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Treatment of CECs by solar driven AOPs

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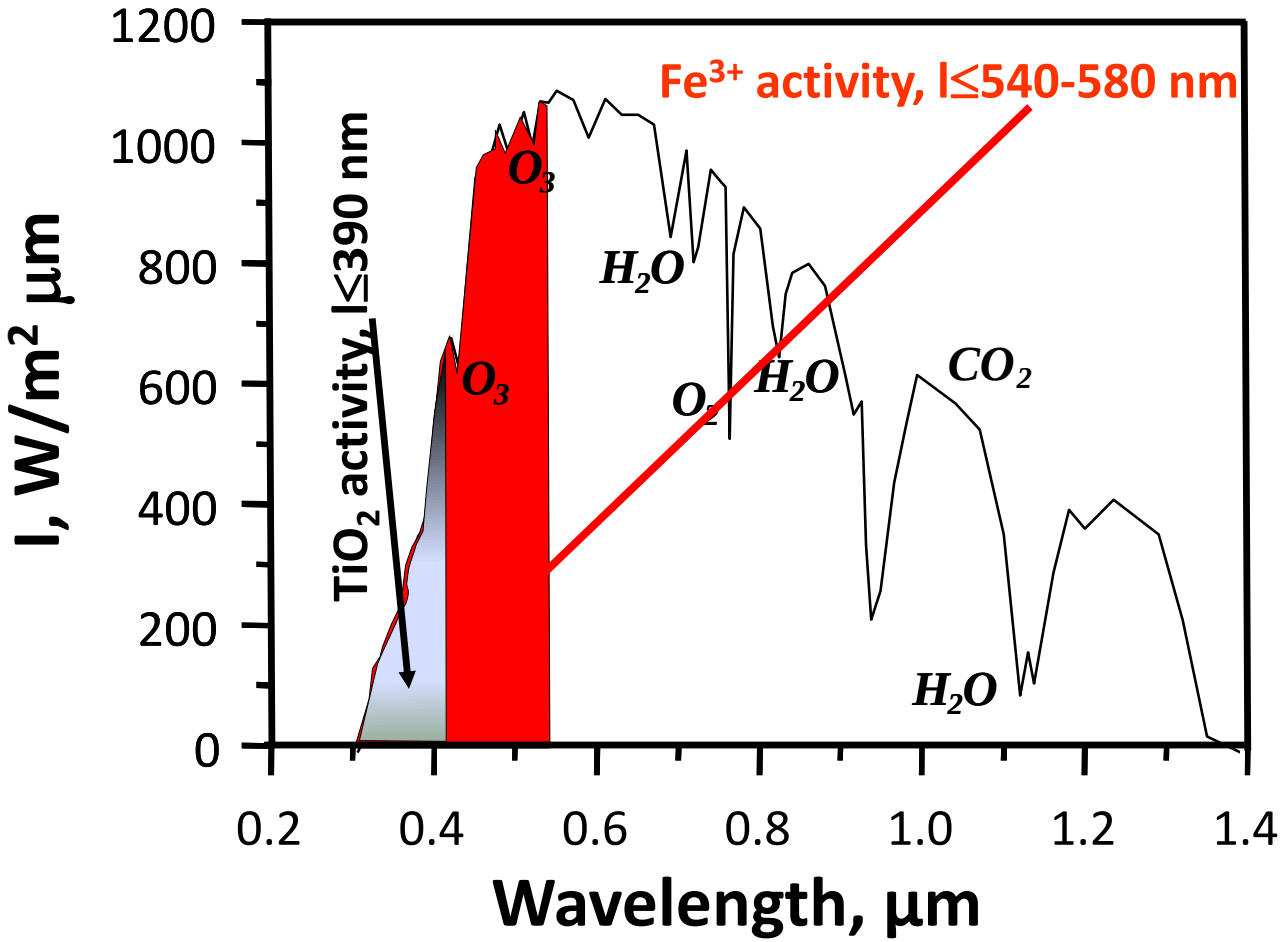
Contents

