Innovative Processes and Practices for Wastewater Treatment and Reuse in the Mediterranean Region

ADVANCED TECHNOLOGIES FOR WASTEWATER TREATMENT

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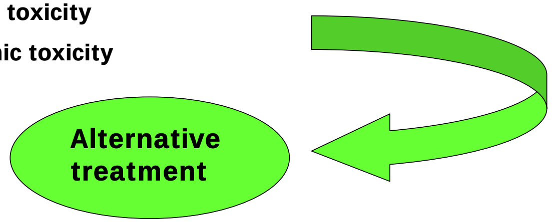
Introduction

Biodegradable substances:

- **Biofilter treatment / activated sludge treatment**

Non-biodegradable substances can show

- **Non-toxic / inert behaviour**
- **Acute toxicity**
- **Chronic toxicity**



Introduction

- Phenols, nitrophenols and halophenols.
- Pharmaceutical compounds (antibiotics, disinfectants...).
- Water disinfection.
- Gasoline additives (MTBE, ETBE,..).
- Chlorinated hydrocarbons (solvents, VOCs, etc).
- Residues from textile industry (dyes).
- Agrochemical wastes (pesticides).

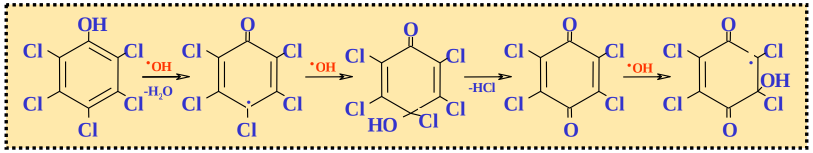
Introduction

Advanced Oxidation Processes are a source of hydroxyl radicals (•OH).

Compound	Oxidation Potential
Fluorine	*2.23*
Hydroxyl radical	*2.06*
Atomic Oxygen	*1.78*
Hydrogen Peroxide	*1.31*
Peroxyradical	*1.25*
Permanganate	*1.24*
Chlorine dioxide	*1.15*
Chlorine	*1.00*
Bromine	*0.80*
Iodine	*0.54*

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

Introduction



•OH

CO_2
Inorganic acids
Water

$$C_nH_mO_pCl_q + \left(\frac{(m-2p)}{4} + n\right)O_2 \rightarrow nCO_2 + \frac{m-q}{2}H_2O + qHCl$$

Introduction

- **AOPs** may be used for **decontamination** of water containing organic pollutants, classified as bio-recalcitrant, and/or for **disinfection** removing current and emerging pathogens.
- The overarching goal for the future of **reclamation and re-use** of water is to capture water directly from non-traditional sources such as industrial or municipal wastewaters and restore it.
- Futuristic direct re-use systems envisioned involve only two steps: a single-stage MBR with an immersed nanofiltration membrane, followed by a **photocatalytic reactor to provide an absolute barrier** to pathogens and to destroy organic contaminants that may pass the nanofiltration barrier.
- Nevertheless, **technical applications are still scarce**. Process costs may be considered the main obstacle to their commercial application

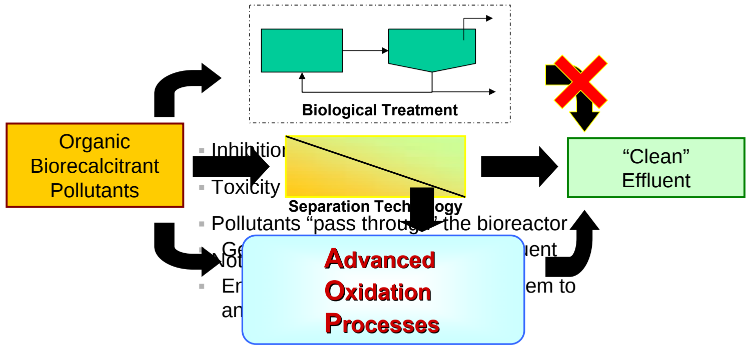
Introduction

PROMISING COST-CUTTING APPROACHES

- Integration of AOPs as part of a **treatment train**.
- To minimize reaction time (i.e. energy) and reagent consumption in the more expensive AOP stage by applying an **optimized treatment strategy**.
- The use of renewable energy sources, i.e., **sunlight** as the irradiation source for running the AOP.

