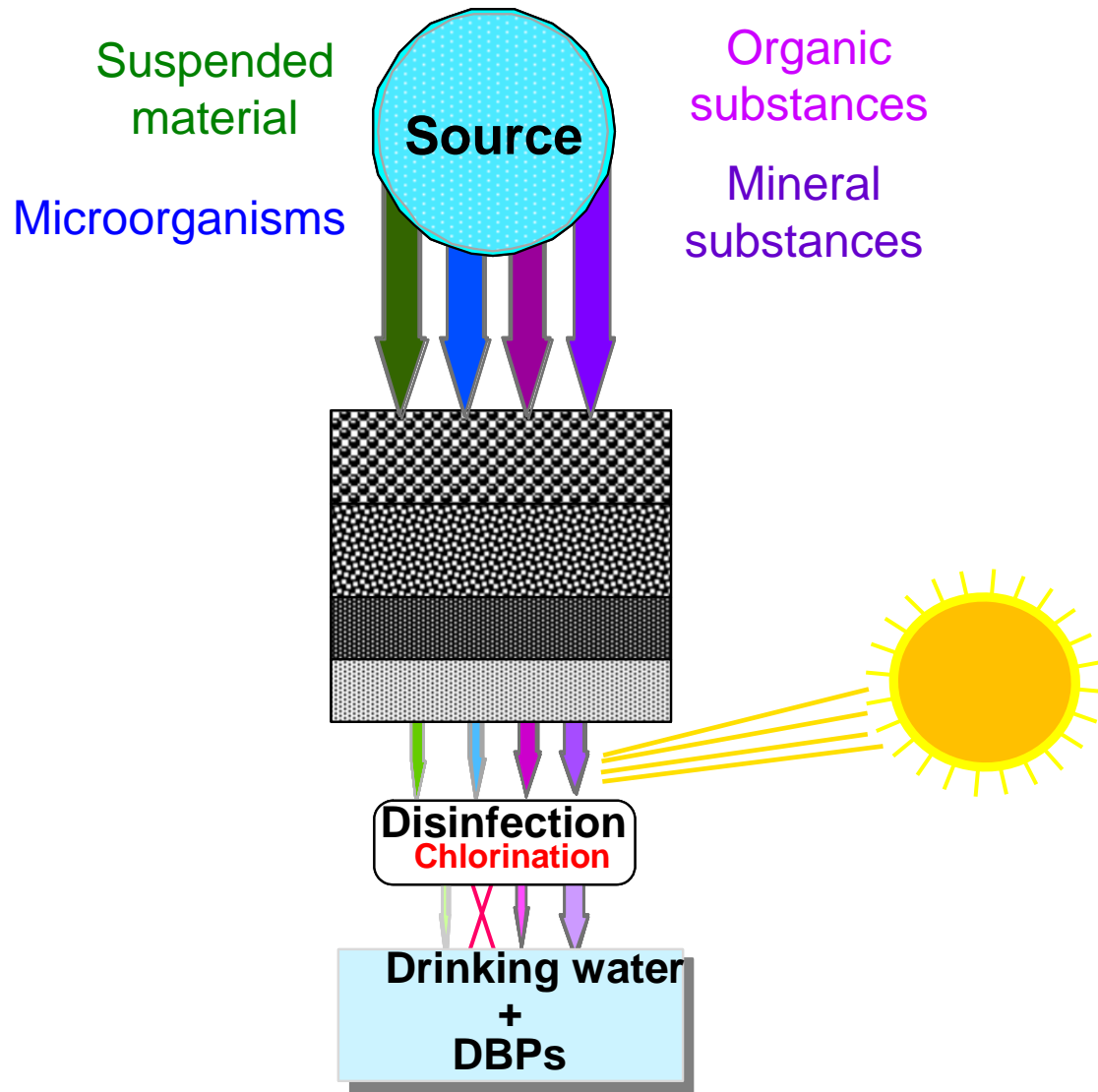
Not DBPs



Aim of the study

- To develop and assess a drinking water and wastewater disinfection process based on solar treatment as:
 - ✓ An alternative to chlorination , by the study of sunlight influence upon the microorganisms
 - ✓ A complement to chlorination, by the study of sunlight influence upon some precursors of the classical disinfection by-products





Schematic representation of the proposed disinfection system

- How this treatment acts ?

Solar irradiation



Absorption

Thermochemistry

Photochemistry

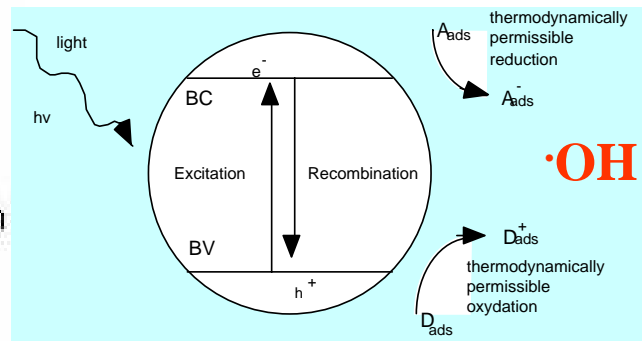
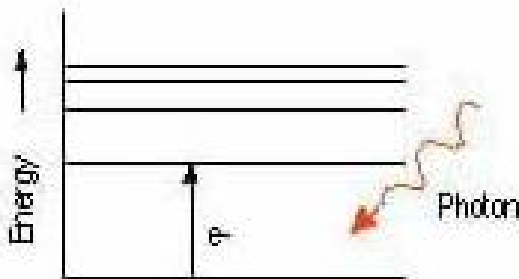
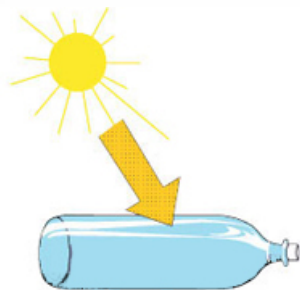