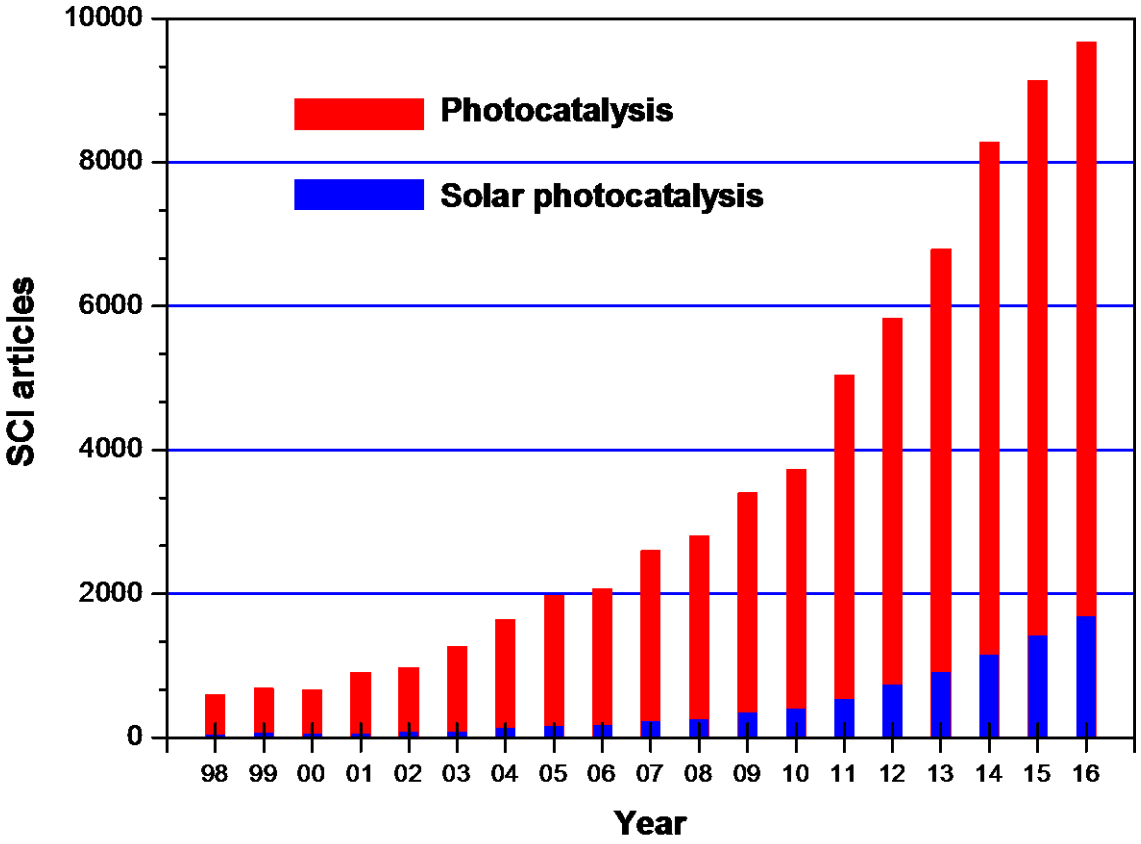
- Solar photo-Fenton.
- Design of the photoreactor.
- Adequate experiments and evaluation of CECs?
- Adequate experiments for plants design and economical approach?
- Other concepts: Fe-complexes
- Combination with other technologies.
- Economic assessment .

Solar photocatalysis



Catalysis Today ***147***, 1–59, 2009.