M.A. Shannon et al., Nature, 452 (2008) 301.
C. Comninellis et al., J. Chem. Technol. Biotechnol., 83 (2008) 769.

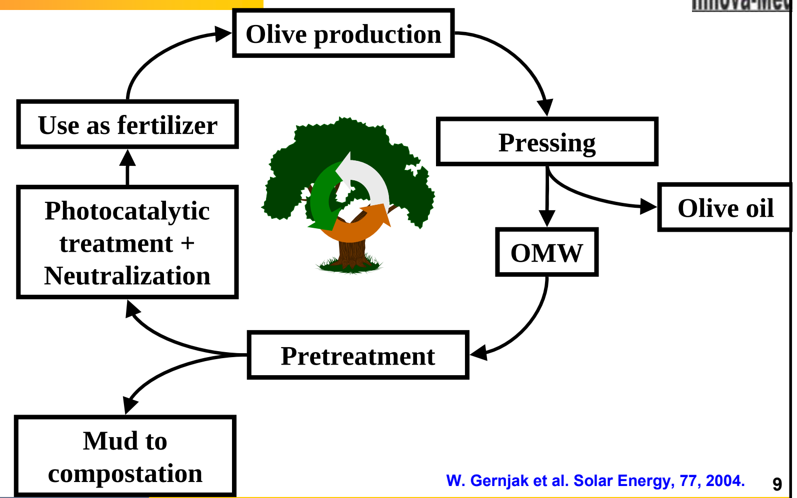
Treatment train



Feasible for accelerating the oxidation and destruction of a wide range of organic contaminants in polluted water

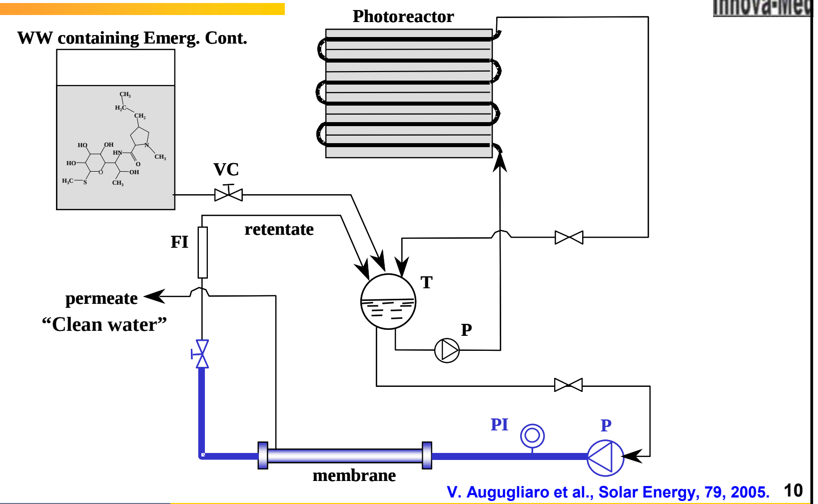
V. Augugliano et al.,, J. Photochem. Photobiol. C: Photochem. Reviews 7 (2007) 123.