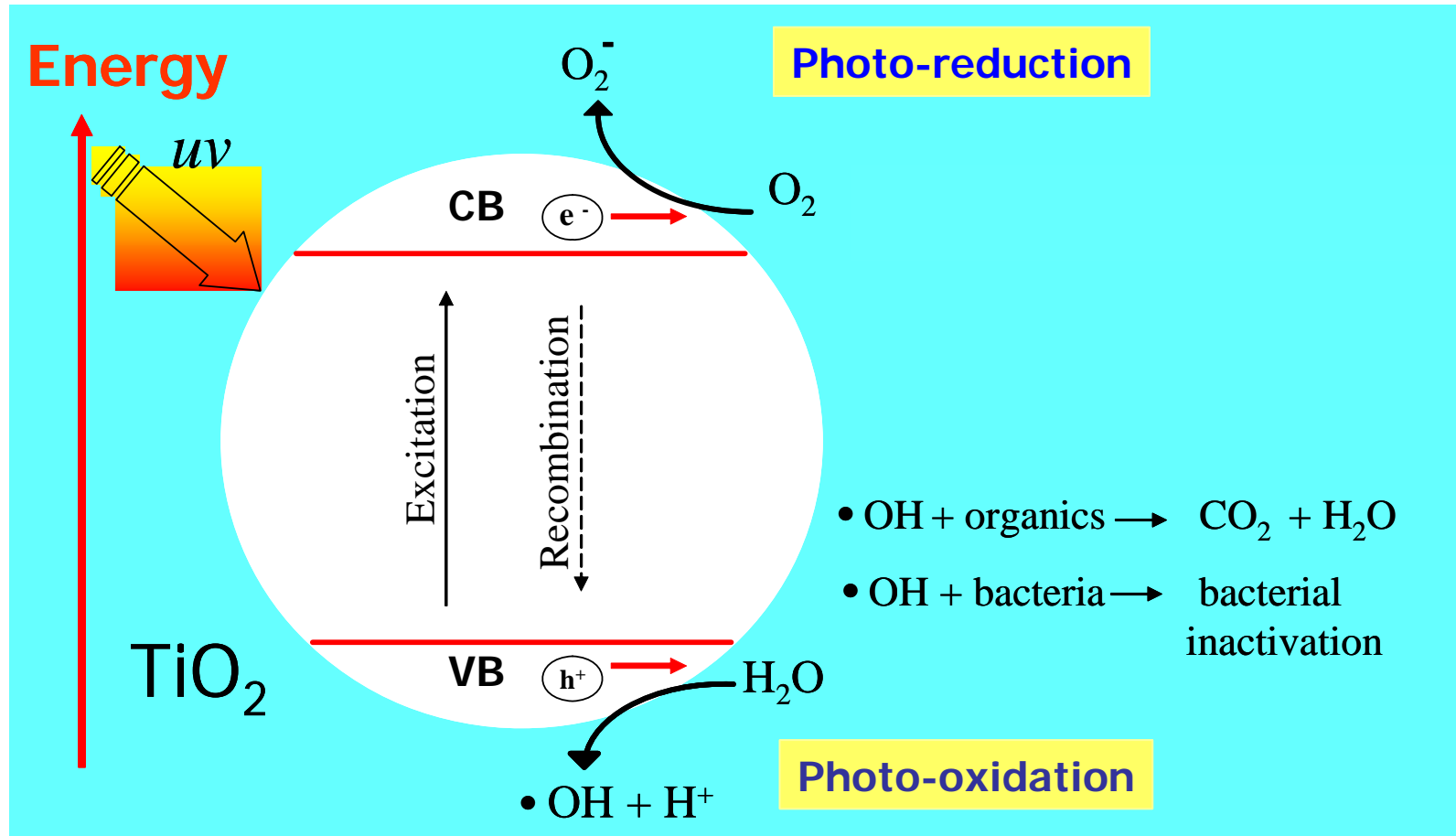
Photo-processes

SODIS



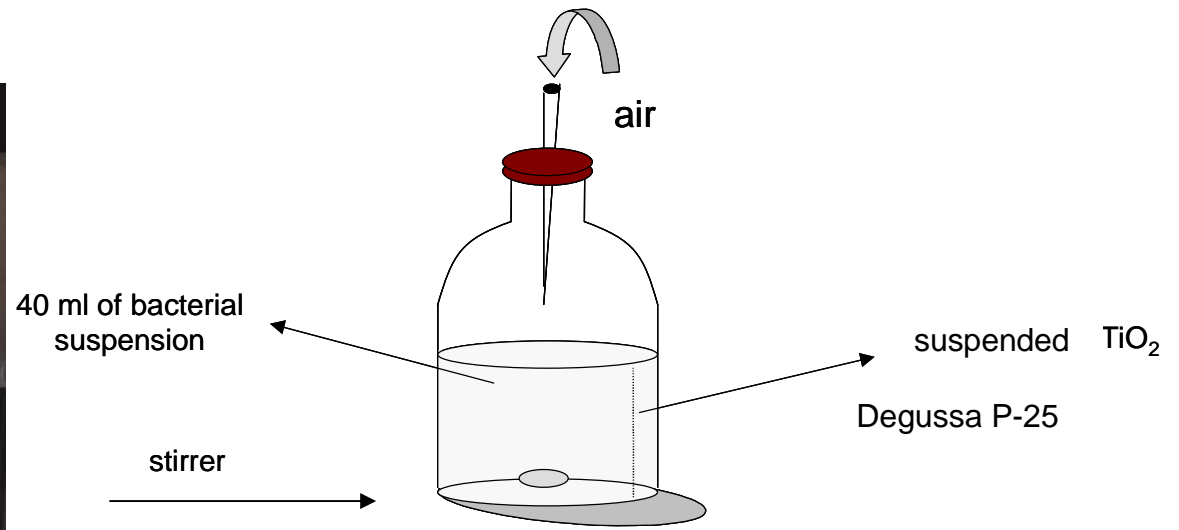
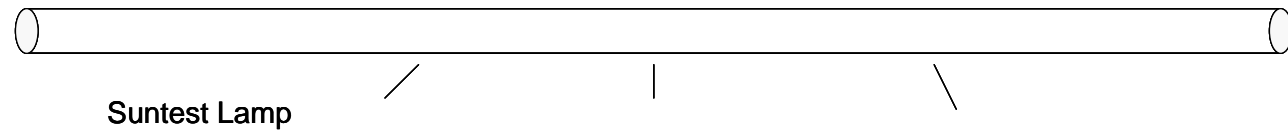
Inactivation of microorganisms by UV-A-radiation and thermal treatment

TiO₂- semiconductor photocatalytic process



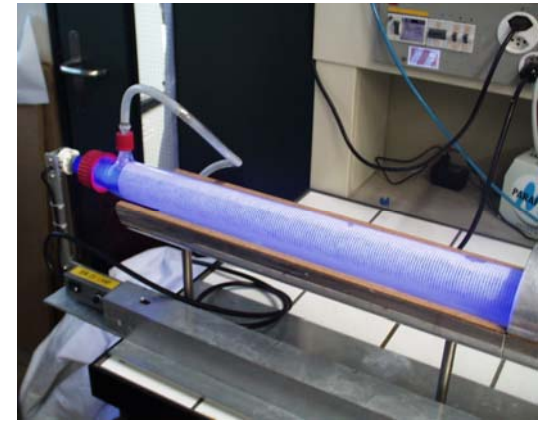
- What about the experimental tools ?

Suntest + reactor



- ✓ A Pyrex glass bottle of 50 ml was used as a batch reactor
- ✓ A Hanau Suntest (AMI) lamp was used as a simulated sunlight

