ADVANCED OXIDATION OF ESTROGENS, ANTIBIOTICS, AND OTHER WATER EMERGING CONTAMINANTS AND THE POTENTIAL FOR SOLAR DETOXIFICATION AND WATER REUSE

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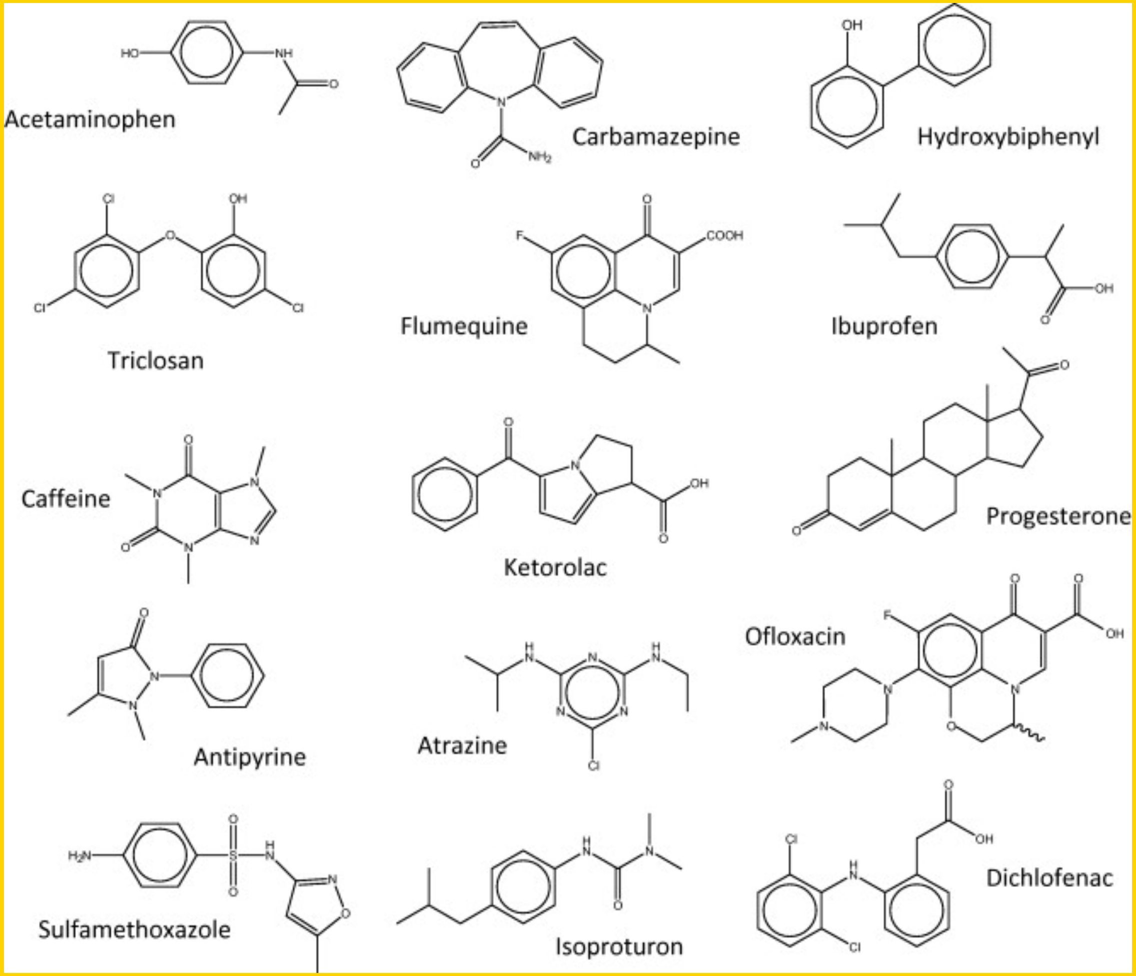
- Yangtze river with red water near Chongqing (China Press) Saturday 9th Sept 2012

Emerging Contaminants of Concern

- Xenobiotics such as drugs, pesticides, pharmaceuticals and EDC have been labelled as Emerging Contaminants
- Sources are industrial and domestic effluents, agricultural run offs, municipal sewage.
- In WWTP ECs are discharged in un-metabolized form or as metabolites
- WWTP treatment technology are very often unable to entirely degrade persistent ECs
- Accumulation in the aquatic environment where they may cause ecological risk, such as interference with the endocrine system of higher organisms, microbiological resistance and accumulation in soil, plants and animals
- Alternative advanced technologies are needed for treatment of WWTP effluents

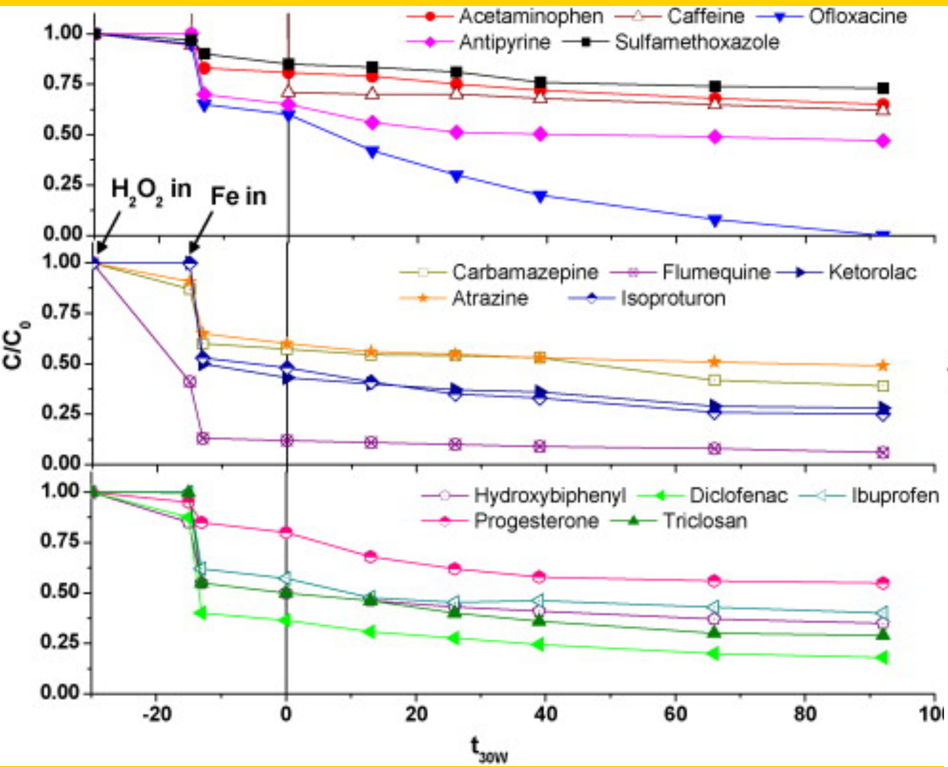
Advanced Oxidation: Solar Photo-Fenton Oxidation Process

- Oxidation of ECs in the presence of light, iron salts and hydrogen peroxide
- Effective for the removal of ECs
- pH < 4 (to prevent iron precipitation)
- Treatment of non-acidic wastewater is too costly because of pH adjustment
- Increase in water salinity

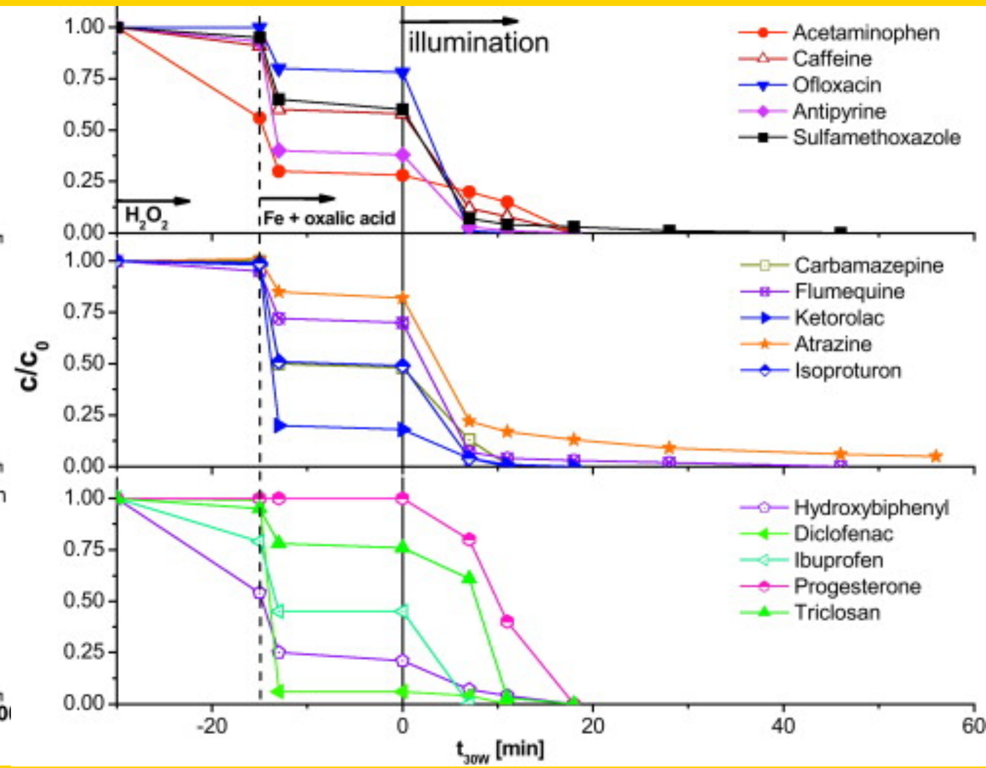


Solar Photo-Fenton Oxidation Process
Secondary biological effluent, El Ejido WWTP, Almeria, Spain

Neutral pH



pH 4



Klamerth et al., Catal. Today 161(2011) 241

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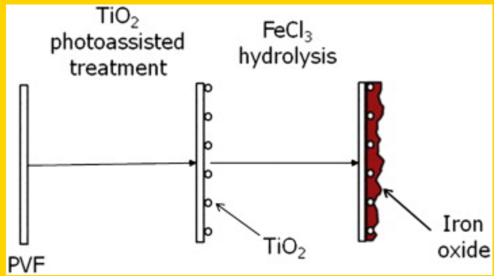
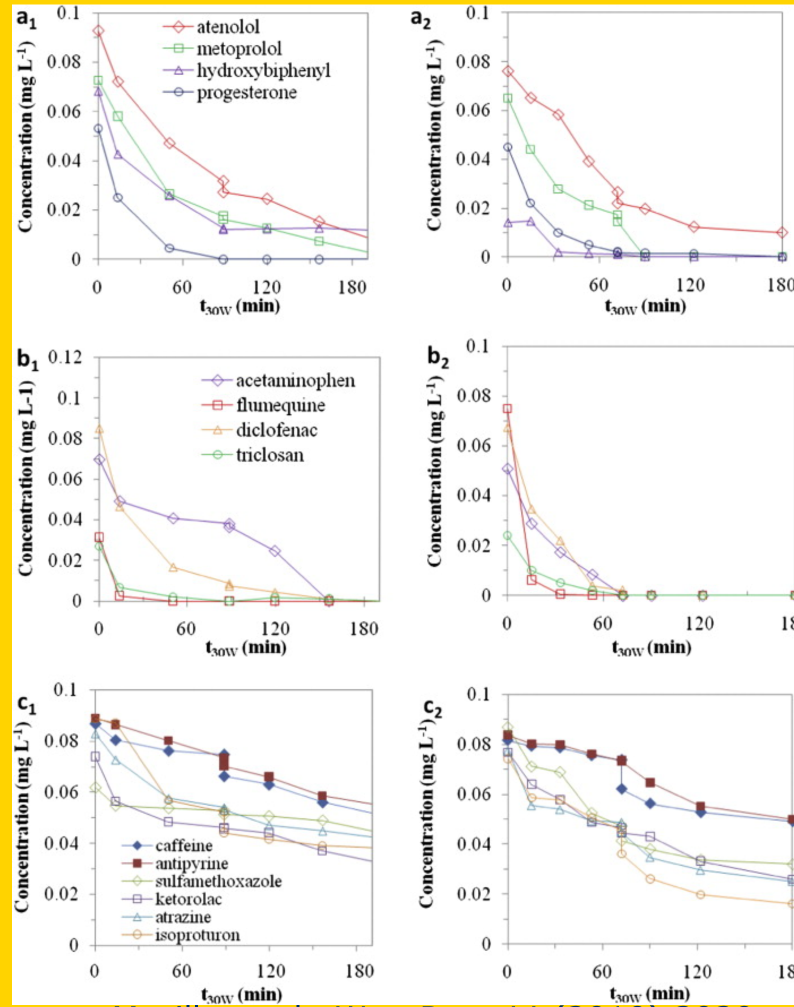
Solar Photo-Fenton Oxidation Process on Immobilized Iron