Treatment train



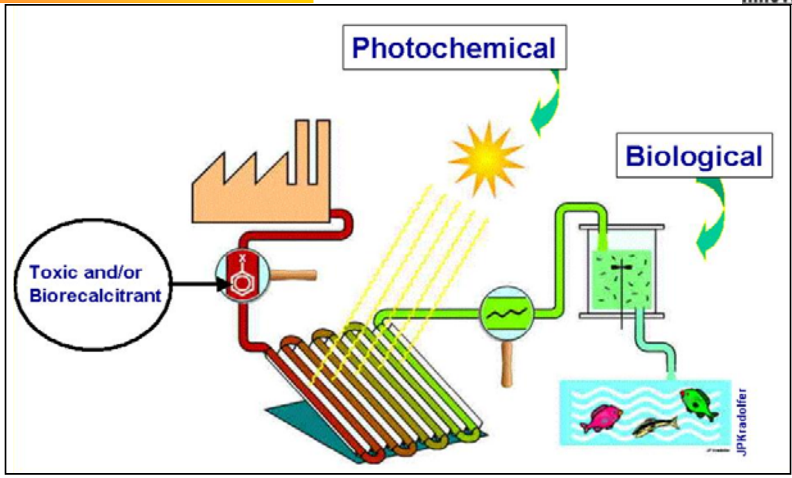
W. Gernjak et al. Solar Energy, 77, 2004.

Treatment train



V. Augugliaro et al., Solar Energy, 79, 2005.

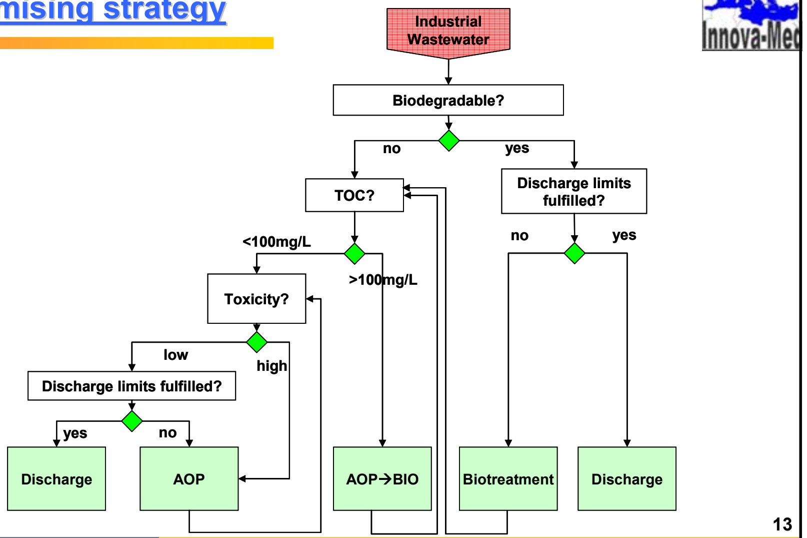
Treatment train



Optimising strategy

Step 1	Check if WW is potentially treatable by AOP and/ or biotreatment	*Wastewater characterisation + check for volatility, solubility, pre-liminary kinetic study*
Step 2	Selection of treatment strategy as a function of wastewater characteristics	*Decision if only AOP, or any treatment train*
Step 3	Develop and optimise coupling strategy	*Various AOPs and treatment trains can be tested.*
Step 4	Pilot-plant studies on process kinetics	*Process optimisation. Strategy depends on problem and AOP.*
Step 5	Theoretical up-scaling	*Necessary for correct posterior economic assessment.*
Step 6	Economic study	*Takes into account investment + O&M costs + their variation depending on process scale.*
Step 7	Choose best-performing AOP	*= AOP that solves given problem (defined by WW characteristic + flowrate) at lowest price.*
Step 8	Final plant design	