Reactors



✓ Simulated sunlight

✓ real Sunlight

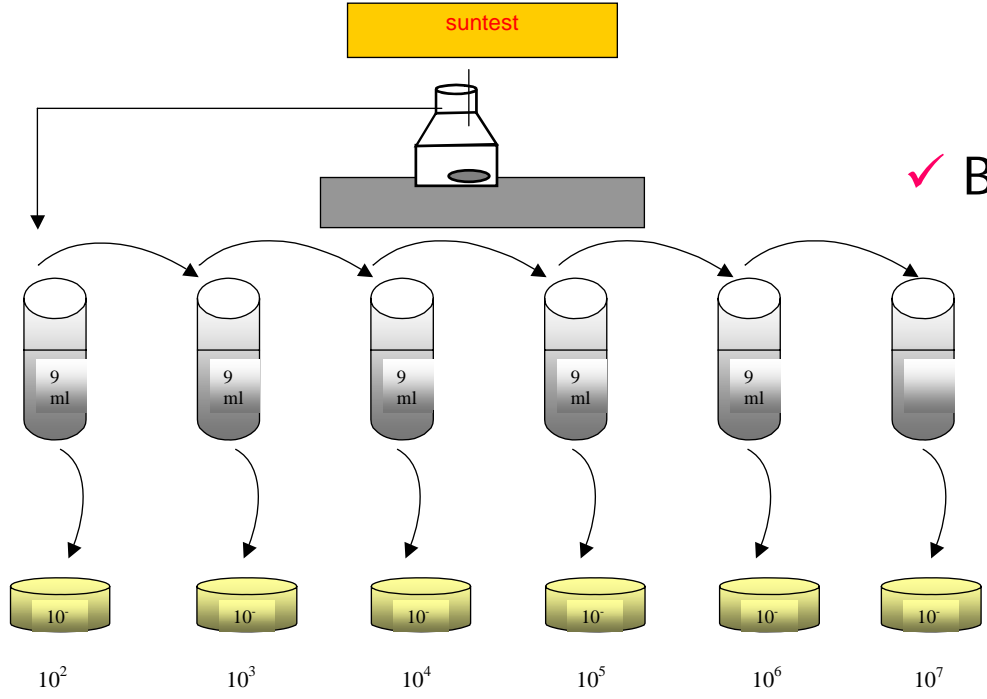
✓ UV-A electric light

✓ TiO_2 P25, *E. coli*, wastewater

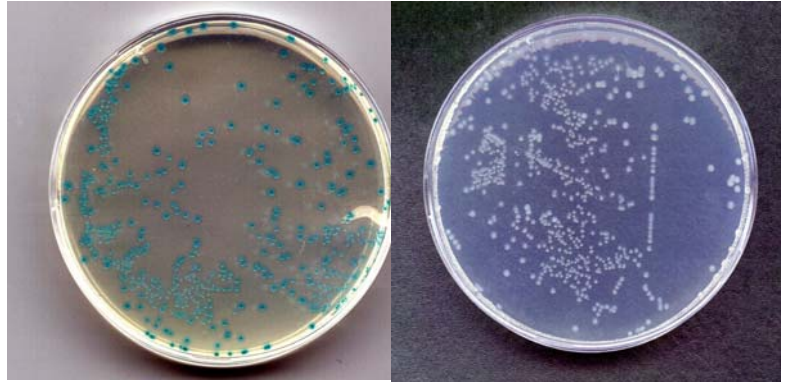
A. G. Rincón and C. Pulgarin. Curso Iguazú, 14-15. 10 2005



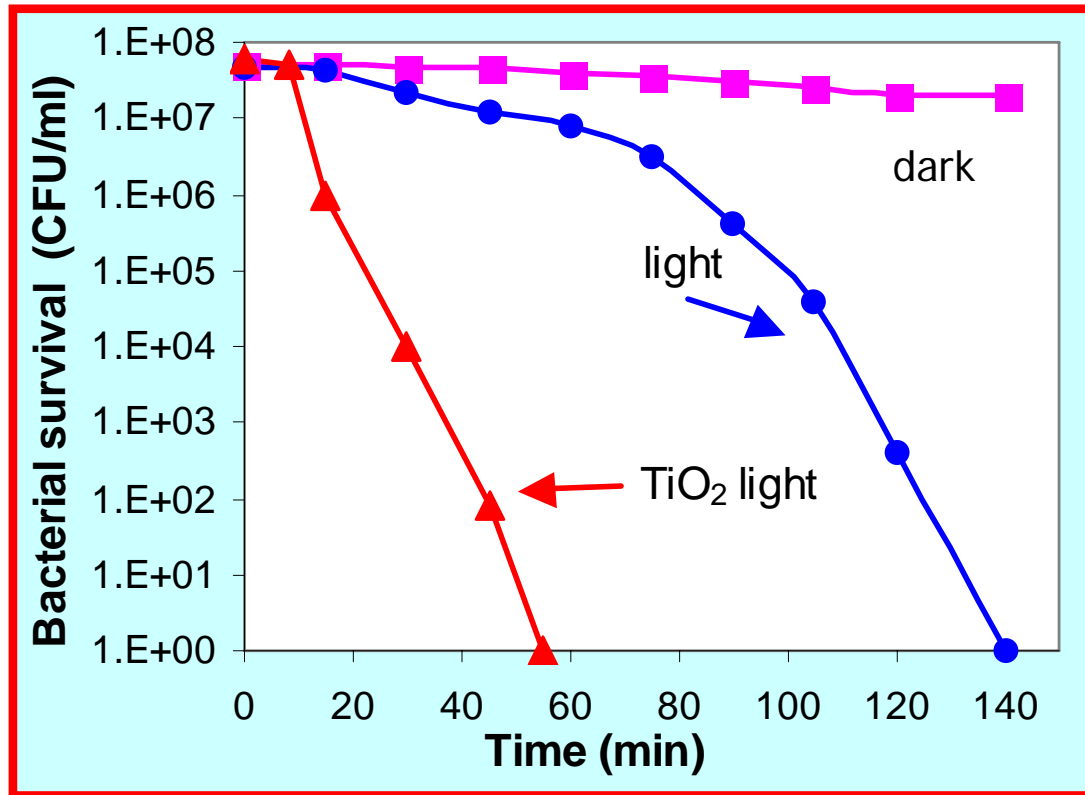
Experimental



✓ Bacterial culturability

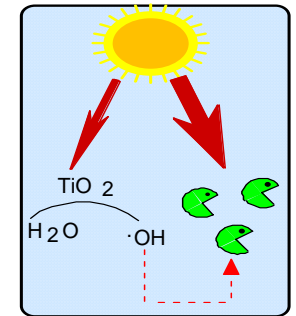
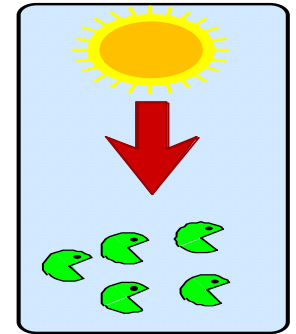


Inactivation of *E. coli* by sunlight



No=10⁷ CFU/ml; TiO₂ 0.75 g/l

✓ *E. coli* inactivation is more efficient in the presence of TiO₂ than without TiO₂