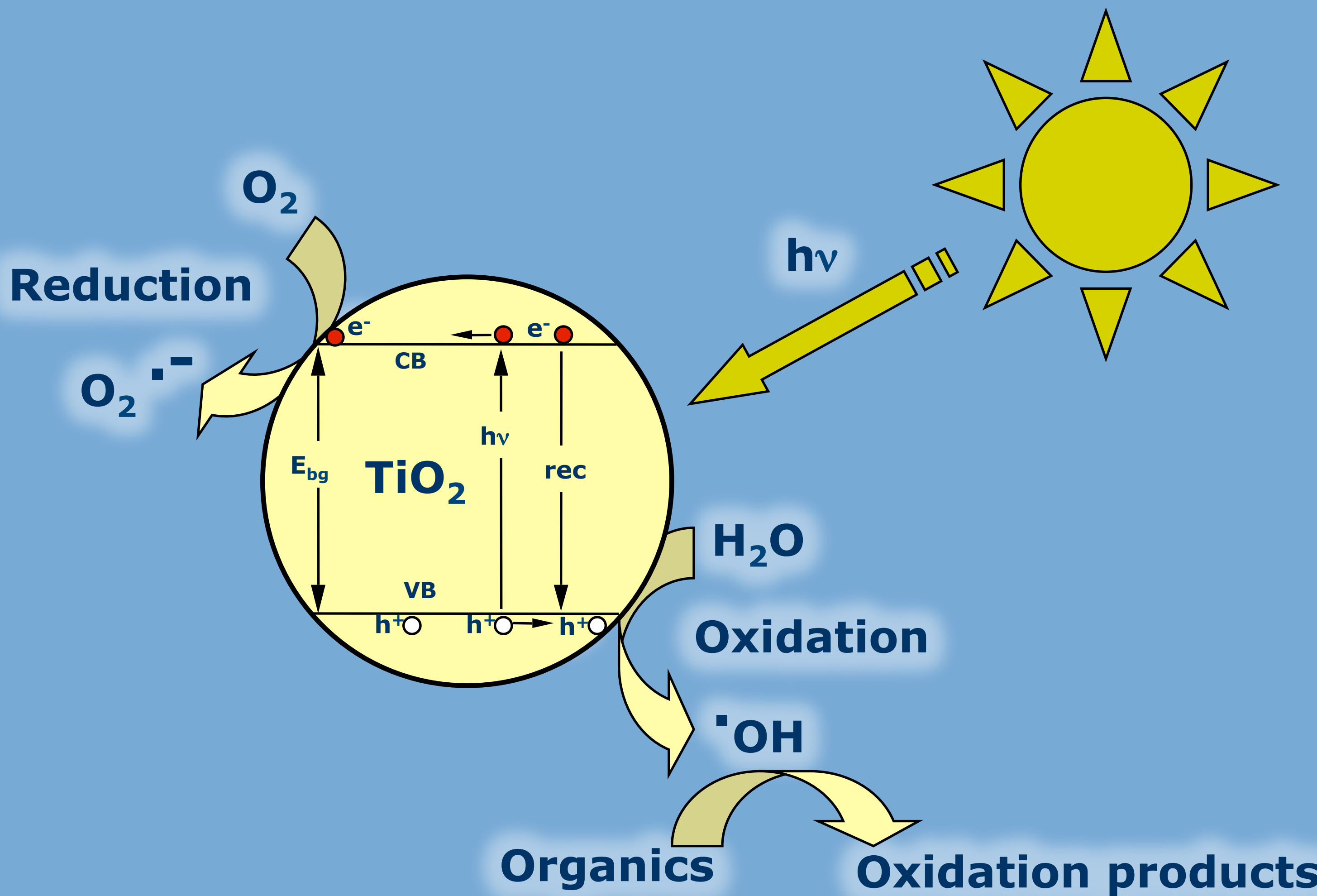


- TiO_2/Fe oxide immobilized on PVF
- Degradation of a mixture of 14 ECs spiked to WWTP in two CPC (8.5 L) at mild pH
- Consecutive runs with 3.1 mM H_2O_2
- Contaminants with Fe(III) chelating groups degraded at faster rates
- Catalyst was active for 20 days without loss of efficiency

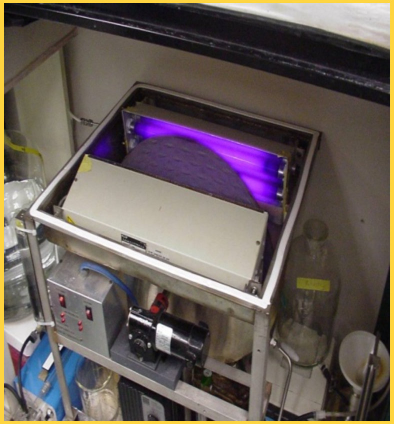


Mazille et al., Wat. Res. 44 (2010) 3029

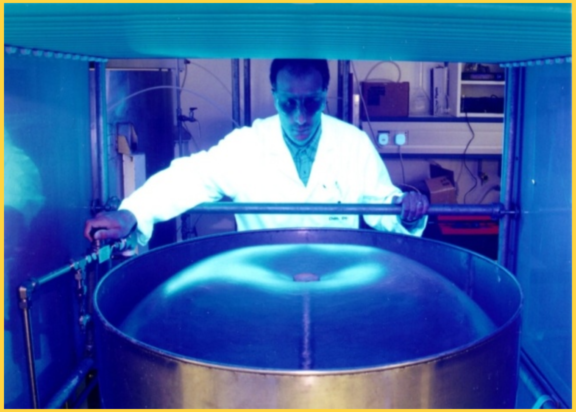
Advanced Oxidation: Heterogenous Photocatalysis



Photocatalytic Reactors: UV Lamp and Solar Reactors



Rotating Disk (Dionysiou)



Fountain (Li Puma)

Parabolic Trough (PSA)

Compound Parabolic Collector (CIEMAT)

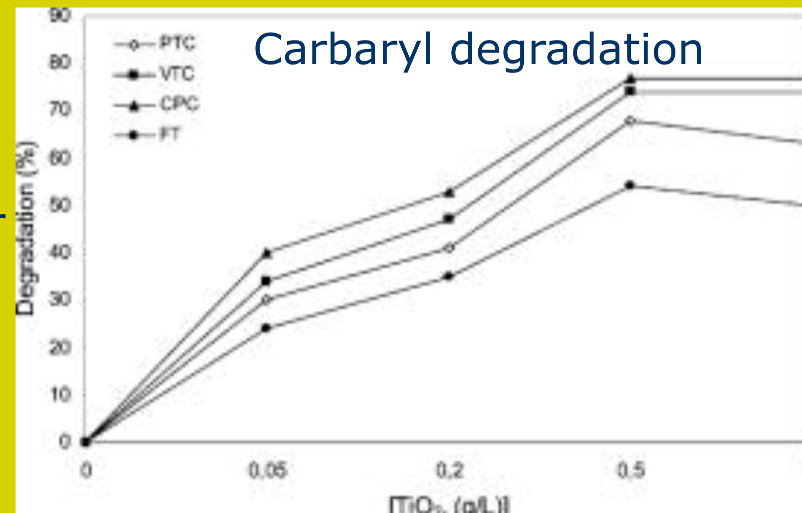
Double Skin (Wolkswagen, Banhemann)

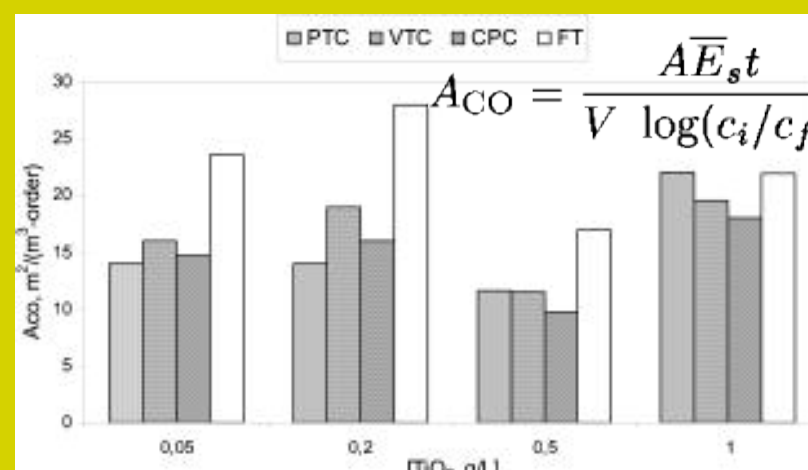
Falling Film (Temine)

Comparison of Solar Photocatalytic Reactors Efficiencies

Bandala and Estrada, J. Solar Energy Eng. 2007, 129, 22.

- Four geometries were tested: Compound parabolic collector (CPC), V-through collector (VTC), parabolic trough collector (PTC) and flat tubular collector (FT)
- TiO2 (P25) slurry suspension





$$A_{CO} = \frac{A\overline{E}_s t}{V \ \log(c_i/c_f)}$$

Compound Parabolic Collector, Commercial Installation, Colombia

- Cross between trough concentrators and one sun systems
- Best optics for non-concentrating systems
- Have the advantage of both systems
- Uses both direct and diffuse sunlight
- High pressure and temperature is allowed
- No vaporisation problems
- Filming of the tube wall can be a problem

Courtesy of Fiderman Machuca, Universidad del Valle, Cali, Colombia

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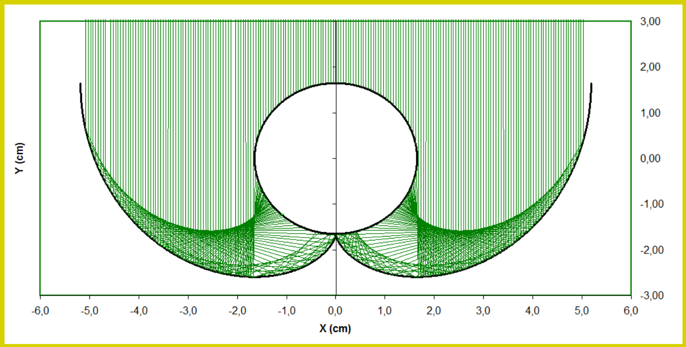
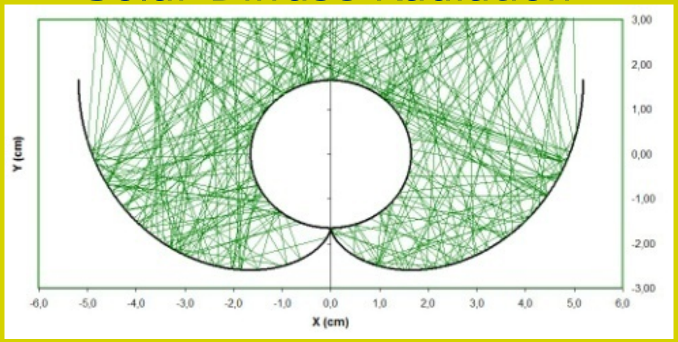
Solar Compound Parabolic Collector (CPC) – Ray Tracing

Colina, Machuca, Li Puma, Environ. Sci. Technol. 43 (2009) 8953

Solar Direct Radiation



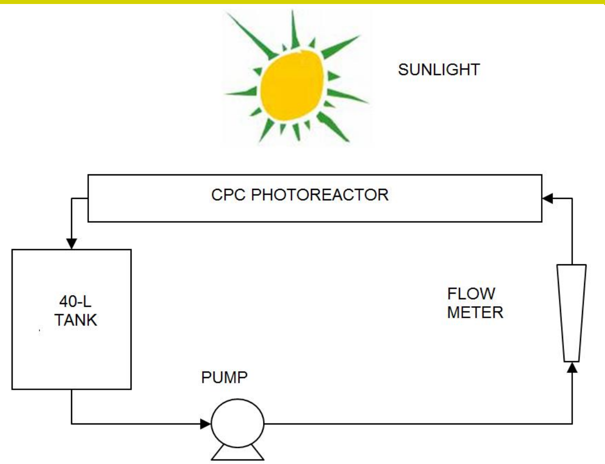
Solar Diffuse Radiation

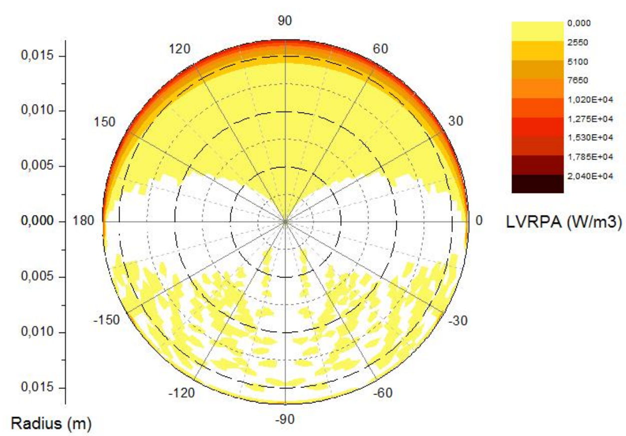


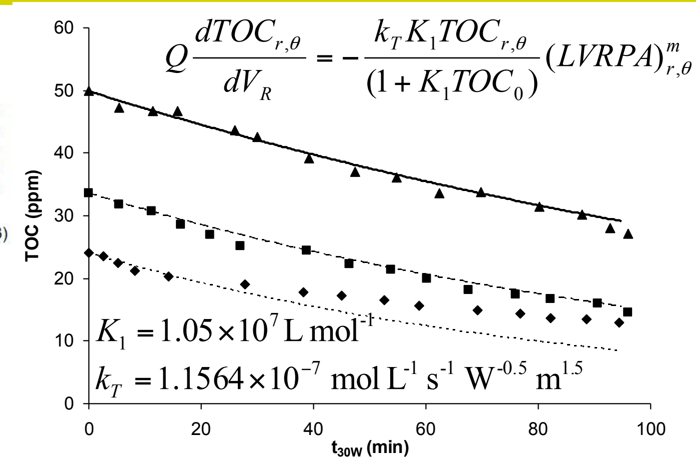
Courtesy of Jose Colina, Universidad de Cartagena, Cali, Colombia

Photocatalytic Mineralization of a Commercial Mixture of Herbicides (2,4-D, Diuron, Ametryne) in a Pilot-Scale Solar CPC Reactor