Optimising strategy



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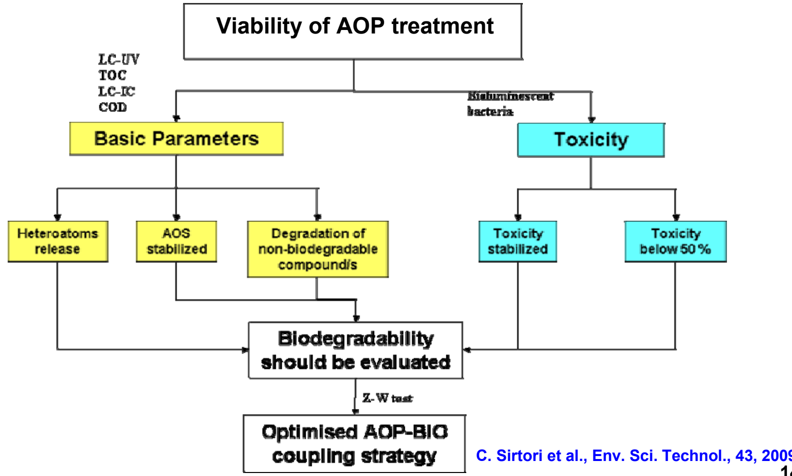
Optimising strategy



C. Sirtori et al., Env. Sci. Technol., 43, 2009.

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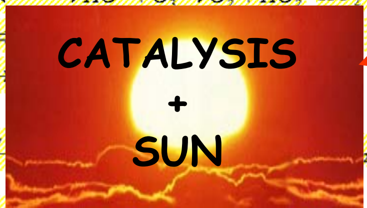
Sunlight as the irradiation source

- H_2O_2/Fe^{2+} (Fenton): $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet$
- H_2O_2/Fe^{2+} (Fe^{3+})/UV (Photo-Fenton): $Fe^{3+} \xrightarrow{h\nu} Fe^{2+} + HO^\bullet$
- $TiO_2/h\nu/O_2$ (Photocatalysis): $TiO_2 \xrightarrow{h\nu} e^- + h^+$
  $h^+ + H_2O \rightarrow {}^\bullet OH + H^+$
- O_3/H_2O_2: $H_2O_2 \xleftrightarrow{H^+} HO^- + O_3 \rightarrow O_2 + HO_2^-$ $\quad HO_2^- + O_3 \rightarrow HO_2^\bullet + O_3^{\bullet-}$
  $HO_3^\bullet \leftarrow$ ... $\quad O_3^{\bullet-} + H^+ \rightarrow HO_3^\bullet$
  $HO_3^\bullet \rightarrow$ ...



- O_3/ UV: $O_3 \xrightarrow{h\nu}$ ... $_2O_2$ $\quad H_2O_2 \xrightarrow{h\nu} 2HO^\bullet$
- H_2O_2/UV: $H_2O_2 \xrightarrow{h\nu} 2OH^\bullet$

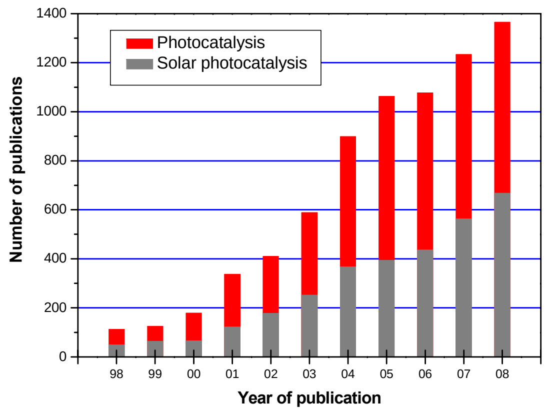
S. Malato et al., Catalysis Today 147, 1, 2009.