Solar photocatalysis



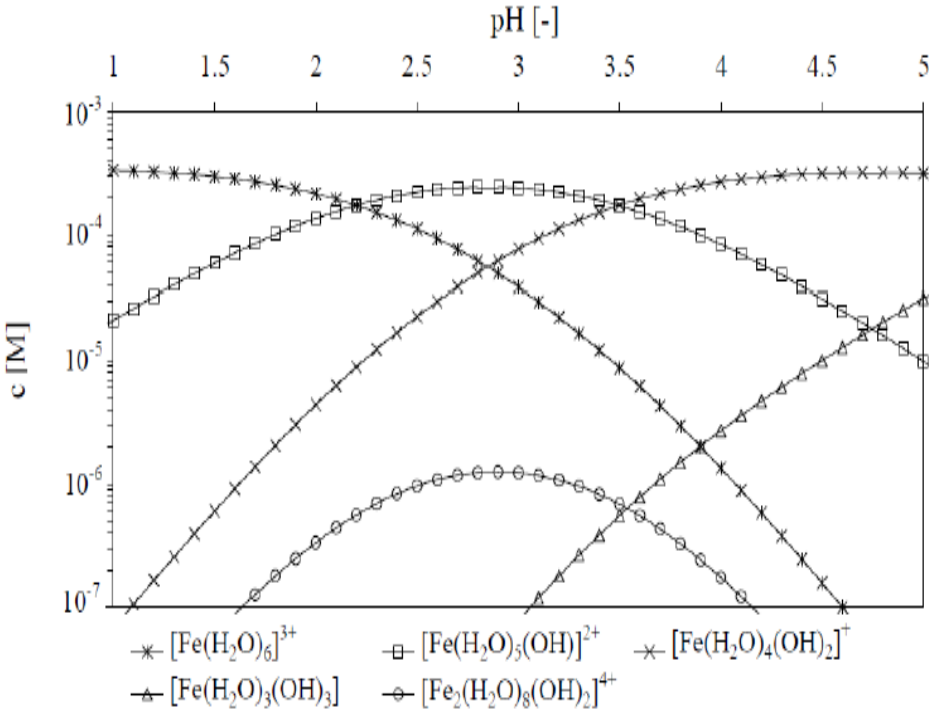
Source: ***www.scopus.com***

Solar photo-Fenton

- Ferric iron forms complexes with water and hydroxyl ligands, some of which photoactive.

$$[Fe^{3+}L] + hv \rightarrow [Fe^{3+}L]^* \rightarrow Fe^{2+} + L^{\cdot}$$

- Fe^{3+} reduction through a Ligand to Metal Charge Transfer....
- Different light absorption properties depending on L



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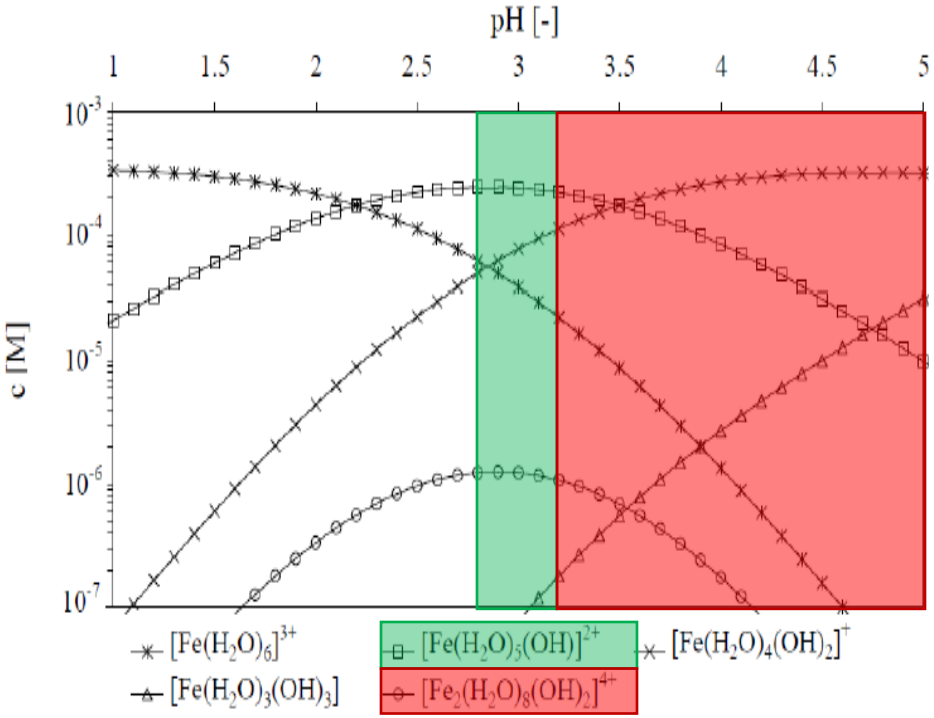

Operational pH range and quantum efficiency of unmodified photo-Fenton (absence of organic ligands) limited to region around pH 3.

Solar photo-Fenton

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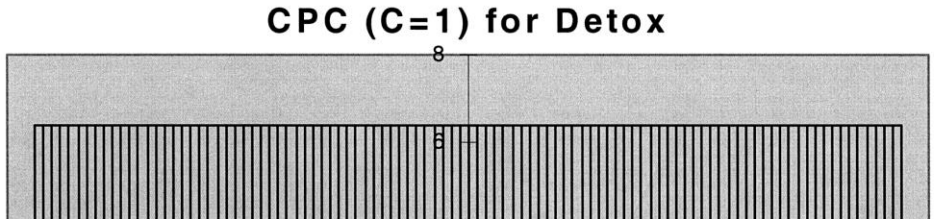
Advantages