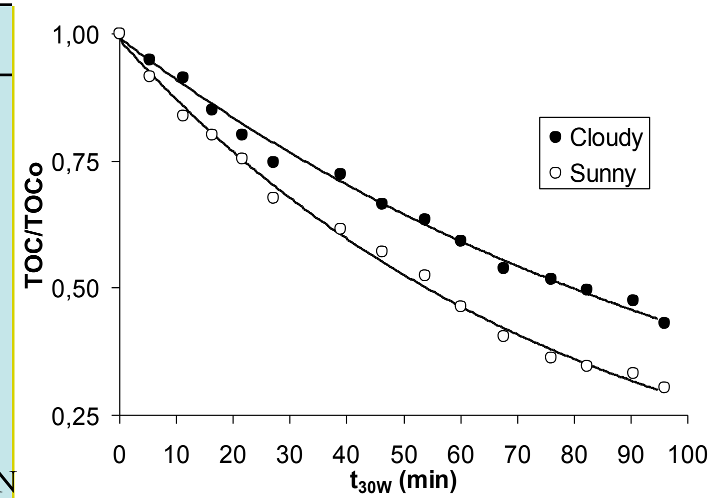
Colina, Machuca, Li Puma, Environ. Sci. Technol. 43 (2009) 8953







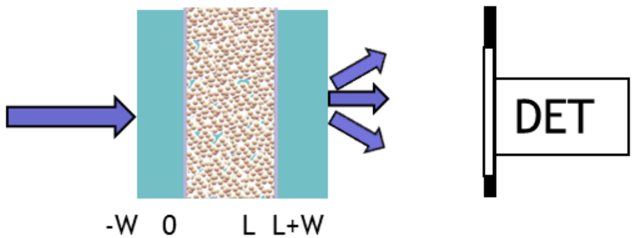
Experimental conditions	
Catalyst load, g/L	0.6
Initial pH of solution	9.0
System total volume, L	20.0
Reactor volume, L	10.3
Tube inner diameter, mm	32.6
Average flow rate, L/min	30.7
Latitude of the site	3°30 N



Photocatalytic Treatment of Emerging Contaminants

- Optimal photocatalyst concentration for industrial wastewater treatment in current solar photoreactor designs is several hundreds of mg/L
- However, the elimination of ECs, which are present at extremely low concentration may be accomplished at much lower catalyst concentrations
- If the catalyst concentration is lowered below the optimum - loss of useful photons – lower reactants conversions
- Laboratory and solar pilot scale experiments were performed with real WWTP effluents to evaluate the kinetics of photocatalytic degradation of 52 ECs under realistic (ppb) concentrations

Extinctance measurement

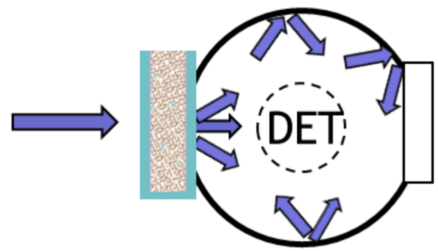


$$EXT_{\lambda} = -log T_{\lambda}$$

$$\beta_{\lambda} = \frac{2.303 EXT_{\lambda}}{L} = \beta_{\lambda}^{*} C_{cat}$$

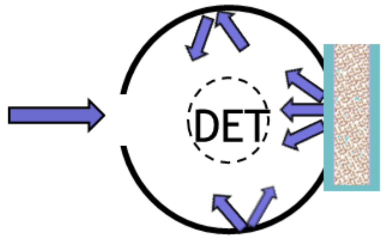
Integrating sphere

DIFFUSE TRANSMITTANCE



$$T_{\lambda} = \frac{q_{\lambda}^{+}(L+W)}{q_{\lambda}^{+}(-W)}$$

DIFFUSE REFLECTANCE



$$R_{\lambda} = \frac{q_{\lambda}^{-}(-W)}{q_{\lambda}^{+}(-W)}$$

Scattering parameters
(regression non-lineal method)

-asymmetry factor (g)
-scattering coefficient (σ)

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Radiative Transfer Equation

$$\mu\frac{dI_\lambda(x,\mu)}{dx}+\underbrace{\kappa_\lambda I_\lambda(x,\mu)}_{\text{Absorption}}+\underbrace{\sigma_\lambda I_\lambda(x,\mu)}_{\text{Out-scattering}}=\underbrace{\frac{\sigma_\lambda}{2}\int_{\mu'=-1}^{1}I_{\lambda'}(x,\mu')\,p(\mu'\to\mu)\,d\mu'}_{\textit{In-Scattering}}$$

boundary conditions

$$I_\lambda(-W,\mu)=I_0\delta(\mu-\mu_0)+\Gamma_1 I_\lambda(-W,-\mu) \qquad (\mu>0)$$

$$I_\lambda(L_{cell},-\mu)=\Gamma_1 I_\lambda(L_{cell},-\mu) \qquad (\mu<0)$$

HG phase function

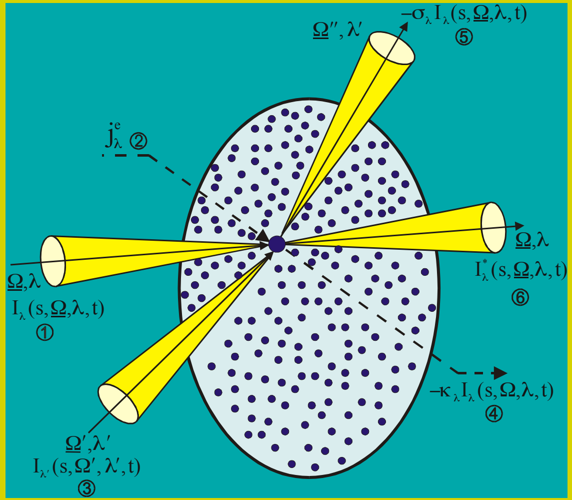
$$p_{HG,\lambda}(\mu_0)=\frac{\left(1-g_\lambda^2\right)}{\left(1+g_\lambda^2-2g_\lambda\mu_0\right)^{3/2}}$$

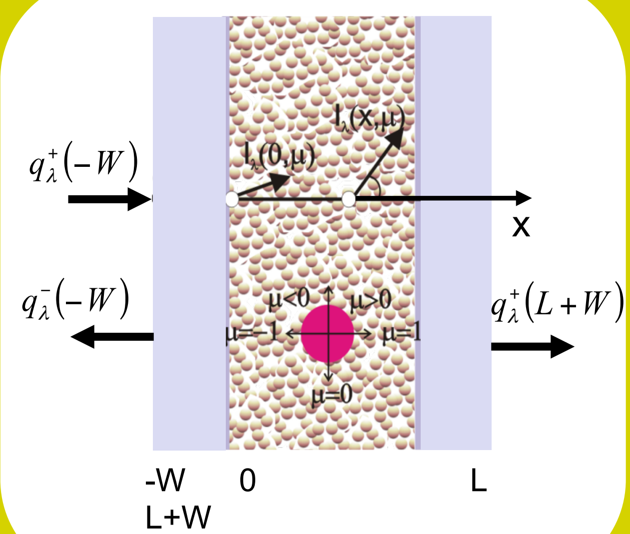
radiation flux

$$q_\lambda^+(-W)=2\pi\int_0^1\mu I_\lambda(-W,\mu)d\mu$$

$$q_\lambda^-(-W)=2\pi\int_{-1}^0\mu I_\lambda(-W,\mu)d\mu$$

$$q_\lambda^+(L+W)=2\pi\int_0^1\mu I_\lambda(L+W,\mu)d\mu$$

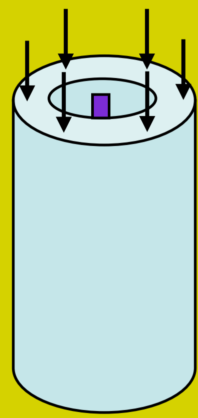


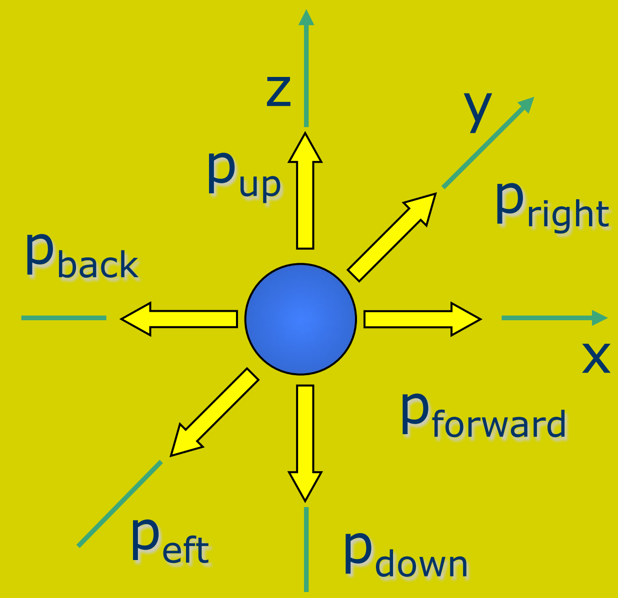


Six-Flux Radiation Absorption-Scattering Model

Li Puma, et al., Environ. Sci. Technol. 38 (2004) 3737; Brucato et al., AIChE J., 52 (2006) 3882; Li Puma and Brucato, Catal. Today 122 (2007) 78.

- Photons are either scattered or absorbed upon colliding a particle
- Scattering randomly follows one of the six Cartesian directions
- Fluid does not absorb radiation
- Uniform distribution of particles





Scattering Albedo

$$\omega = \frac{\sigma}{\sigma + \kappa}$$

$$\sigma = \int_{\lambda_{min}}^{\lambda_{max}} \sigma_\lambda I_\lambda d\lambda \Bigg/ \int_{\lambda_{min}}^{\lambda_{max}} I_\lambda d\lambda$$

$$\kappa = \int_{\lambda_{min}}^{\lambda_{max}} \kappa_\lambda I_\lambda d\lambda \Bigg/ \int_{\lambda_{min}}^{\lambda_{max}} I_\lambda d\lambda$$

$$p_{up} = p_{down} = p_{left} = p_{right} = p_{side}$$

$$\boxed{4\ p_{side} + p_{forward} + p_{backward} = 1}$$

Optical Thickness

$$\tau = (\sigma + \kappa) c_{cat} \delta$$

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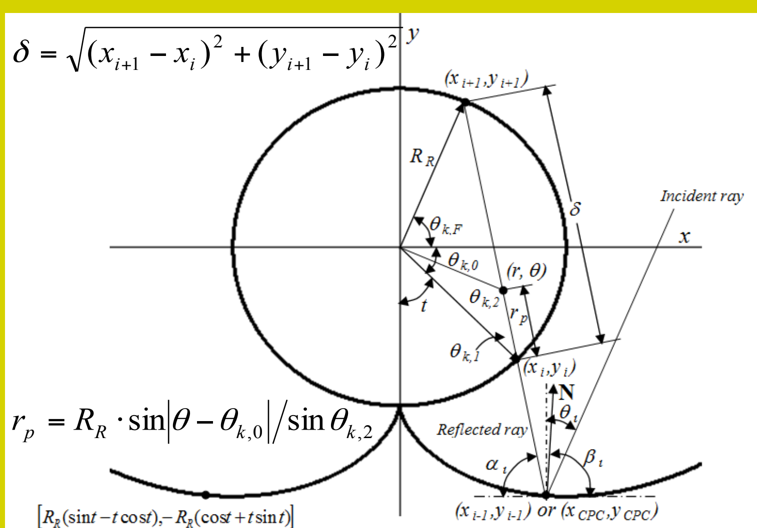
$$LVRPA = \frac{\tau_{app} I_0}{\omega_{corr}(1-\gamma)} \frac{\eta}{(1-\eta)R}\left[\left(\omega_{corr} - 1 + \sqrt{1-\omega_{corr}^2}\right)\exp(-\tau_{app}\xi^*) + \gamma\left(\omega_{corr} - 1 - \sqrt{1-\omega_{corr}^2}\right)\exp(\tau_{app}\xi^*)\right]$$

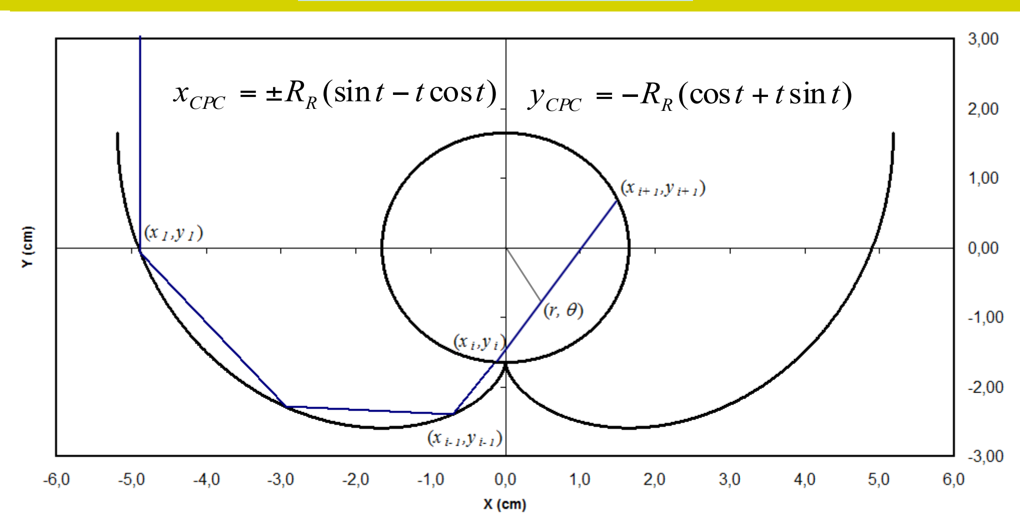
Apparent Optical Thickness $\tau_{app} = a\tau\sqrt{1-\omega^2_{corr}}$