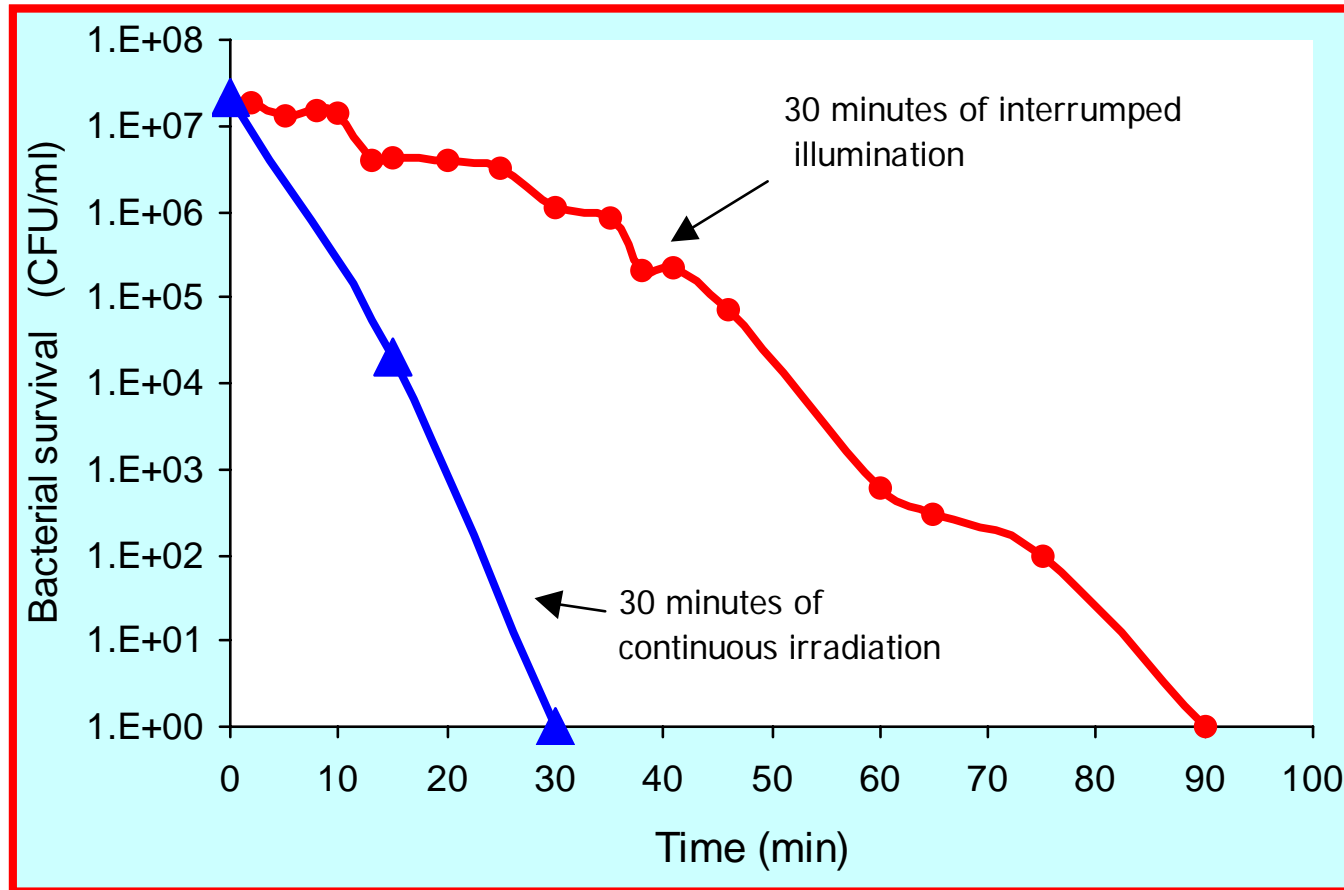
Physicochemical and catalytical aspects

- Intermittence of illumination
- Light intensity
- Temperature
- Turbidity
- Fixation of catalyst
- Commercial catalyst
- Catalyst concentration



- What is the behavior of bacteria under intermittent illumination?

Interruption of illumination

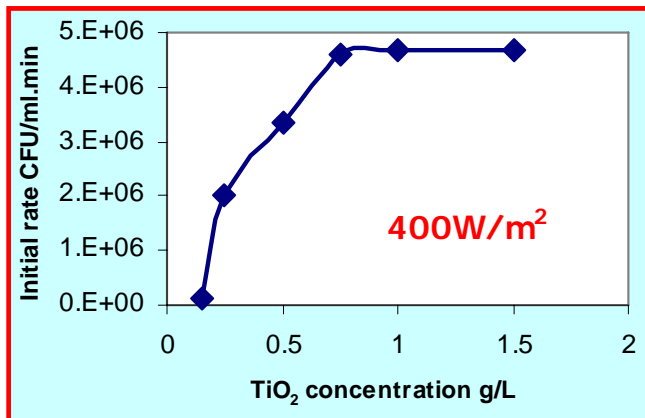
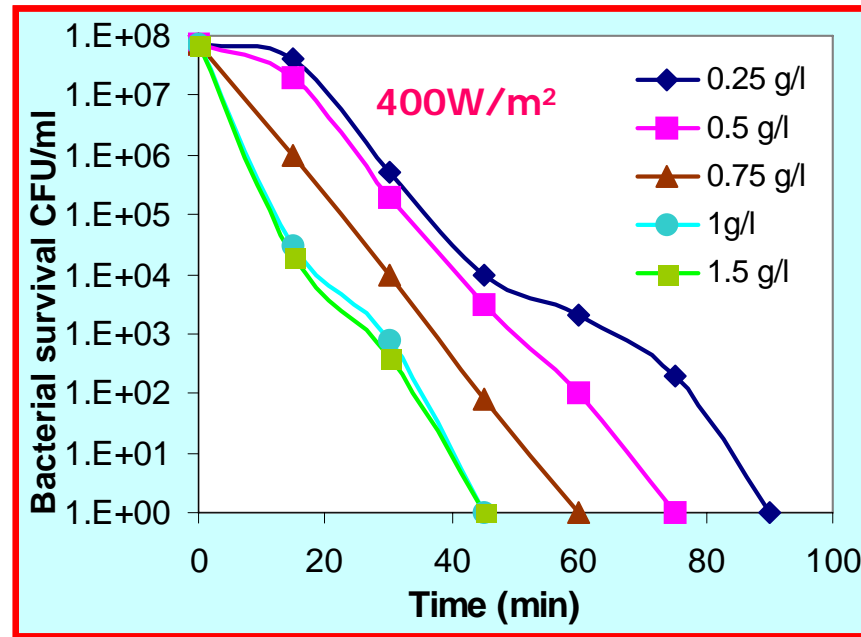


✓ Continuous irradiation was more efficient than intermittent irradiation. TiO_2 P25 1g/l



- What is the optimal amount of photocatalyst?