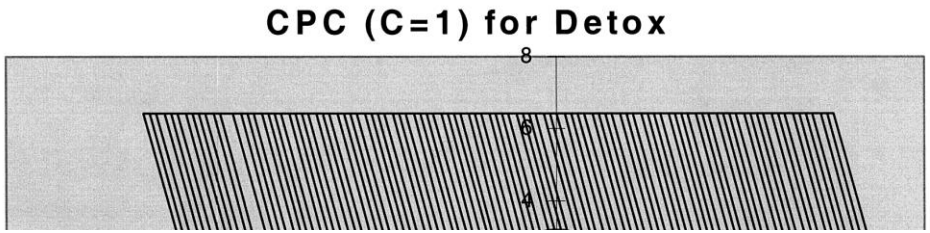
- Highly oxidative $HO^{\bullet}$ can attack and degrade most organic structures.
- Very fast.
- Modest cost of reagents (iron, H_2O_2, and acids/bases for pH control).
- Fe^{3+} to Fe^{2+} photoreduction possible with solar radiation.

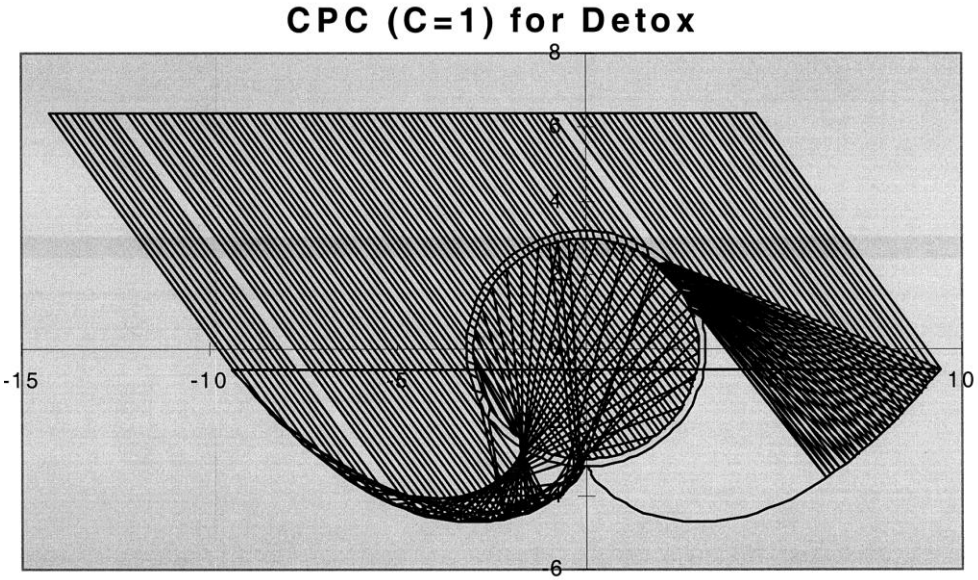
Disadvantages

- Requires strict pH control
- Use of pH controlling reagents (acids and bases) increases salinity of treated water.
- Some anions present in natural water (such as CO_3^{2-}/HCO_3^-, PO_4^{3-}) scavenge $HO^{\bullet}$, effectively stopping the process.
- Non selectivity of $HO^{\bullet}$ means that biodegradable components are also targeted.