Optical Thickness $\tau = (\sigma + \kappa)c_{cat}\delta$

Snell's law (multiple ray reflections)

$$I_{0,reflected} = I_0\psi^n$$





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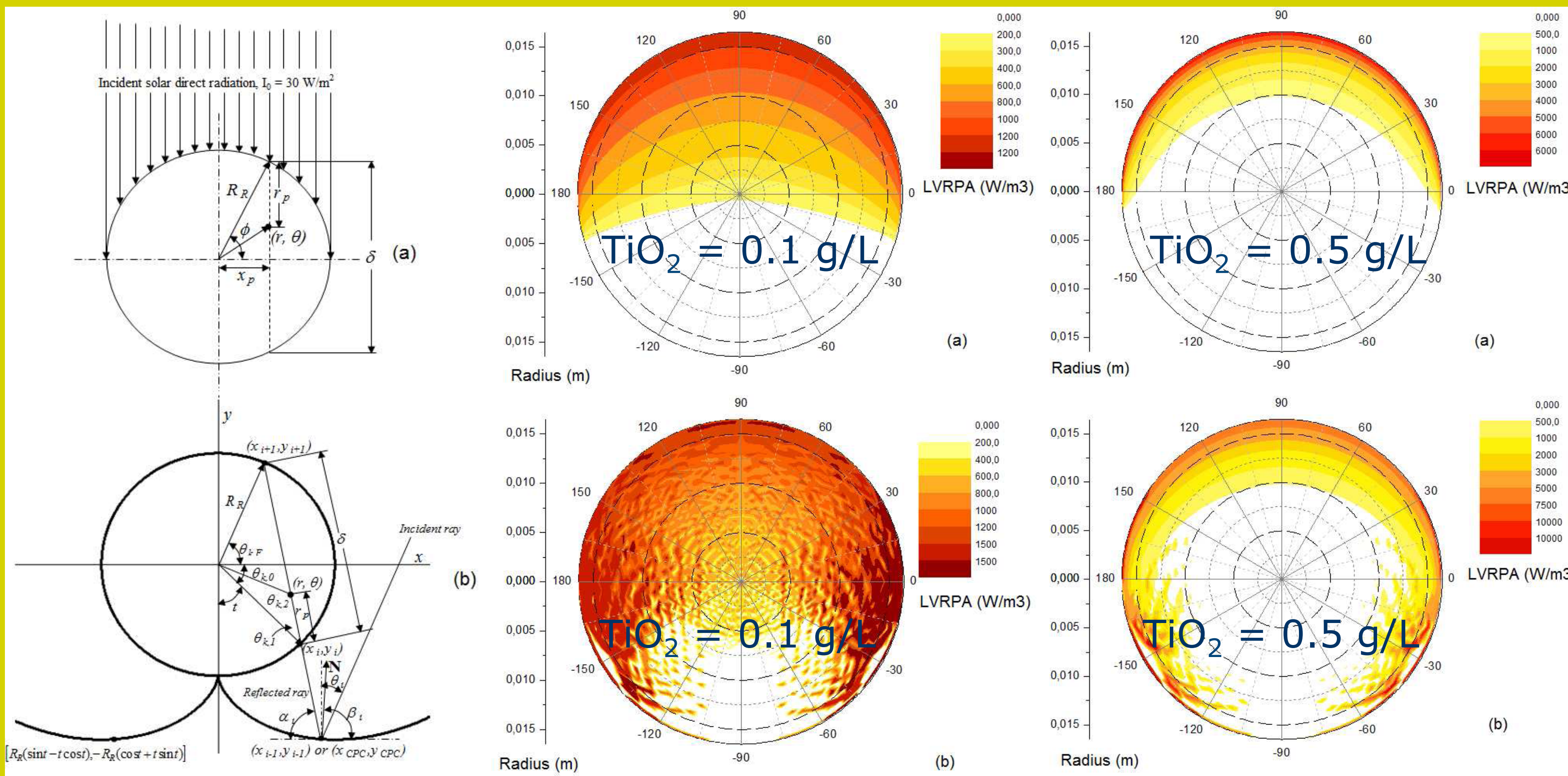
Radiation Absorption in Tubular and CPC Solar Photoreactors

Colina, Machuca, Li Puma, Environ. Sci. Technol. 44 (2010) 5112

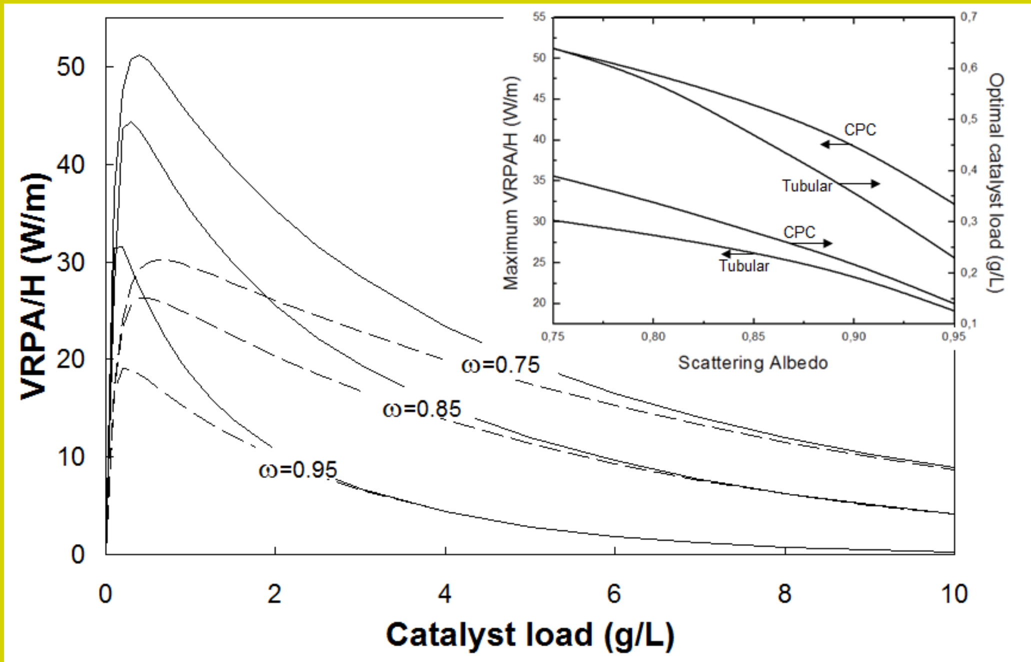


$$LVRPA = \frac{\tau_{app} I_0}{\omega_{corr}(1-\gamma)} \frac{\eta}{(1-\eta)R}\left[\left(\omega_{corr}-1+\sqrt{1-\omega_{corr}^2}\right)\exp(-\tau_{app}\xi^*)+\gamma\left(\omega_{corr}-1-\sqrt{1-\omega_{corr}^2}\right)\exp(\tau_{app}\xi^*)\right]$$

Optimum Catalyst Loading – Validation Against Literature

Colina, Machuca, Li Puma, Environ. Sci. Technol. 44 (2010) 5112

- CPC – 70% higher radiation absorption than tubular reactor: agrees with data of degradation of oxalic acid (Bandala, 2004) and methylene blue (Arias, 2008)
- CPC requires 39% less catalyst to operate under optimum conditions
- Scattering albedo of TiO_2 (Degussa P25) under solar radiation is 0.88: **Optimal catalysts TiO_2 concentration is 0.21 g/L in a 32 mm CPC reactor** – agrees with experimental data of degradation of many pollutants (Malato, 2004); 2,4-DCP (Gimenez 1999); 4-CP (Guillard, 2003); PCP (Minero, 1996)

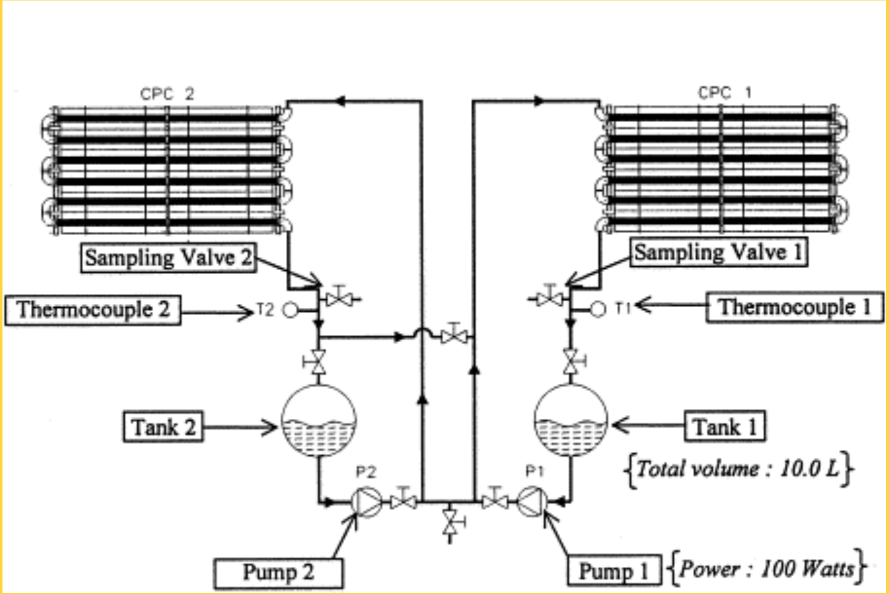


Secondary biological effluents El Ejido WWTP, Almeria, Spain - 89 contaminants detected by HPLC-QTRAP-MS, 52 were quantified (DOC = 13-23 mg/L, IC = 110-132 mg/L, COD = 43-63 mg/L)

Contaminant	C_0 (ng/L)	Contaminant	C_0 (ng/L)	Contaminant	C_0 (ng/L)	Contaminant	C_0 (ng/L)
4-AA	1315	**Citalopram HBr**	17	**Ibuprofen**	726	**Primidone**	50
4-AAA	12702	**Clarithromycin**	54	**Indomethacine**	437	**Propanolol**	17
4-FAA	4617	**Codeine**	192	**Isoproturon**	172	**Propyphen.**	32
4-MAA	2824	**Cotinine**	287	**Ketoprofen**	428	**Ranitidine**	710
Antipyrine	681	**Diazepan**	68	**Lincomycin**	192	**Salbutamol**	81
Atenolol	1241	**Diclofenac**	4425	**Mefenamic Acid**	18	**Simazine**	704
Atrazine	305	**Diuron**	1081	**Mepivacaine**	28	**Sulfadiazine**	36
Azithromycin	69	**Erythromycin**	78	**Naproxen**	2968	**Sulfamethazine**	236
Benzafibrate	44	**Famotidine**	19	**Nicotine**	450	**Sulfamethoxazol**	999
Caffeine	17175	**Fenofibric Acid**	142	**Norfloxacin**	29	**Sulfapyridine**	131
Carbamazepine	114	**Furosemide**	100	**Ofloxacin**	1614	**Terbutaline**	85
Chlorfenvin.	29	**Gemfibrozil**	2622	**Paraxanthine**	17750	**Trimethoprim**	1661
Ciprofloxacin	305	**Hydrochlorothia.**	780	**Pravastatin**	75	**Velafaxime**	539

Pilot Scale Experiments: Sunlight Irradiation (PSA, Almeria, Spain)

Prieto-Rodriguez, et al. , J. Hazard. Mat. 211-212 (2012) 131



- We followed the degradation of 16 ECs (90% of pollutant load)
- The remaining 36 ECs (10% of pollutant load) were represented as a cumulative concentration

PHOTOREACTOR CONFIGURATION 1

- Two CPC modules with twelve, 32 mm O.D. Pyrex tubes per module – the same as in the laboratory scale reactor
- Total irradiated volume = 22 L
- Total irradiated area = 3.1 m^2
- Total volume in the system = 35 L

PHOTOREACTOR CONFIGURATION 2

- Two CPC modules with ten, 50 mm O.D. Pyrex tubes per module
- Total irradiated volume = 45 L
- Total irradiated area = 4.5 m^2
- Total volume in the system = 60 L