Sunlight as the irradiation source

Photochemical AOPs

AOP	key reactions	wavelength
UV/ H_2O_2	$H_2O_2 + h\nu \rightarrow 2\ OH^\bullet$	$\lambda < 300$ nm
UV/ O_3	$O_3 + h\nu \rightarrow O_2 + O\ (^1D)$ $O\ (^1D) + H_2O \rightarrow 2\ OH^\bullet$	$\lambda < 310$ nm
UV/H_2O_2/ O_3	$O_3 + H_2O_2 + h\nu \rightarrow O_2 + OH^\bullet + OH_2^\bullet$	$\lambda < 310$ nm
UV/ TiO_2	$TiO_2 + h\nu \rightarrow TiO_2\ (e^- + h^+)$ $TiO_2(h^+) + OH^-_{ad} \rightarrow TiO_2 + OH_{ad}^\bullet$	$\lambda < 390$ nm
photo-Fenton	$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^\bullet + OH^-$ $Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + H^+ + OH^\bullet$	$\lambda < 580$ nm

Sunlight as the irradiation source



(source: www.scopus.com, 2009, search terms "photocatalysis" and "solar" within these results)

Sunlight as the irradiation source

The SOLARDETOX Consortium (Brite-Euram III Program, Contract No. BRPR-CT97-0424) has installed during 1999 <u>the first European Solar Detoxification Plant.</u> Main plant characteristics are:

- **CPC surface: 100 m^2**
- **Treatment volume: 800 L.**
- **Batch Operation**
- **Automatic operation**

Sunlight as the irradiation source

Solar field figures:

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

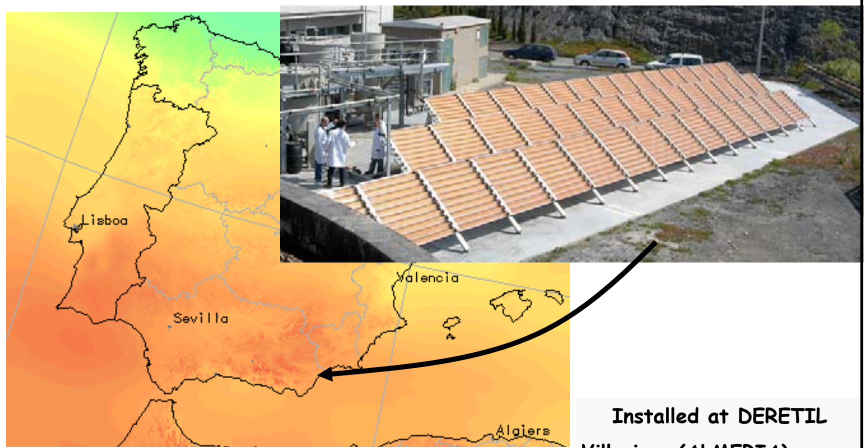
b) 4 parallel rows with **14 modules** each mounted on a 37º-tilted platform (local latitude)

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

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

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

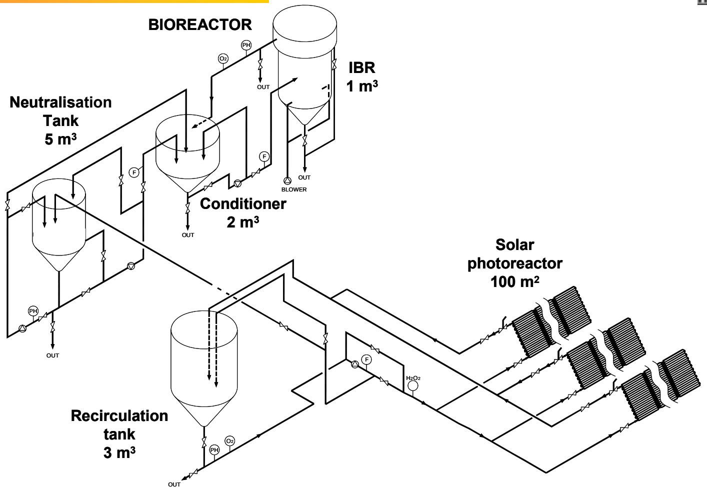
Sunlight as the irradiation source



Installed at DERETIL Villaricos (ALMERIA)