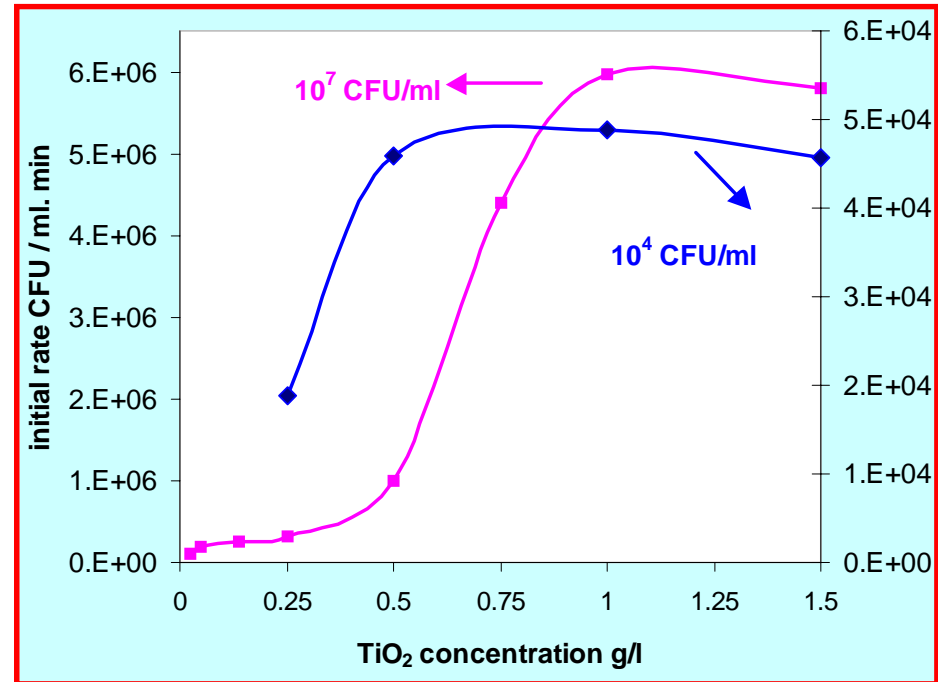
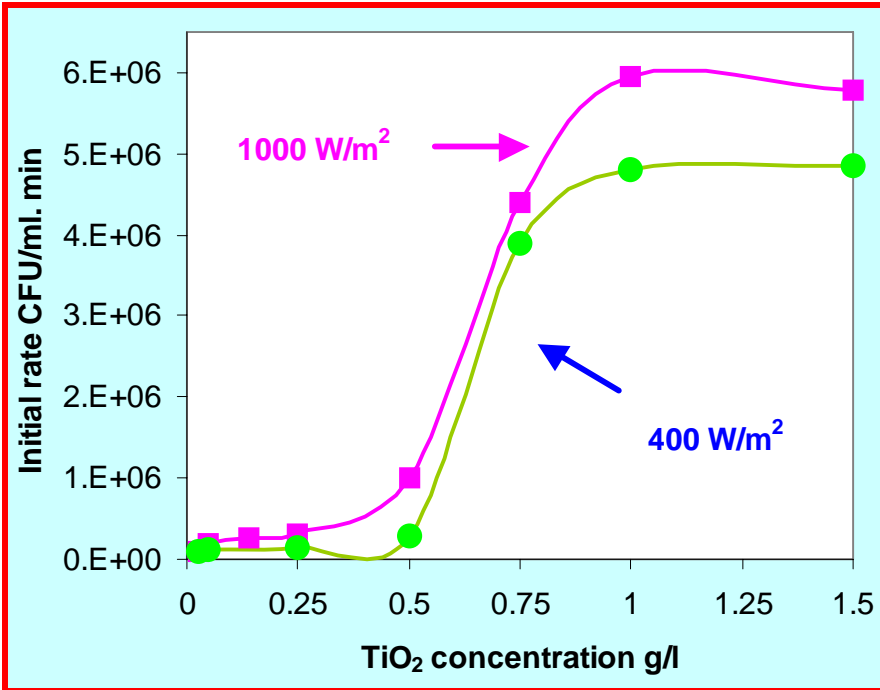
TiO₂ concentration



✓ The initial rate increases with the amount of catalyst up to a level corresponding to complete absorption of the incident light by TiO₂ (screen effect)



TiO₂ concentration



- ✓ The initial rate increases with the amount of catalyst up to a level corresponding to complete absorption of the incident light by TiO₂ (screen effect)
- ✓ The optimal TiO₂ concentration varies as a function of light intensity and initial bacterial concentration



Physicochemical and catalytic aspects

- ⊙ Direct germicidal action of light with the addition of TiO_2 is more efficient than the action of light alone.
- ⊙ Intermittency of irradiation decrease the bacterial inactivation rate
- ⊙ It is necessary to overpass a threshold of TiO_2 concentration before to observe a significant bacterial inactivation.
- ⊙ The optimal TiO_2 concentration depends on different parameters as initial bacterial concentration, light intensity and the chemical composition of water. In our condition, the optimal values are generally ranged between 0.5 and 1 g/l.

- The chemical substances present in the water have an effect on the disinfection?

Chemical parameters

- Natural inorganic substances: (+) (-)
- Effect of synthetic and natural mixtures of organic and inorganic substances (+)(-)
- H_2O_2 , O_2 (+)
- Specific organic substances (-)

Rincón, A.G and Pulgarin C. *Appl. Catal. B: Environ.* 51 (2004), 283-302

Rincón, A.G et al. *J. Photochem Photobiol. A: Chem.* 139 (2001), 233



Biological aspects:

- Influence of physiological state of bacteria and number of transfers
- Influence of initial bacterial concentration
- Definition of the effective disinfection time (EDT)
- Post irradiation events
- Response of natural bacterial community to photocatalytic treatment

EDT

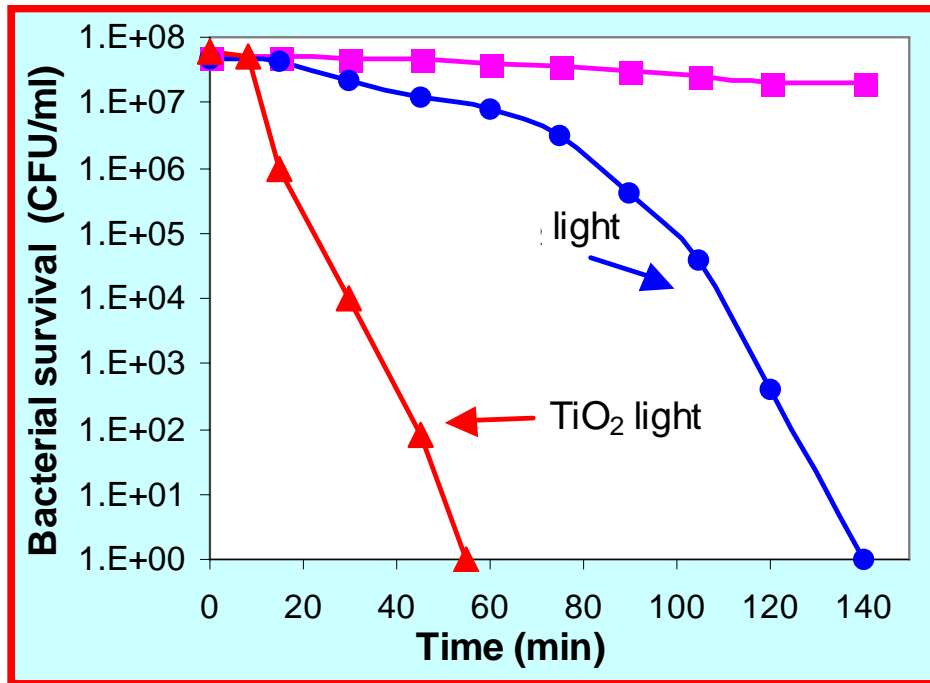
- « Efficient Disinfection Time » is defined as the the treatment time required to prevent any bacterial regrowth during the subsequent 24 or 48 h in the dark, after stopping the phototreatment.