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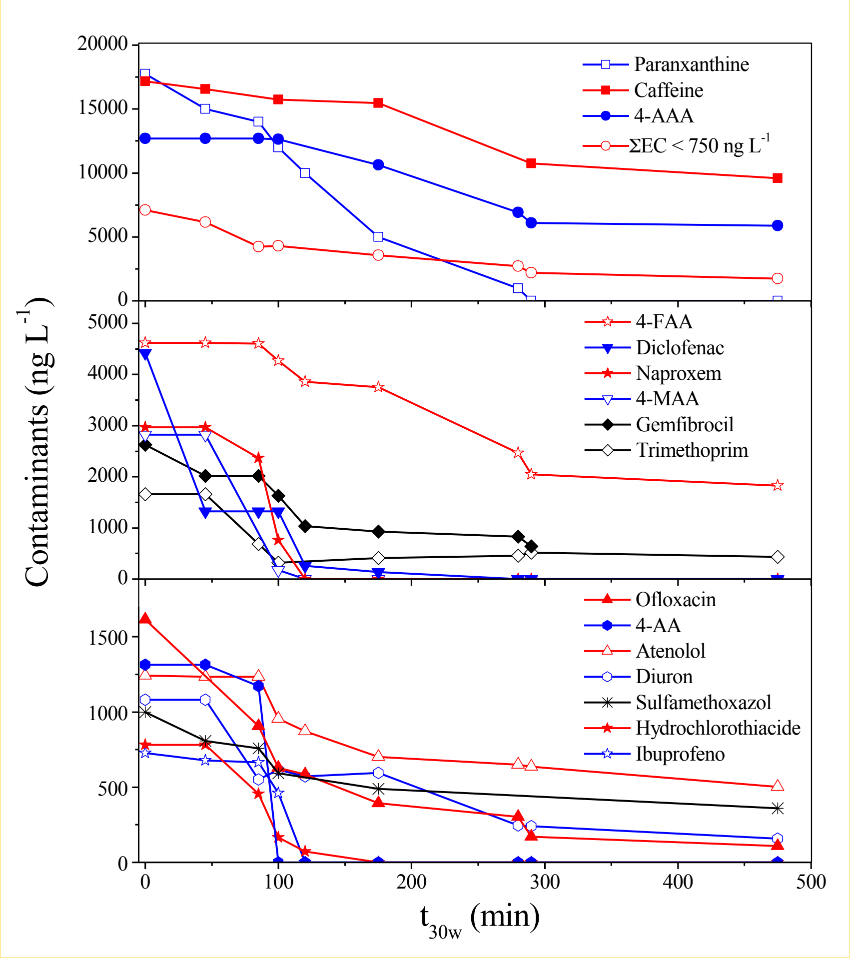
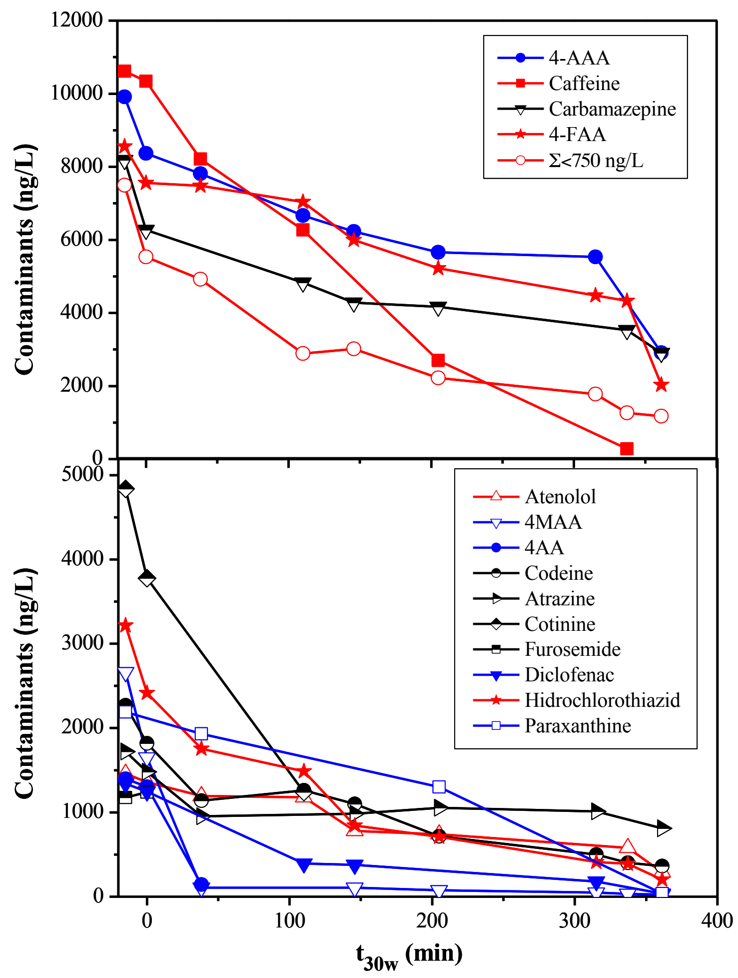
Treatment of WWTP Secondary Biological Effluent (El Ejido WWTP, Almeria, Spain)

Prieto-Rodriguez, et al. , J. Hazard. Mat. 211-212 (2012) 131

CONFIGURATION 1



CONFIGURATION 2



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Radiation Absorption Optimization in Tubular and CPC Solar Photocatalytic Reactors

Colina, Machuca, Li Puma, Environ. Sci. Technol. 44 (2010) 5112

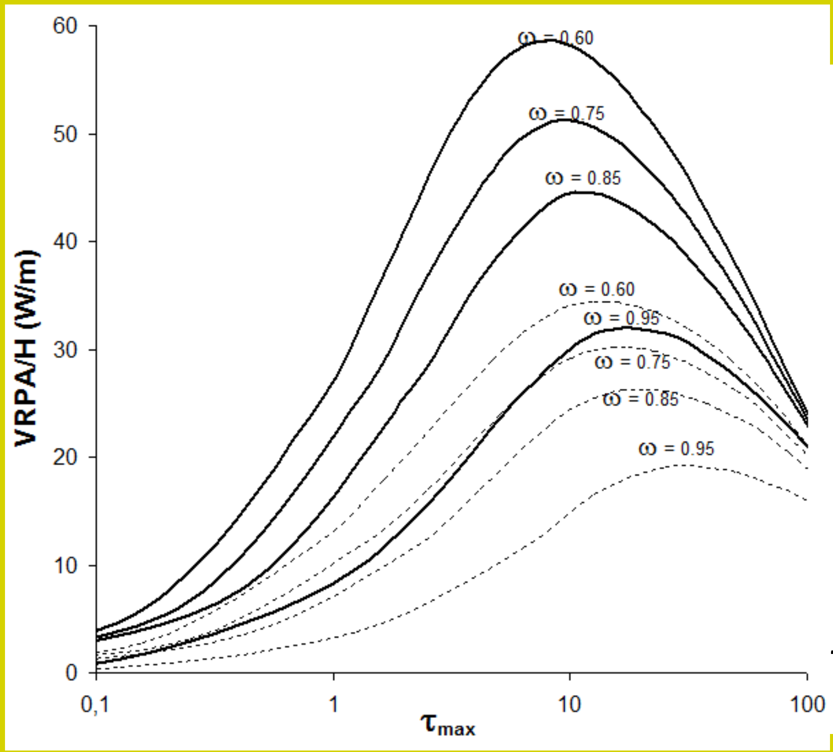


Table 2. Radiation absorption in the pilot scale photoreactors estimated from modeling the CPC by ray-tracing coupled with the six-flux absorption-scattering model [17].

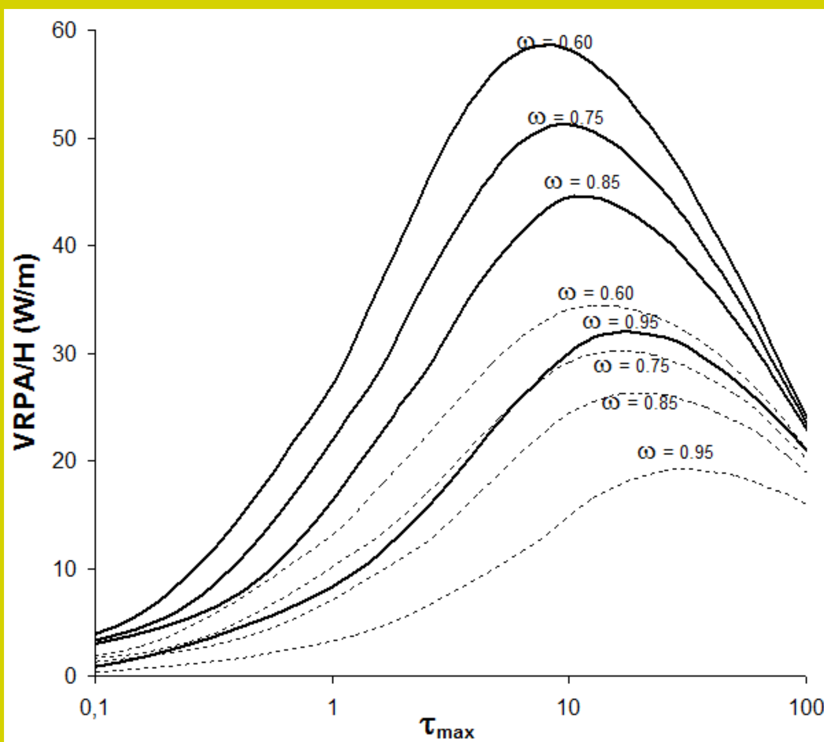
	Photoreactor I	Photoreactor II
TiO_2 P25 loading [mg/L]	20	20
Inner tube diameter [mm]	29.2	46.4
Optical thickness, τ	0.86	1.36
Radiation absorbed per unit length [W/m]	12.6	36.9
Maximum rate of photon absorption[W/m] (i)	41.6	66.1
Radiation absorption efficiency	30.3%	55.8%

$$d = \frac{\tau}{(\sigma + \kappa) C_{cat}}$$

Radiation Absorption Optimization in Tubular and CPC Solar Photocatalytic Reactors of Any Diameter

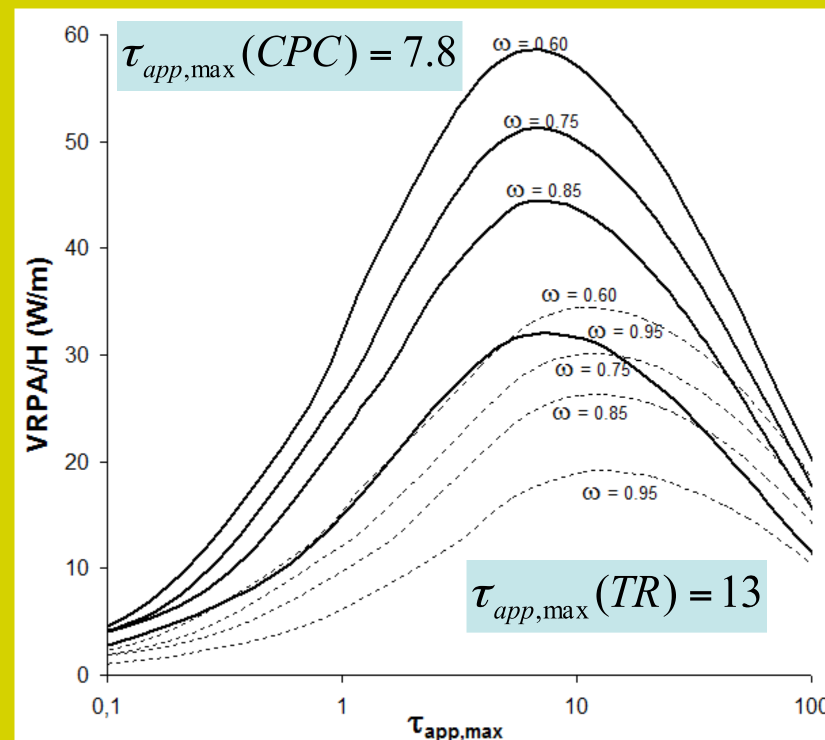
Colina, Machuca, Li Puma, Environ. Sci. Technol. 44 (2010) 5112

Optical Thickness (max)



$$\tau_{max} = (\sigma + \kappa) C_{cat} (2R_R)$$

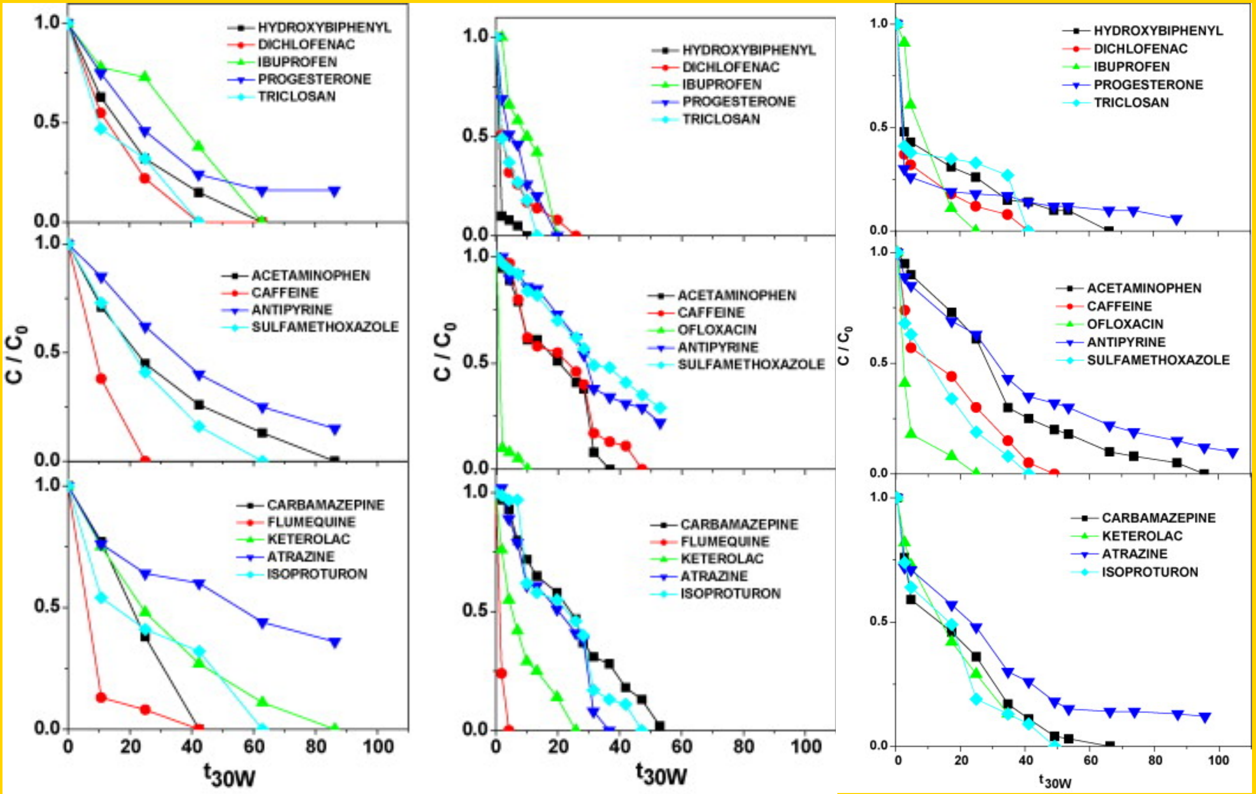
Apparent Optical Thickness (max)



$$\tau_{app,max} = a \tau_{max} \sqrt{1 - \omega^2{}_{corr}}$$

Treatment of ECs using Immobilized TiO_2

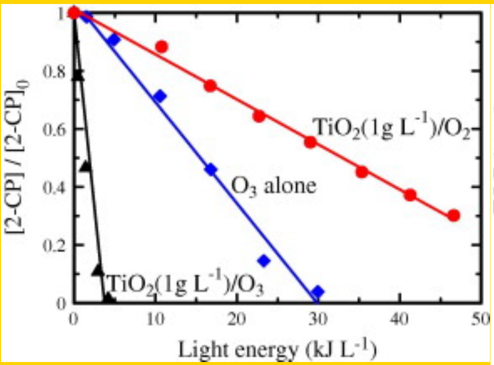
Slurry (5 g/L) | Immobilized (first cycle) | Immobilized (fifth cycle)

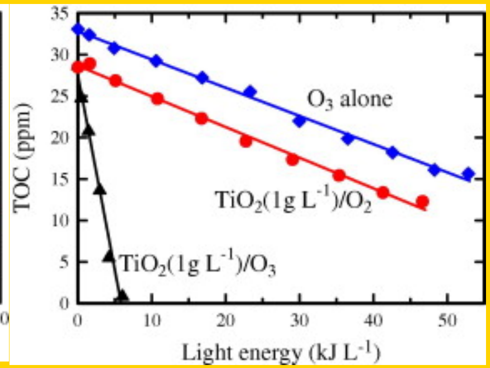


- Sol-gel deposition of TiO_2 on glass spheres
- Slurry and immobilized catalyst: Degradation rates appear to be similar
- But slurry reactor was not operated efficiently (optimum TiO_2 should be 0.2 g/L).