http://www.psa.es/webeng/projects/cadox/index.html

Sunlight as the irradiation source



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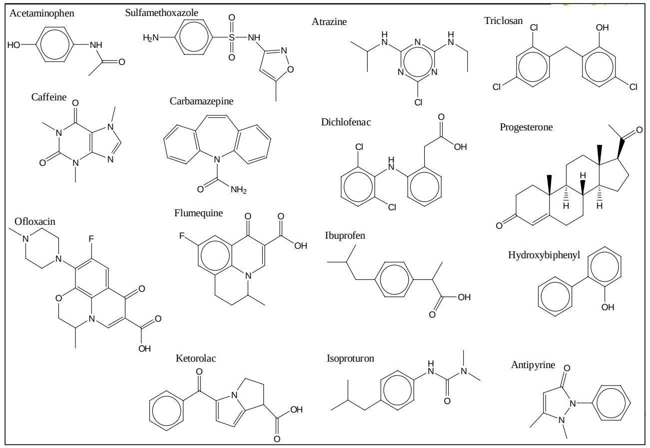
Water Reuse by AOPs (photo-Fenton)

Selected ECs



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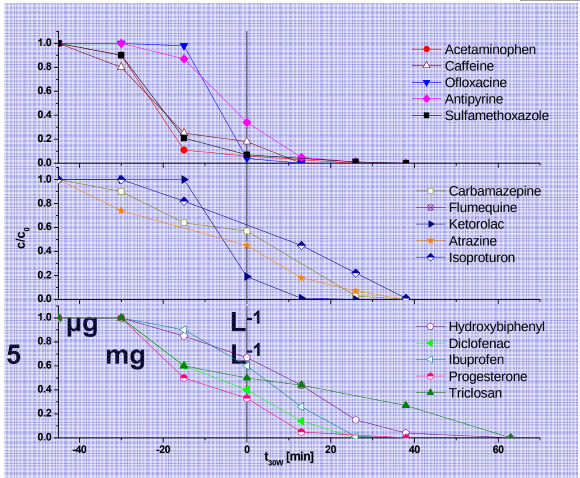
Water Reuse by AOPs (photo-Fenton)

Photo-Fenton experiments with real waste water from the MWTP El Ejido:

COD_0: 77 mg L^{-1}
DOC: 22 → 14 mg L^{-1}
pH: 7.7 → 2.9
used 43 mg L^{-1} H_2O_2

c_0 = 5 µg L^{-1}
c_0(Fe) = 5 mg L^{-1}
pH~3



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Water Reuse by AOPs (photo-Fenton)

Treatment of real waste water (MWTP, El Ejido) with 5 mg L^{-1} Fe, pH ~3.5, 2 x 50 mg L^{-1} H_2O_2, and the analysis with HPLC-QTRAP-MS.
51 substances were detected and successfully degraded (until LOD), with the exception of Nicotine (166→47 ng L^{-1}), Caffeine (3100→8 ng L^{-1}), Chlorfenvinphos (640→99 ng L^{-1}), Cotinine (225→11 ng L^{-1}).

t30W [min]	Nicotine	Atenolol	Ranitidine	4-MAA	4-AA	Parax anthine	Metronid azole	Caffeine	4-AAA	4-FAA	Trimetho prim	Ofloxacin	Ciproflo xacin	Mepiva caine	Meto prolol	Antipyrine	Propan olol
inicial	166	627	162	9884	2257	3080	16	782	4615	2236	26	1139	392	25	15	49	0
-30	159	534	0	104	0	1818	6	3152	2291	1168	17	554	163	17	13	707	15
0	245	170	0	0	0	1747	0	1291	1104	467	0	58	0	4	4	520	0
19	133	0	0	0	0	0	0	12	20	0	0	0	0	0	0	20	0
59	119	0	0	0	0	0	0	8	0	0	0	0	0	0	0	0	0
100	63	0	0	0	0	0	0	12	0	0	0	0	0	0	0	0	0
140	47	0	0	0	0	0	0	8	0	0	0	0	0	0	0	0	0