Rincón, A.G and Pulgarin C. *Appl. Catal. B: Environ.* 49 (2004), 99



Post irradiation events

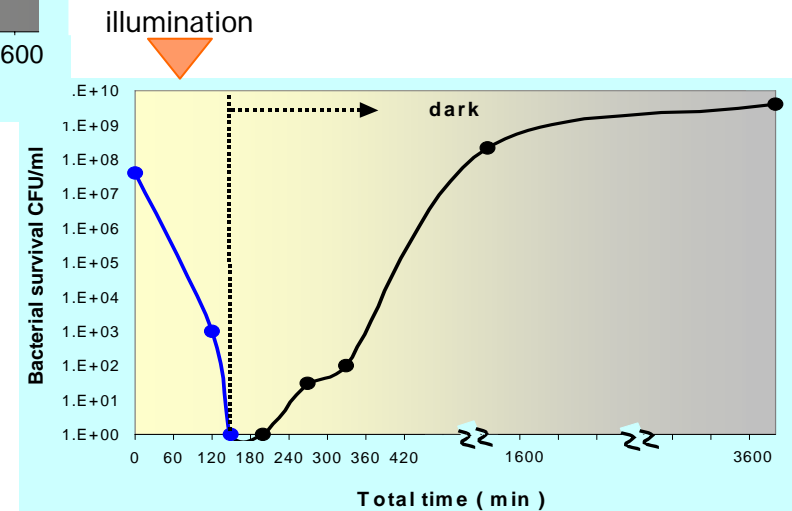
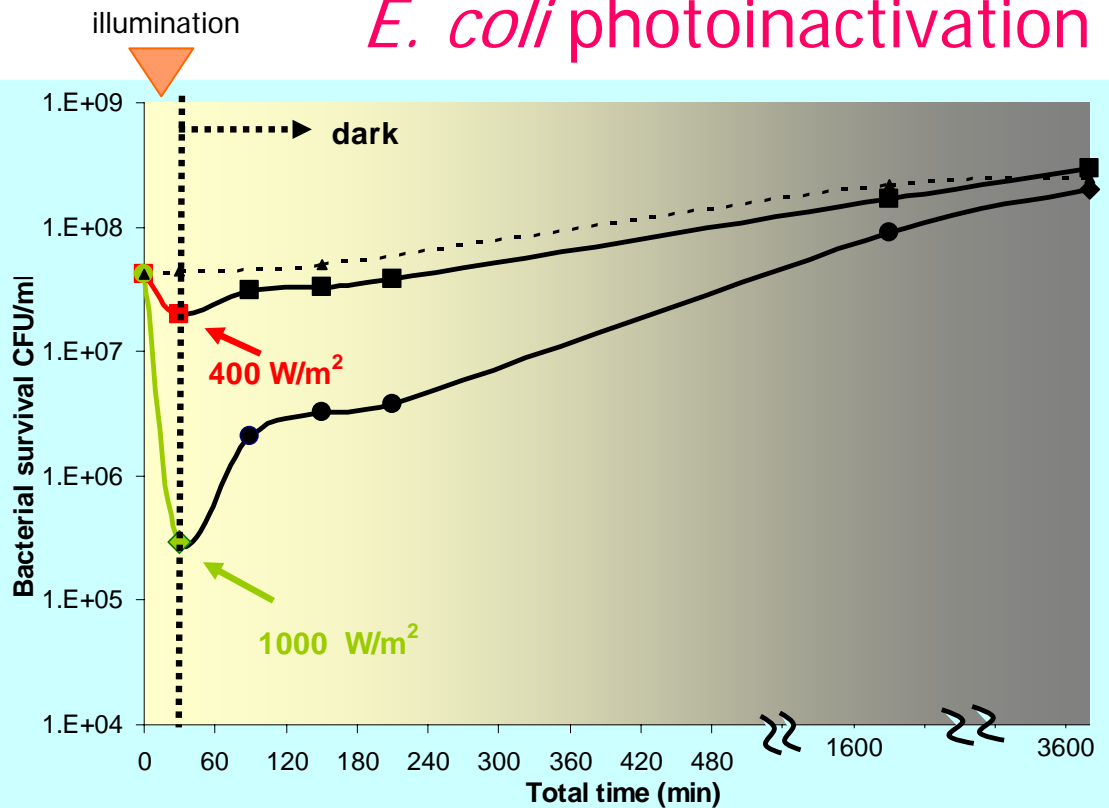
What is the durability of the photodisinfection ?



After 24 h in the dark, no bacteria were detected for photocatalytic system but not for the system without illumination

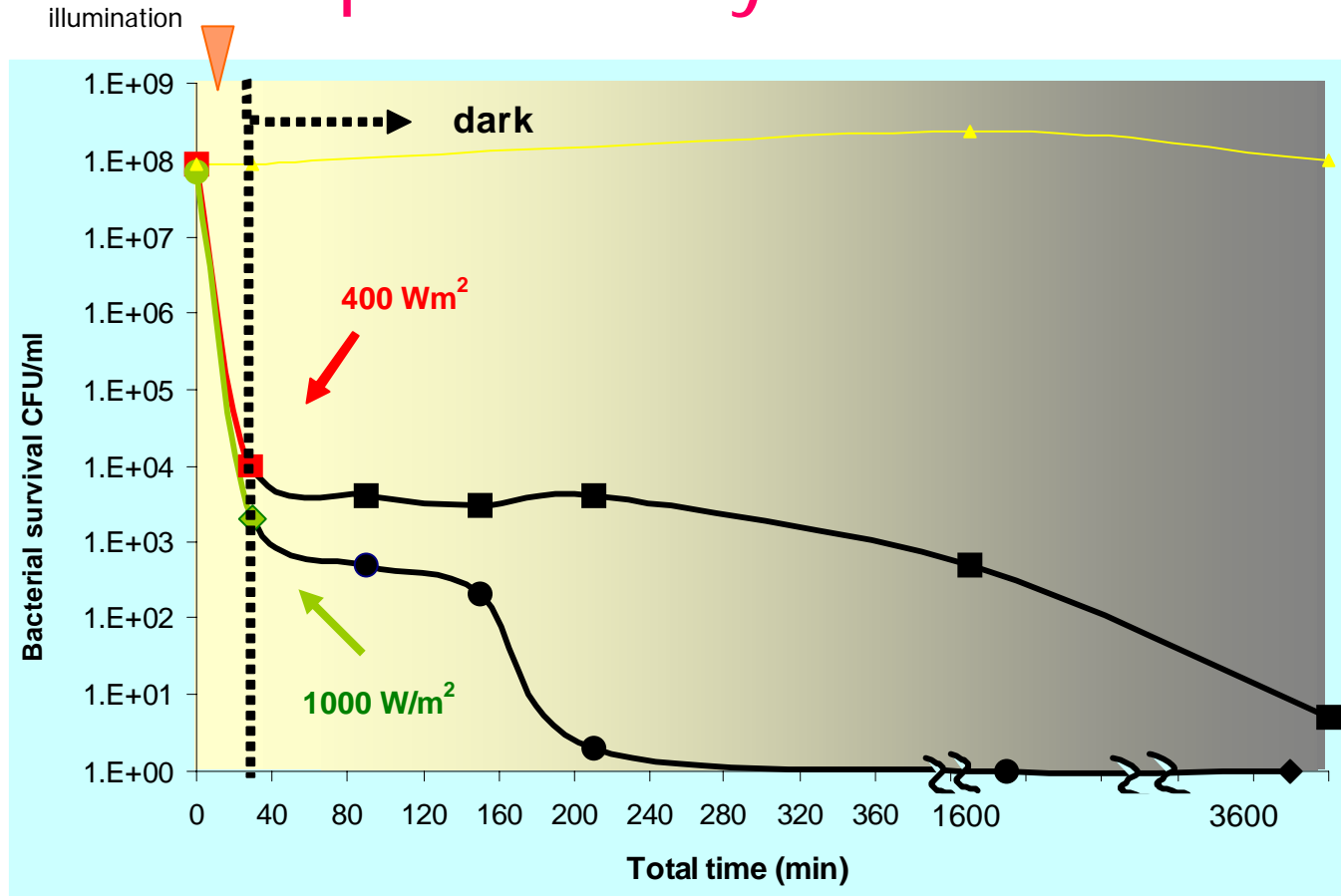
- What does it happens after stopping illumination before total lost of bacterial culturability?.

E. coli photoinactivation without TiO₂



✓ At 30 min of irradiation, the bacteria are not completely destroyed when illumination is stopped. Bacterial concentration increase in the dark.