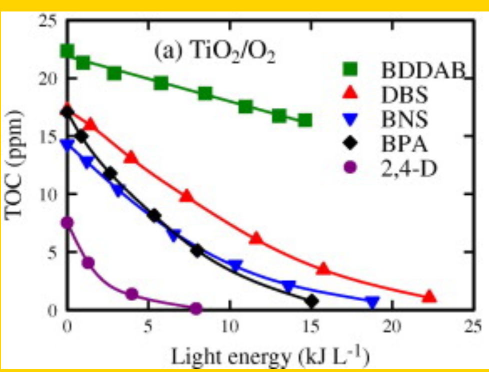
Miranda-Garcia et al., Catal. Today 151 (2010) 107

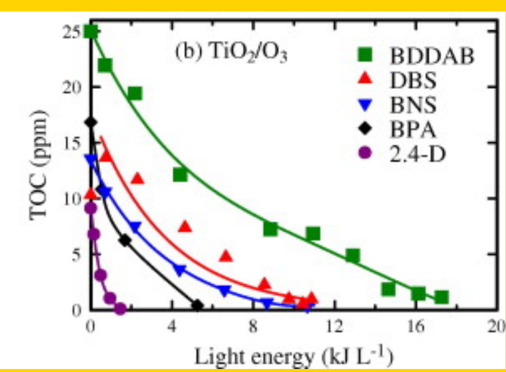
Solar Photocatalytic Ozonation

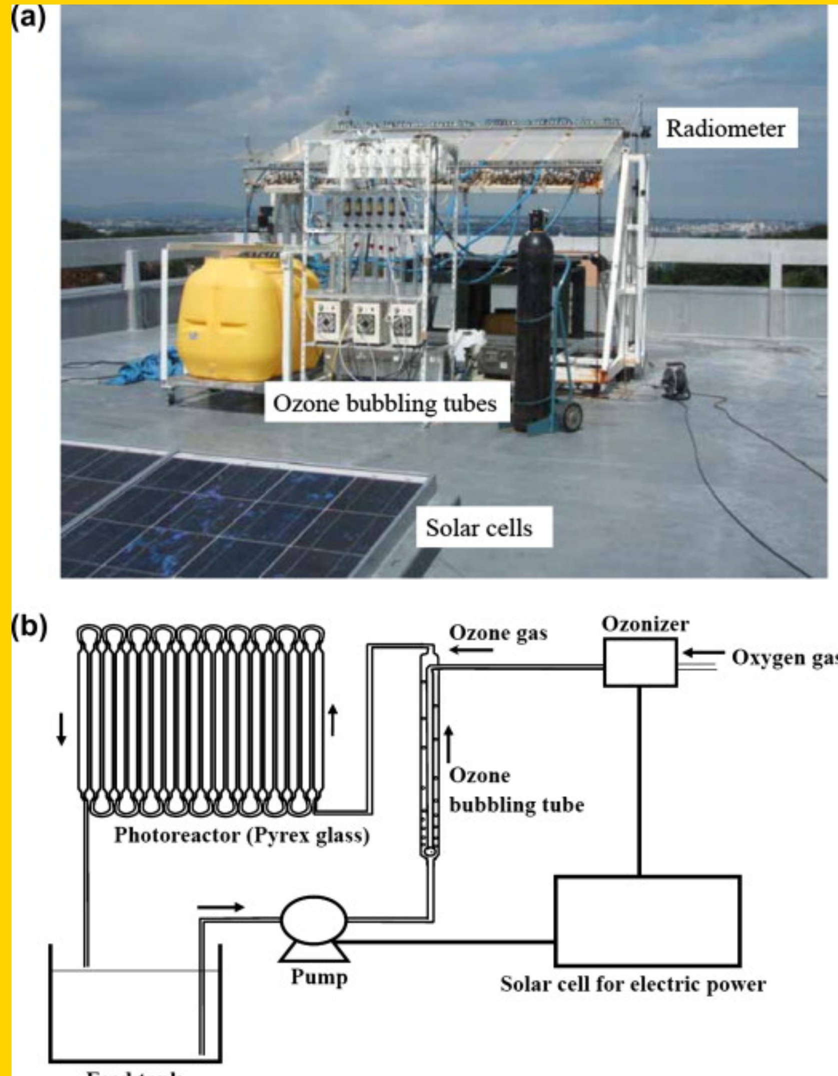




- BDDAB - benzyldodecyldimethylammonium bromide
- DBS – dodecylbenzenesulfonate
- BNS – butylnaphtalenesulphonate
- BPA – bisphenol-A
- 2,4-D – 2,4-dichlorophenoxyacetic acid

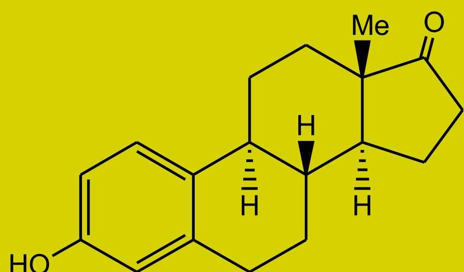




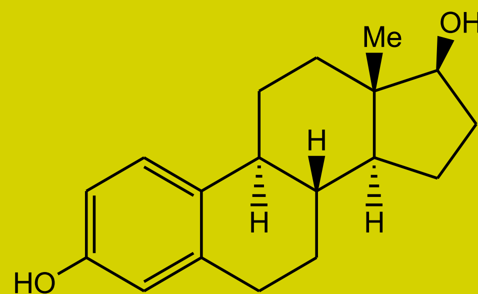


Oyama et al., Solar Energy 85 (2011) 938

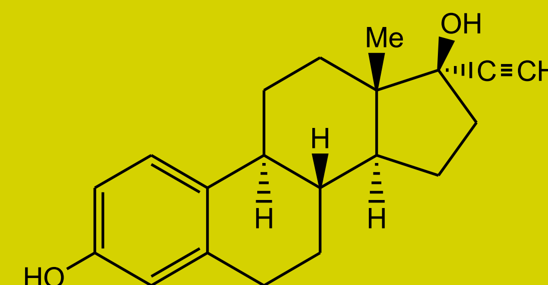
Photodegradation of Estrogens



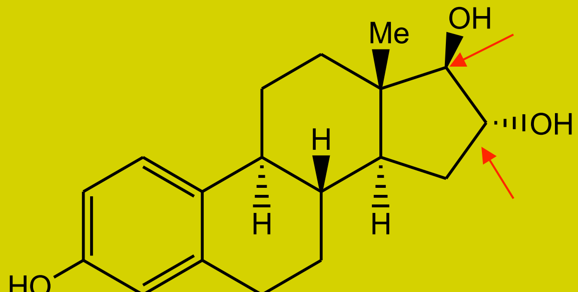
estrone (E1)



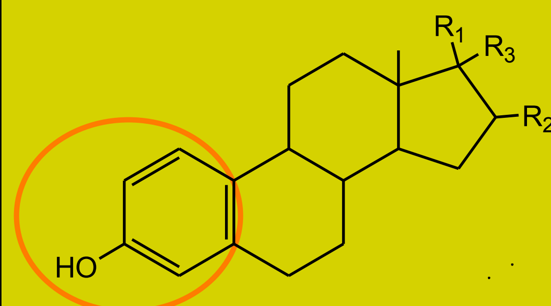
17-β-estradiol (E2)



17α-ethynylestradiol (EE2)



estriol (E3)



	R_1	R_2	R_3
Oestriol	OH	OH	H
17α–eO	OH	H	HC≡C
Oestrone	=O	H	H
17β–O	H	H	H

Estrogenic activity: E2 > EE2 > E1 and E3

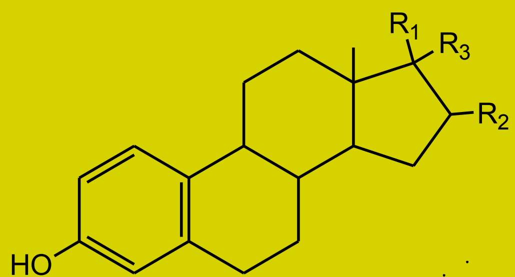
Photocatalysis & Photoreaction Engineering