Design of the photoreactor







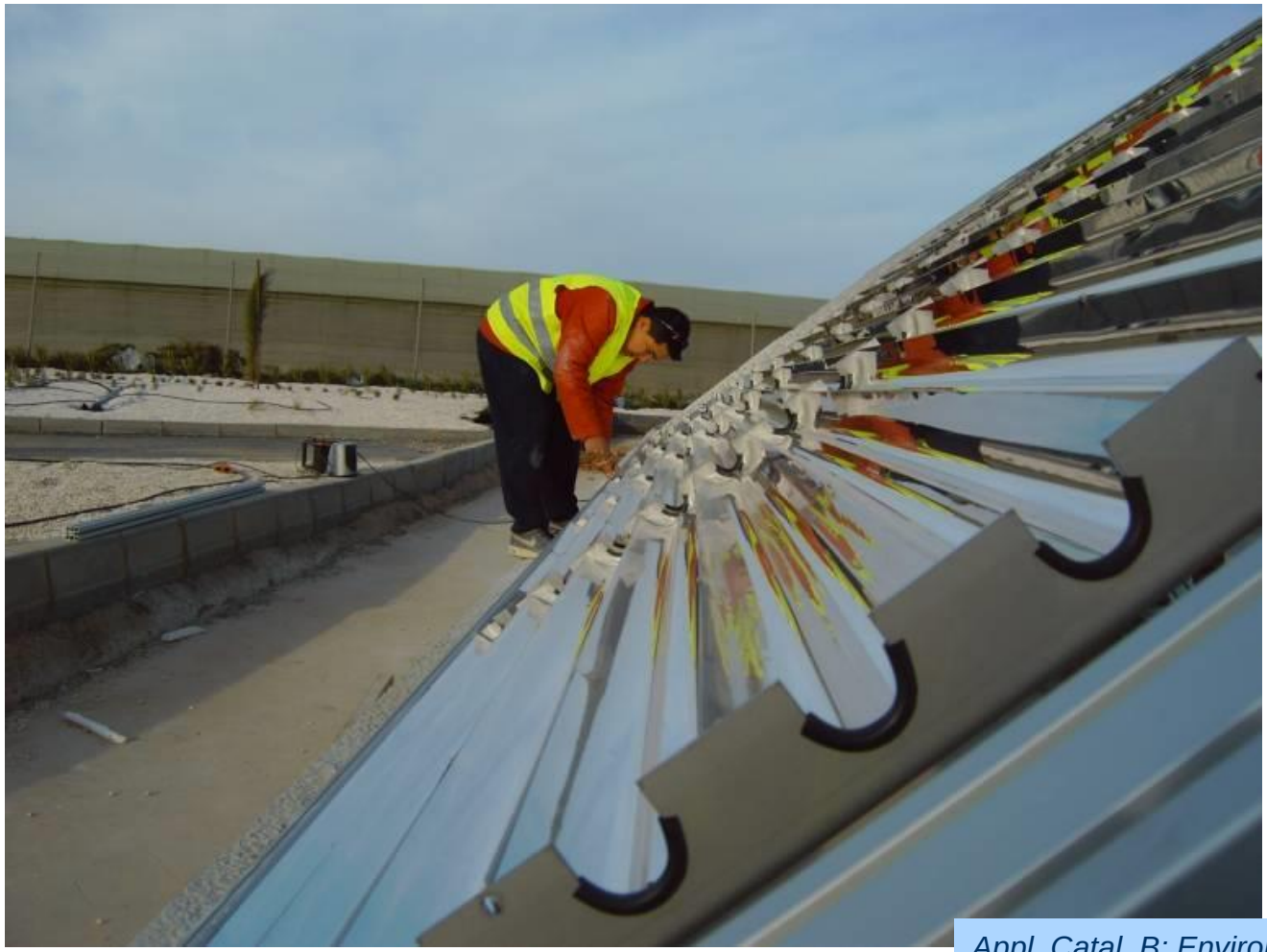
1 Sun CPCs

- ✓ ***Turbulent flow conditions***
- ✓ ***No vaporization of volatile compounds***
- ✓ ***No solar tracking***
- ✓ ***No overheating***
- ✓ ***Direct and Diffuse radiation***
- ✓ ***Low cost***
- ✓ ***Weatherproof (no contamination)***

Design of the photoreactor

Appl. Catal. B: Environ., ***170***, 90-123, 2015.