E. coli photocatalytic inactivation

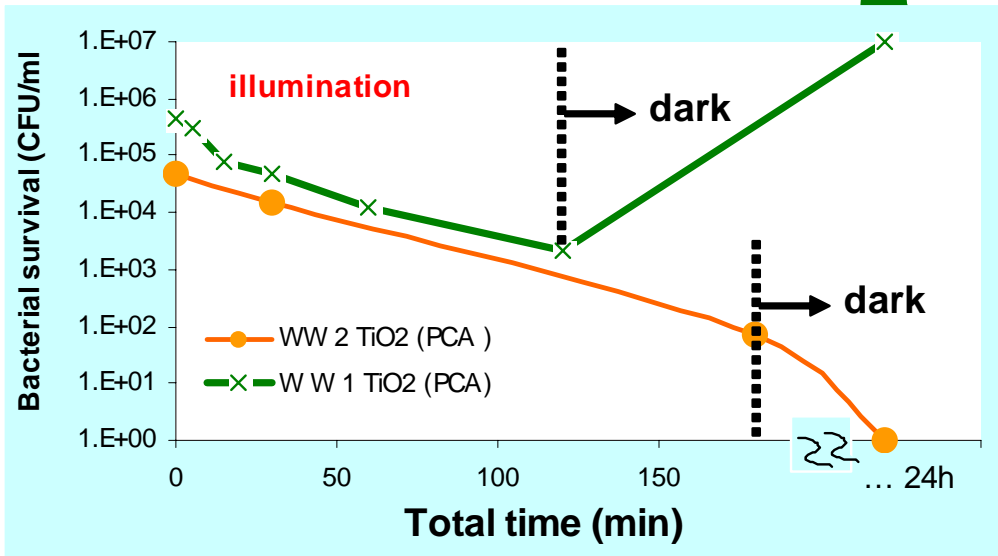


- ✓ After the irradiation in the presence of TiO_2 , bacterial survival keeps decreasing
- ✓ A « residual disinfection effect » was observed in the dark
- ✓ An increase in light intensity, increases also the post irradiation effect in the dark

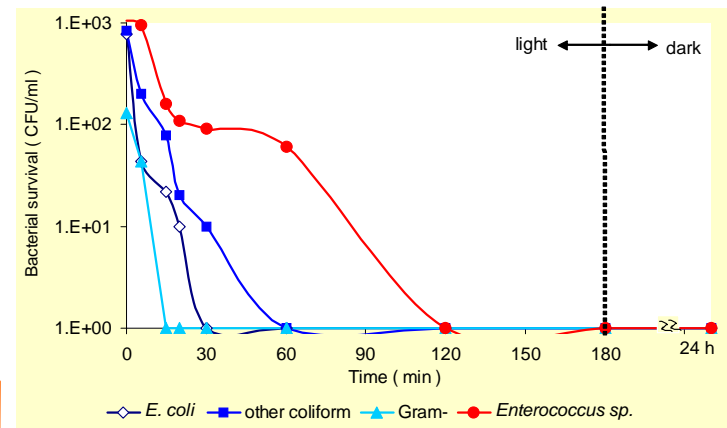
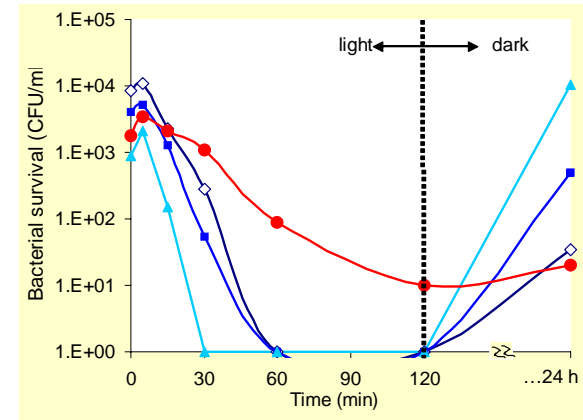


Effect of the photocatalytic process on a real wastewater containing microbial community

Vidy, Lausanne Switzerland



1 g/l TiO₂, 2 and 3 h of irradiation 1000 W/m²



- ✓ 3 h of illumination was the time required to rise a bactericide effect
- ✓ No bacterial recovery was observed.
- ✓ EDT24: **efficient disinfection time**

Rincón, A.G and Pulgarin C. *Appl. Catal. B: Environ.* 49 (2004), 99



What is the sensitivity of different type of bacteria to the photocatalytic treatment?

- Reactor: Suntest
- Illumination time: 3h
- TiO₂ concentration: 1g/l
- Initial concentration of bacteria and total inactivation time for each groupe of bacteria

Wastewater-Switzerland

- *E. coli*: 9X10² CFU/ml, 30 min
 - Colifoms: 4X10³ CFU/ml, 1h
 - *Enterococcus*: 2X10³ CFU/ml, 2h
-

- Reactor: Suntest
- Illumination time: 3h
- TiO₂ concentration: 0.5 g/l
- Initial concentration of bacteria and total inactivation time for each groupe of bacteria

Wastewater-Colombia

- *E. coli*: 8X10² CFU/ml, 2h
- *Shiguella*: 4X10² CFU/ml, 1.5h
- *Salmonella*: 6X10¹ CFU/ml, 1h



Biological aspects

- ✓ A “Residual disinfecting effect” is observed after stopping of illumination
- ✓ The sensitivity of different groups of bacteria to the photocatalytic treatment depends on the type of bacteria.
- ✓ *E.coli*, is the more sensitive to the photocatalytic process in all the studied conditions.



- Scaling up is possible?

Field scale experiments for drinking water production

Water from the Lemán Lake contaminated with *E. coli* K 12 was exposed to sunlight in different seasons.

- Effect of the volume of phototreated water
- Water disinfection in the presence and absence of TiO_2
- Post irradiation events
- Cost estimation of the water disinfection by photocatalysis

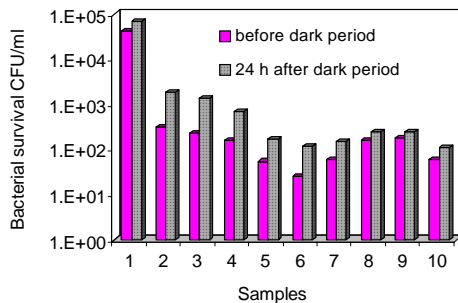
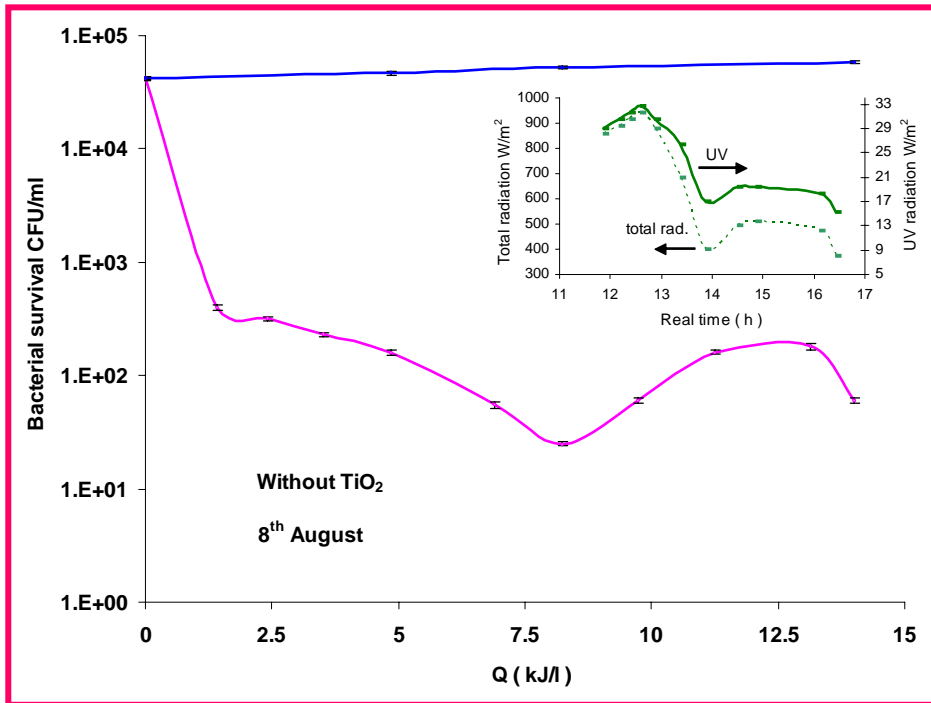
Photocatalytic treatment as a final treatment for drinking water production