Department of Chemical Engineering

Loughborough University

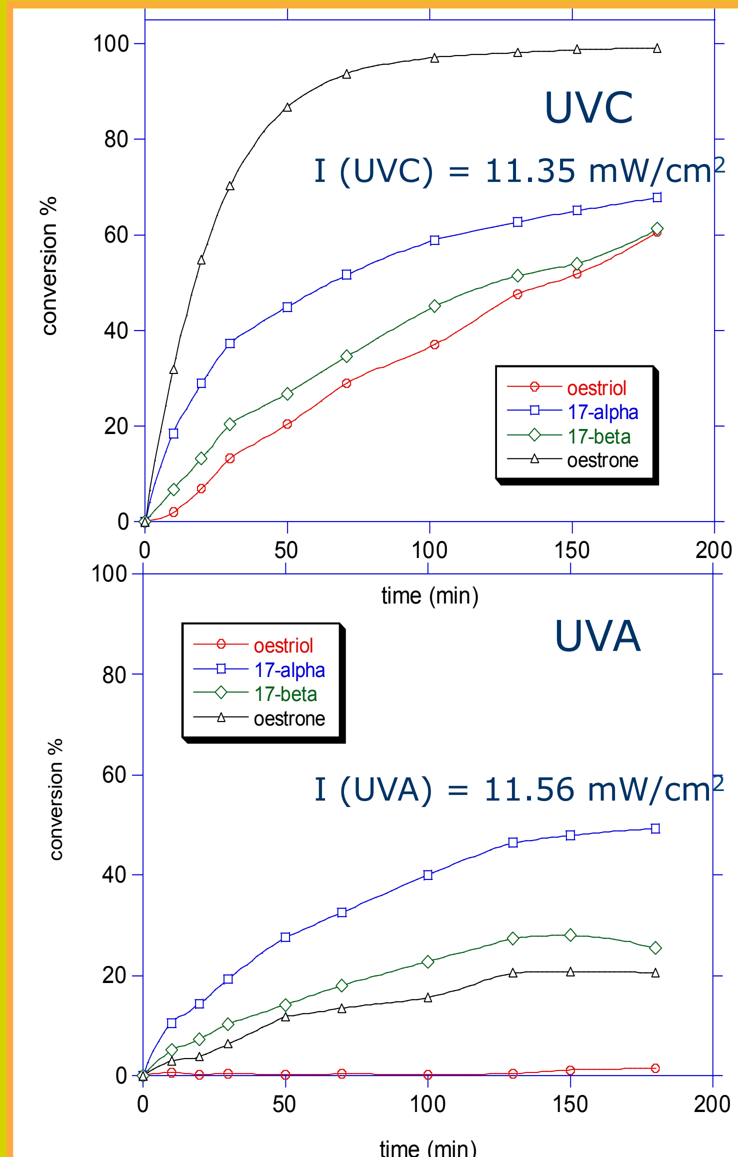
UVA and UVC Photolysis

Li Puma et al., Appl. Catal. B: Environ. 99 (2010) 388

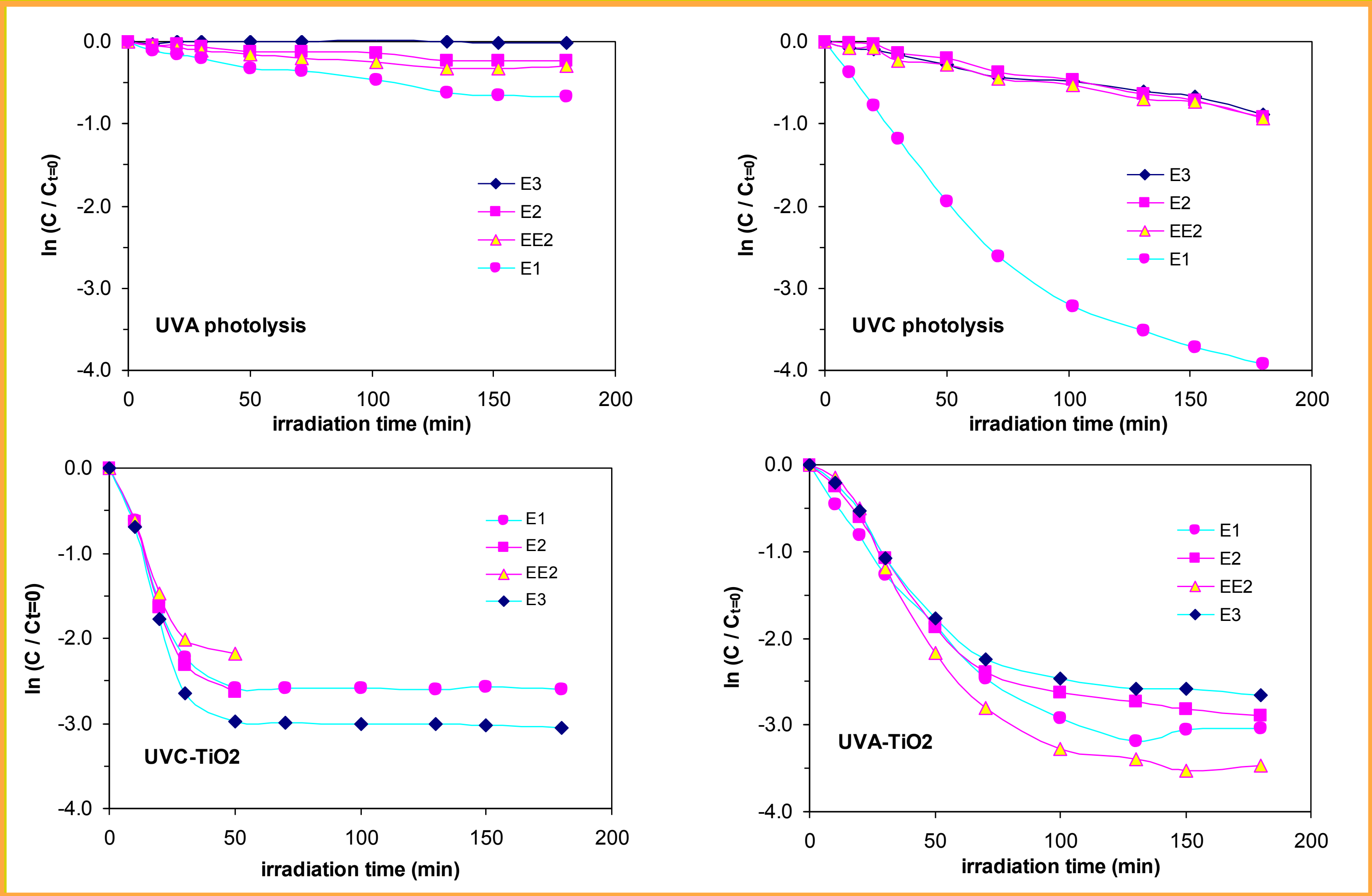


	R_1	R_2	R_3
Oestriol	OH	OH	H
17α–eO	OH	H	HC≡C
Oestrone	=O	H	H
17β–O	H	H	H

- Basic steroid structure. Aromatic ring responsible for the absorption properties in the UV, due to $\pi \rightarrow \pi^*$ transition at $200 < \lambda < 250$ nm
- Higher absorption and reactivity under UVC irradiation is expected from structural considerations
- Moderate degradation of estrogens with UVA, no degradation for estriol
- With UVC irradiation, photolysis highly increases for all components in the mixture. Much faster degradation of estrone



Degradation Kinetics of Estrogens Mixtures



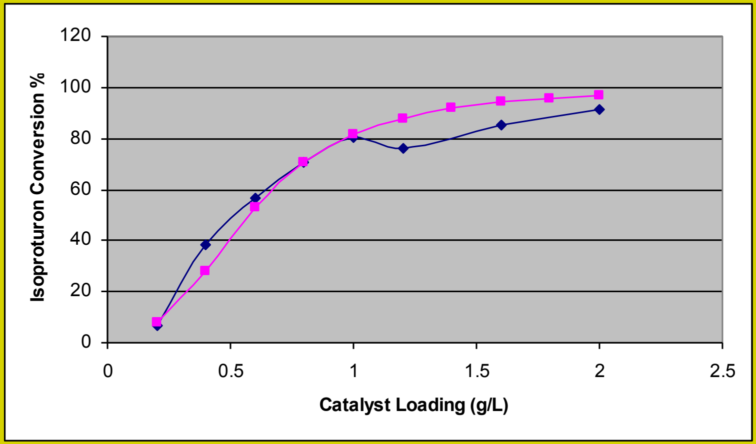
Li Puma et al., Appl. Catal. B: Environ. 99 (2010) 388

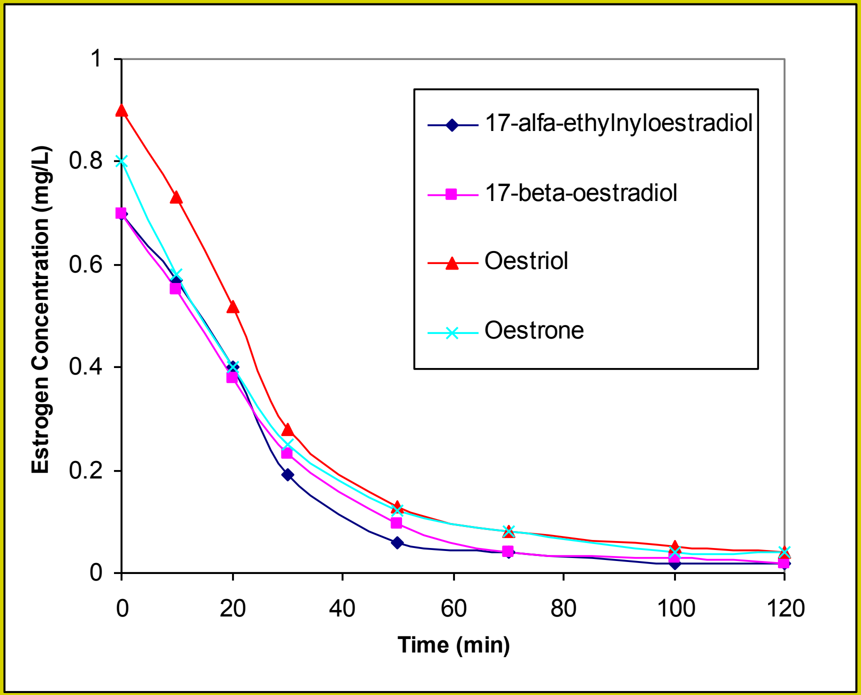
Estrogens Degradation in a Fountain Photocatalytic Reactor

Li Puma and Yue, *Ind. Eng. Chem. Res*. 40 (2001) 5162; *Chem Eng. Sci.* 56 (2001) 2733 and 56 (2001) 721

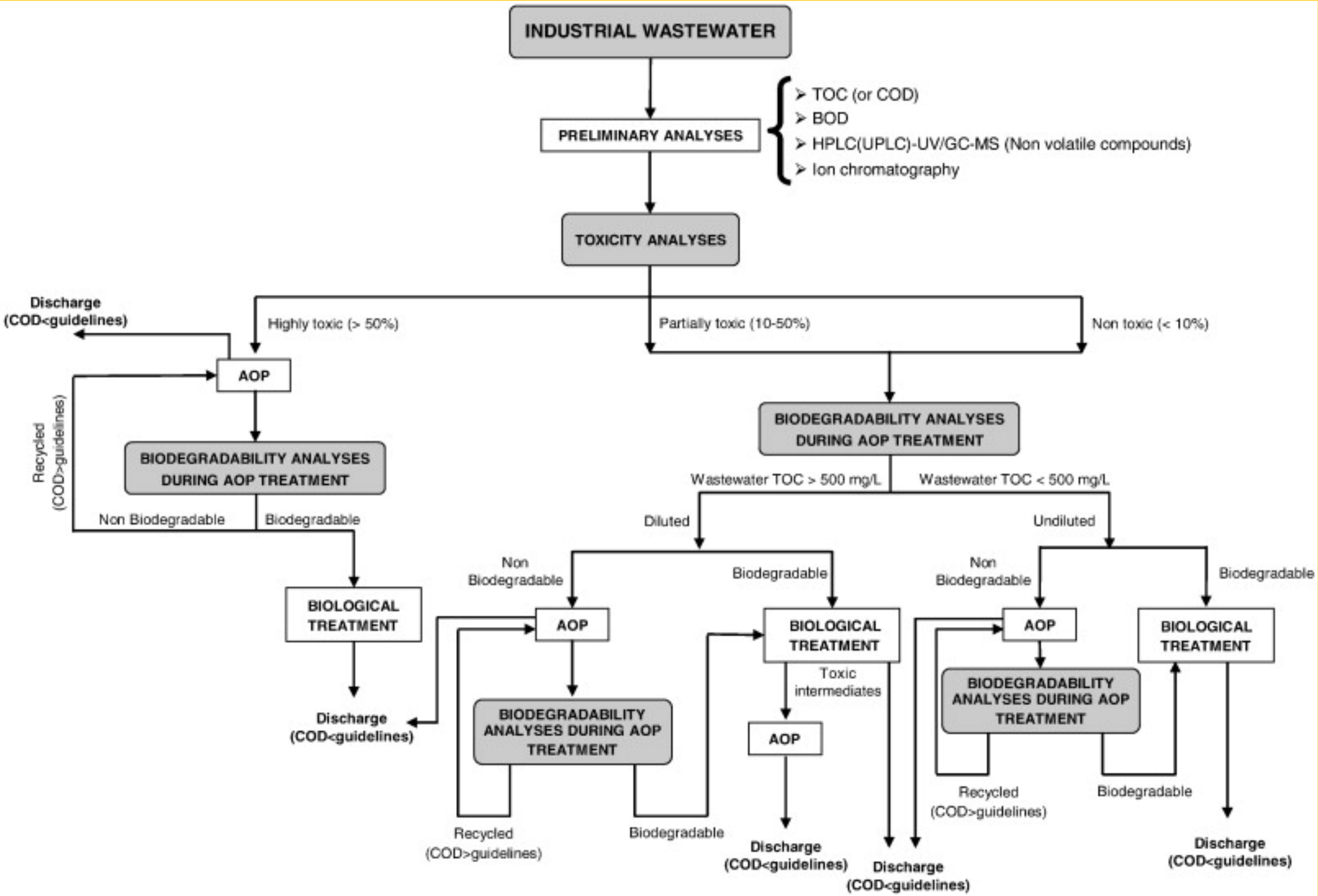
Prof. Li Puma with Fountain Photoreactor

- Umbrella shape unsupported water fountain
- High photocatalyst activation
- High oxygen mass transfer rate
- Can use both direct and diffuse sunlight



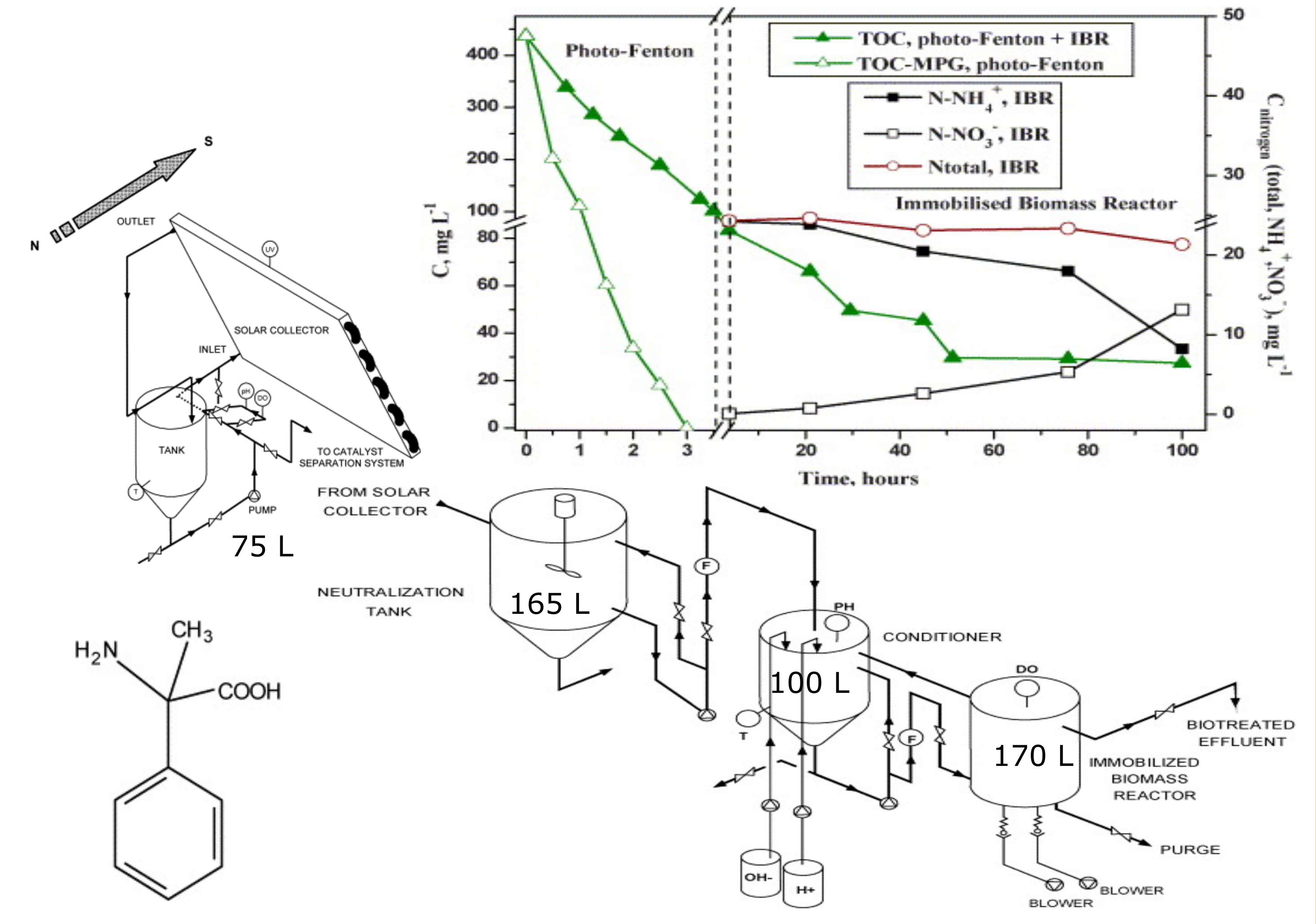


Integration of Advanced Oxidation and Biodegradation



Oller et al., Sci. Total Environ. 409 (2011) 4141

Photo-Fenton and IBR: α-Methylphenylglycine (MPG)