t30W [min]	Erythro mycin	Sulfame thoxazole	E.Carbam azepine	Carbam azepine	Simazine	Isopro turon	Atrazine	Keto profen	Diazepan	Indome thacine	Fenofibric Acid	Mefenamic Acid	Chlorfen vinphos	Cotinine	Sulfa pyridine	Linco mycin	Azithro mycin
inicial	80	284	11	89	8	0	0	261	9	98	81	27	51	172	161	61	75
-30	0	17	3	64	5	13	11	104	6	22	21	9	640	159	12	27	44
0	0	71	0	11	0	0	2	45	0	0	6	0	375	225	31	0	0
19	0	0	0	0	0	0	0	0	0	0	0	0	37	66	0	0	0
59	0	0	0	0	0	0	0	0	0	0	0	0	52	17	0	0	0
100	0	0	0	0	0	0	0	0	0	0	0	0	17	11	0	0	0
140	0	0	0	0	0	0	0	0	0	0	0	0	99	11	0	0	0

t30W [min]	Norfl oxacin	Primidone	Citalopram HBr	Famo tidine	Amitriptylin HCl	Clarithro mycin	Nadolol	Velafa xime	Furos emide	Diclof enac	Benza fibrate	Gem fibrozil	Hidrochlo rothiazide	Diuron	Salicilic Acid	Prava statin	Ibuprofen
inicial	179	82	219	20	22	109	13	188	429	793	205	2968	314	213	48	426	181
-30	103	40	126	9	12	26	7	100	49	261	33	567	64	77	6	0	615
0	0	13	0	0	0	0	0	0	0	86	12	643	45	0	0	0	212
19	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
59	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
100	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	454
140	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Water Reuse by AOPs (photo-Fenton)

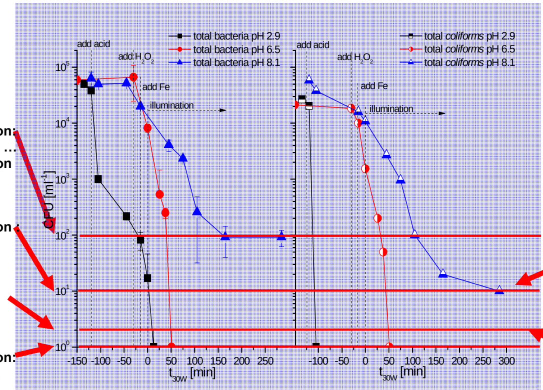
Samples were inoculated on agar plates and incubated at 37ºC for 24 h
Effects of pH, H_2O_2, Fenton, and photo-Fenton are observable.

Agricultural irrigation: Trees, cereal crops, … Industrial use for non food processes (100 CFU mL^{-1})

Agricultural irrigation: pastures, fields…, (10 CFU mL^{-1})

Urban irrigation: Gardens,… (2 CFU mL^{-1})

Agricultural irrigation: Fresh vegetables…, (1 CFU mL^{-1})



Spanish Norm for the reuse of water 1620/2007

Environmental use: Aquifer recharge (10 CFU mL^{-1})

Recreation use: Golf courses, … (2 CFU mL^{-1})

Concluding remarcks

To lead to industry application it will be critical that the AOPs can be developed up to a stage, where the process:

- is cost-efficient compared to other processes.
- is robust, i.e. small to moderate changes to the wastewater stream do not affect the plant's efficiency and operability strongly.
- is predictable, i.e. process design and up-scaling can be done reliably.
- is easy to implement, i.e. suppliers and engineering companies can start marketing the process without huge initial investment costs, which could only be recovered by high turnovers.
- is easy to operate and maintain, operation error must not lead to "catastrophic events".
- is safe regarding the environment (minimize risks of leakage, discharge of not sufficiently treated effluent).
- gives additional benefit to the industry applying the process (e.g. giving the company the image of being "green").

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