Compound parabolic collector (CPC) placed at the EPFL.

- ❖ Photocatalytic disinfection via TiO_2
- ❖ Water from Lemman Lake contaminated with *E. coli* was exposed to sunlight

Water disinfection in the absence of TiO_2 - post irradiation effects

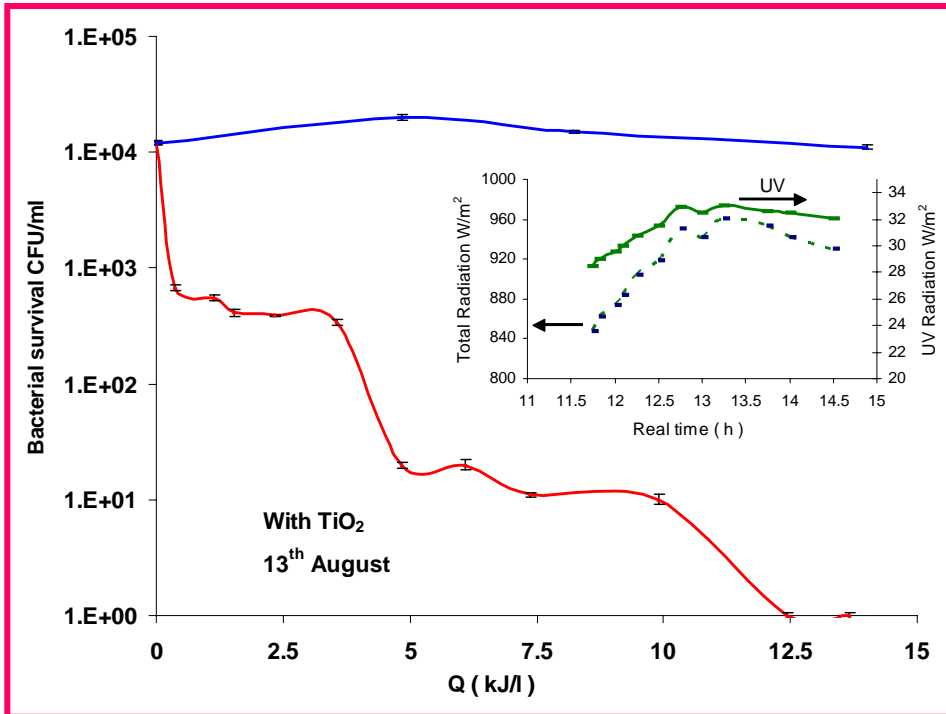


❖ Bacterial concentration slightly re-increases:

- some bacteria recover their culturability;
- decrease of UV intensity and modification of the visible spectral composition of sunlight
- there is possibly a replication of the remaining culturable cells.

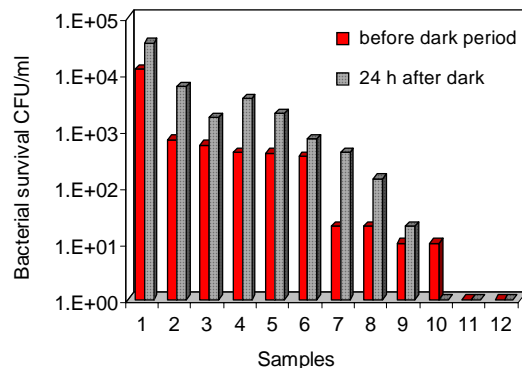
❖ Total disinfection was not reached during illumination and bacterial recovery was observed even before the illumination stopped as well as in the post irradiation period EDT_{24} was not reached.

Photocatalytic treatment as a final treatment for drinking water production



✓ Active *E. coli* concentration decreases as the accumulated energy increases and arrives to non-detectable level (<1 CFU/ml) when 12.5 kJ/l are applied

✓ No bacterial recovery was observed after 24 h after stopping of treatment, while regrowth was observed if stopped in middle of exposure EDT₂₄ was reached.



Solar UV dose

$$\text{dose} = I \times t_r$$

I: average intensity, W/m²

t_r: residence time, h

Exp.3 began in the late afternoon when visible light has different spectral characteristics. Solar UV intensity was lower (18.9 W/m²) than that of the exp. 5 (37.2 W/m²).

Experiment. Date	TiO ₂ (g/l)	V _{TOT} (l)	Bacterial load (CFU/ml)	UV average (W/m ²)	% bacterial inactivation	UV dose (Wh/m ²)	Period of treatment (h:min)
1. January 17, 2003 ^a	0.1	70	1200000	7.20	99.99167	9.87	12:00-16:00
2. January 20, 2003 ^a	0.1	70	807000	4.92	99.99876	6.75	12:30-16:30
3. August 19, 2003 ^a	0.1	70	295000	18.98	99.8986	19.52	15:30-18:30
4. September 4, 2003	0.1	70	514000	33.83	99.9961	23.20	13:05-15:05
5. August 21, 2003	0.1	70	414000	37.28	99.9976	17.04	12:20-13:40
6. August 15, 2002 ^a	--	70	220000	36.24	99.9909	37.28	11:30-14:30
7. May 16, 2002 ^a	--	70	400000	36.77	99.9405	37.82	12:20-15:20
8. September 20, 2003 ^a	--	70	365000	23.92	99.4247	43.74	10:50-16:10

dose necessary to inactivate approximately 99.9900 % of *E. coli* using a CPC reactor in Lausanne Switzerland.

^a undetectable value (< 1 CFU/ml) was not reached during irradiation

The UV solar dose necessary to reach a target disinfection level is not a good indicator to predict the impact of the solar photocatalytic process on bacteria.



General conclusions

- ❖ A systematic study on the effect of physicochemical, biological and chemical parameters on photocatalytic disinfection.
- ❖ An intensive work with a solar reactor (70 l) demonstrated the feasibility, of the scaling up of the system.
- ❖ The definition of efficient disinfection time (EDT_x) as a parameter of control for photocatalytic disinfection. The EDT_x depends on the mentioned photochemical and biological aspects. EDT_x should be determined for each specific condition, Thereafter the obtained EDT value can be raised of a certain percentage in order to introduce a range of security.

Thanks for your attention