Oller et al., Catal. Today 122 (2007) 150

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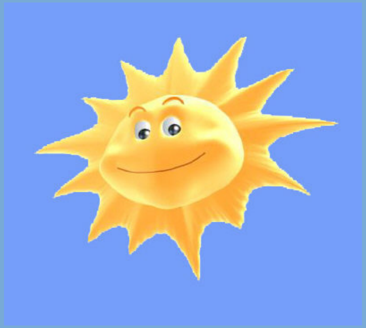
"Solar Hydrogen" uses Renewable Natural Resources

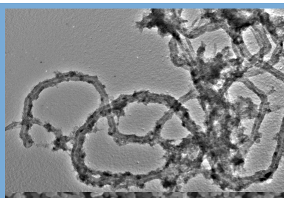
Biomass (Waste)

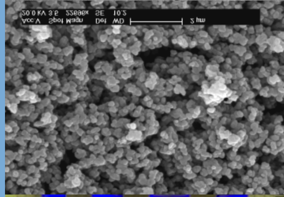
Nanostructured Photocatalyst

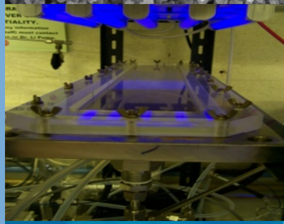


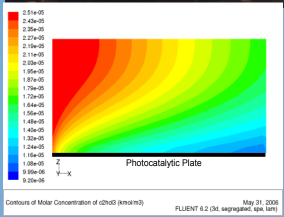
Solar light

Water









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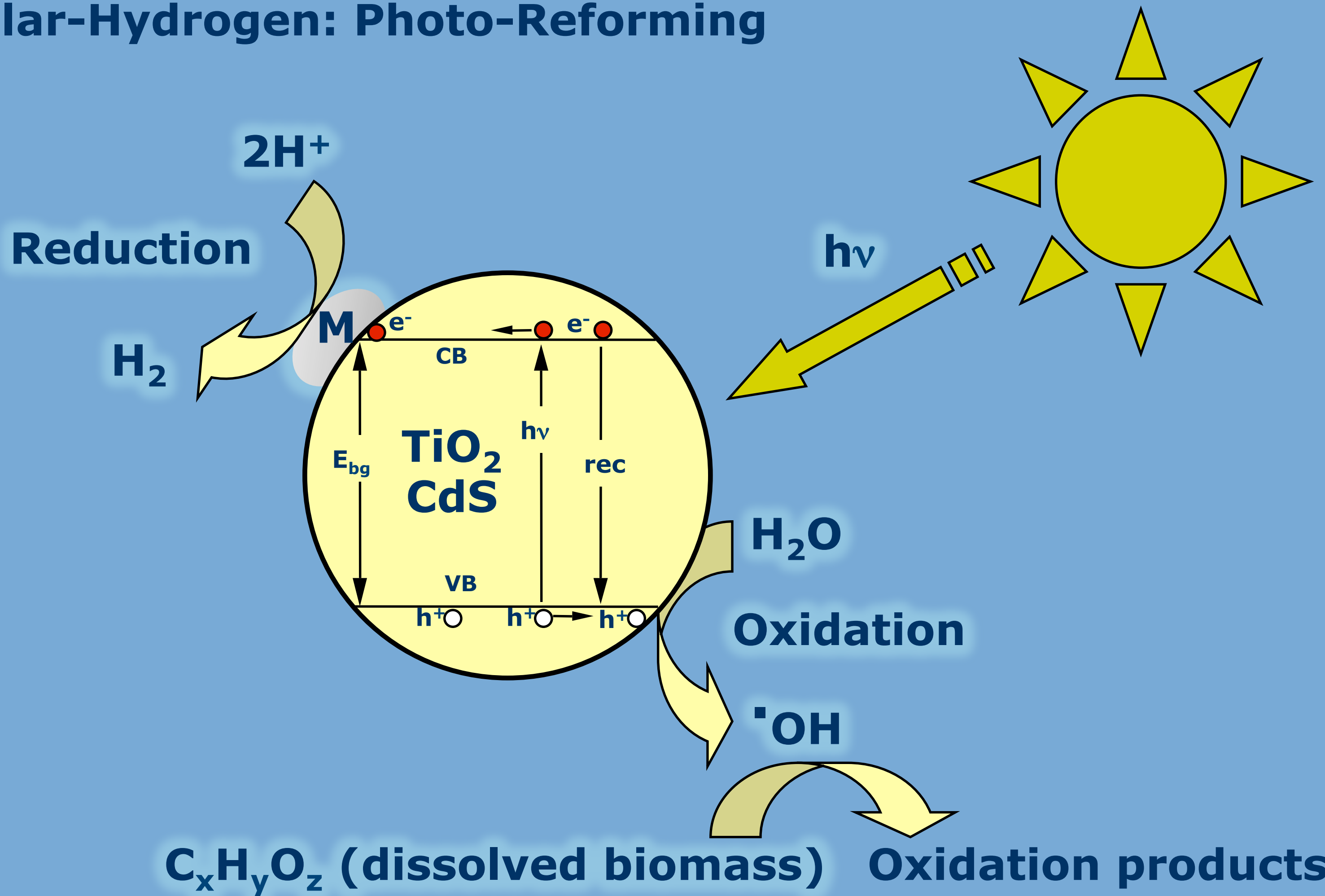
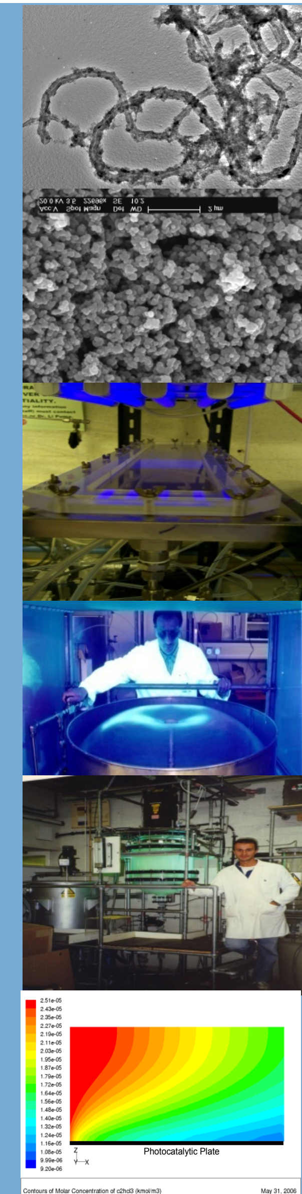
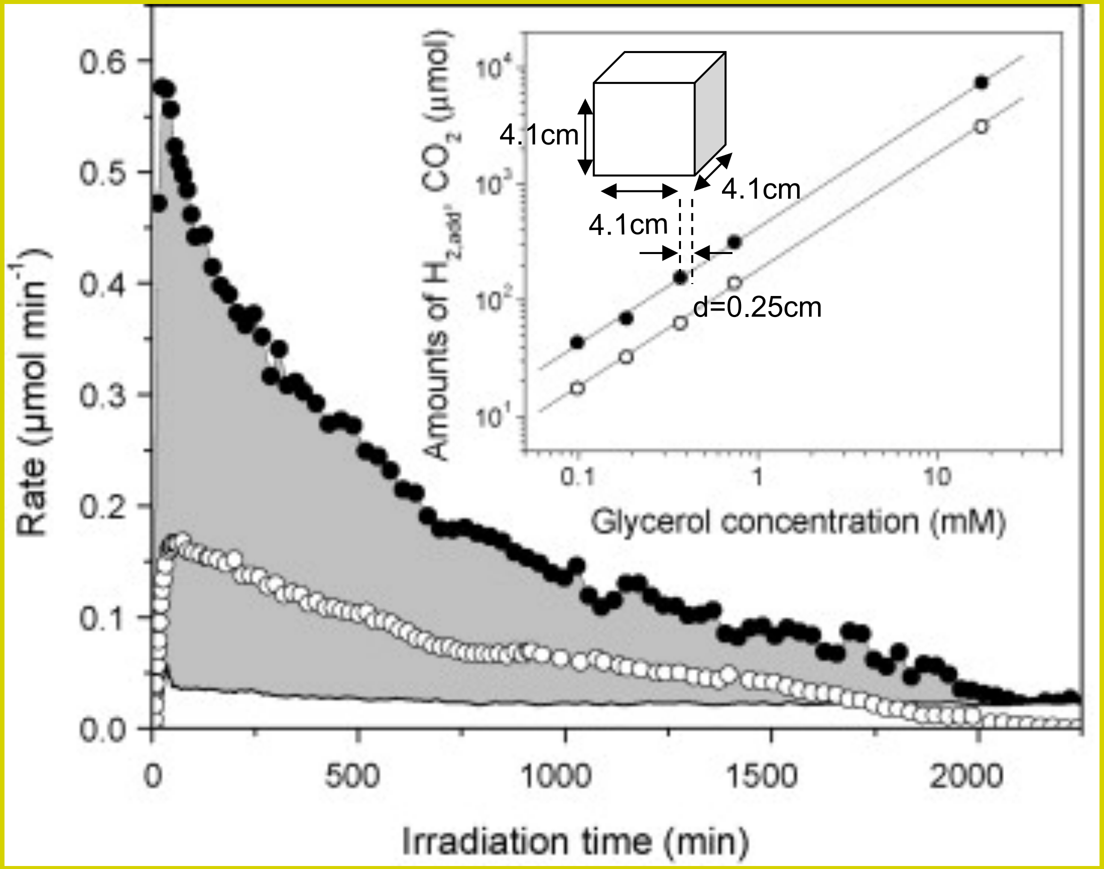
Solar-Hydrogen: Photo-Reforming





$$C_xH_yO_z + (2x - z)H_2O \xrightarrow[h\nu \geq E_{bg}]{Pt/TiO2} xCO_2 + (2x - z + y/2)H_2$$

Photocatalytic Reforming of Glycerol on Pt/TiO_2



Daskalaki and Kondarides, Catal. Today, 144 (2009) 75

$$C_3H_8O_3 + 3H_2O \rightarrow 3CO_2 + 7H_2$$

- Cell, cubical shape photoreactor irradiated by simulated solar light
- One-order of magnitude increase in the rate of H_2 evolution compared to pure water
- Stoichiometric production of H_2 and CO_2

Scale-up 3: Pilot Scale Solar Photoreactor

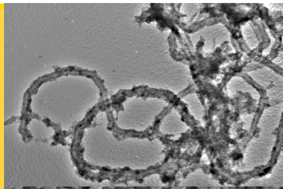
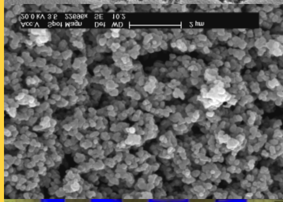
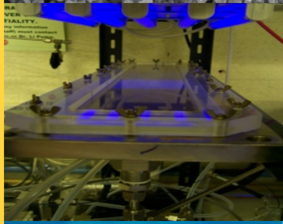
- Continuous production of hydrogen from glycerol wastewater @ 300 micromole/min - Prof. Li Puma – Loughborough University

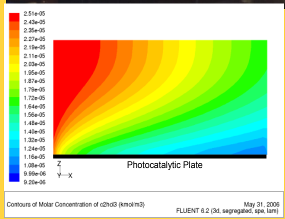
Using Biomass Derivatives As Sacrificial Agents

- Carbohydrates from food manufacturing industries
- Cellulose from paper making
- Lactose from dairy industries
- Maltose from fermentation industries
- Sulfite refinery wastewater from gasoline desulfurization

Conclusions

- Solar powered advanced oxidation - effective process for the treatment of ECs in WWTP effluents
- Large diameter CPC treat ECs efficiently using low catalyst concentrations
- Optimization of solar reactor for ECs treatment – use lowest catalyst concentration and larger reactor diameter, related to the total pollutant load – lower cost of catalyst recycling
- More engineering pilot and large scale demonstration studies should be carried out at different scales –home/domestic, semi-industrial, industrial and municipal
- Photocatalytic reforming of biomass waste may provide an efficient and low cost method for production of renewable hydrogen from waste biomass

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"Application of Nanotechnology in the Energy Business"

Prof. Kondarides, Verykios and Lianos at Patras University

Contact: Gianluca LI PUMA (g.lipuma@lboro.ac.uk)

Environmental Nanocatalysis & Photoreaction Engineering – Department of Chemical Engineering, Loughborough University

Further details:

PCO of ECs in WWTP- Prieto-Rodriguez, et al. , *J. Hazard. Mat*. 211-212 (2012) 131.

Solar photoreactor design - Colina-Marquez et al., *Environ. Sci. Technol.* 44 (2010) 5112.

PCO of Pesticides - Colina-Marquez et al., *Environ. Sci. Technol.* 44 (2009) 8953.

Advanced oxidation of estrogens - Li Puma et al., *Appl. Catal. B: Environ.* 99 (2010) 388

Photoreforming of waste: Daskalaki et al., *Environ. Sci. Technol.* 44 (2010) 7200