Design of the photoreactor



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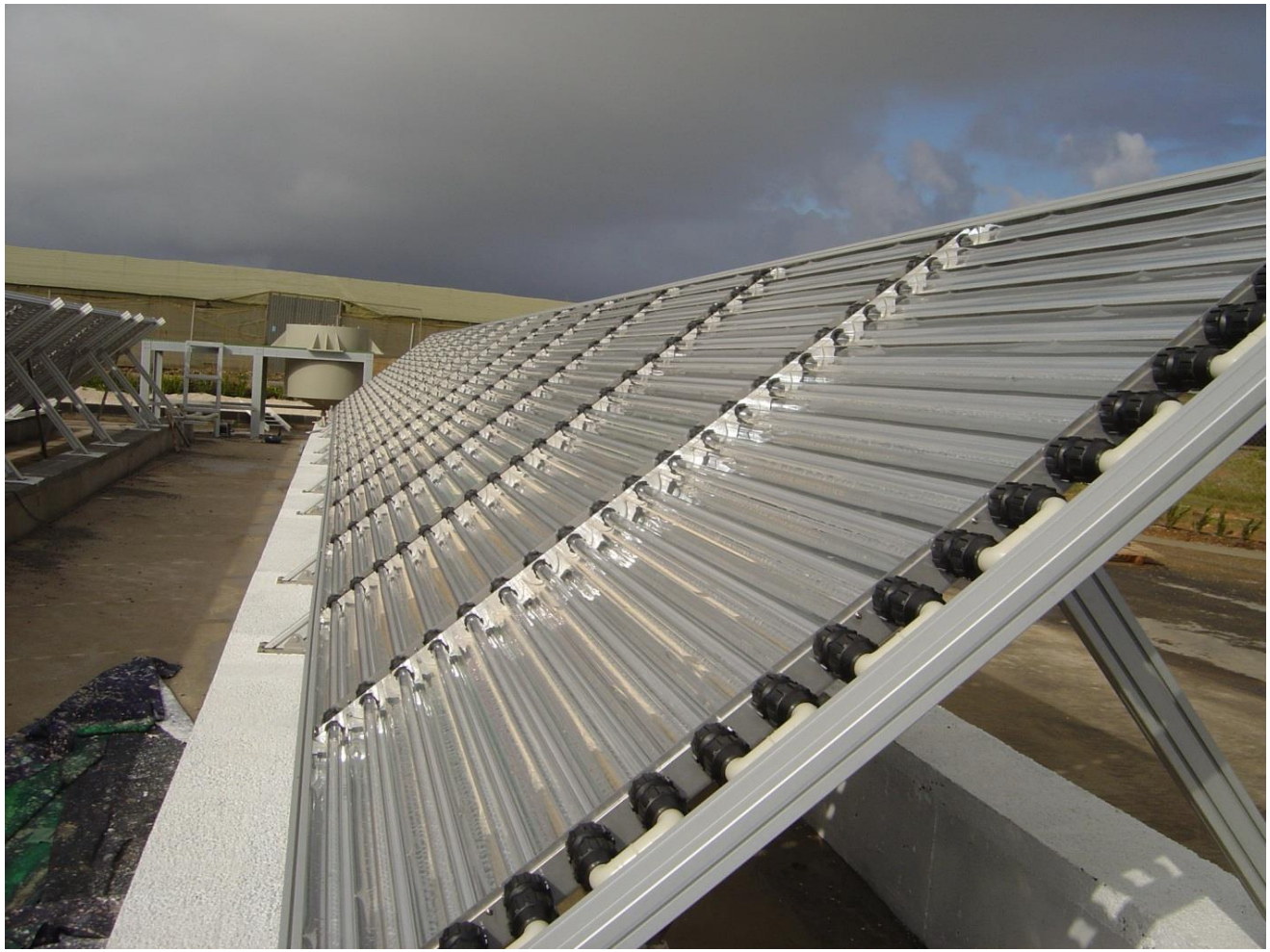

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Design of the photoreactor

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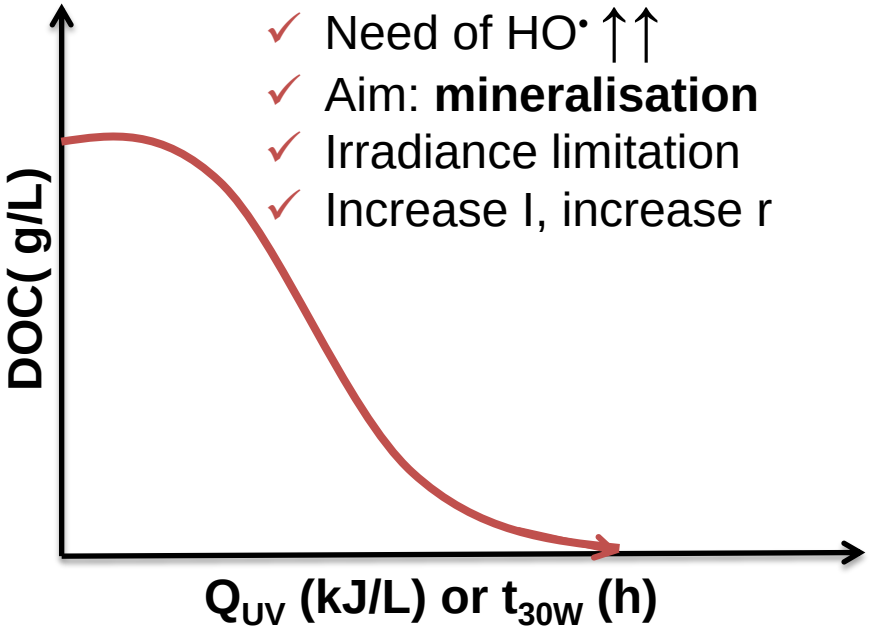
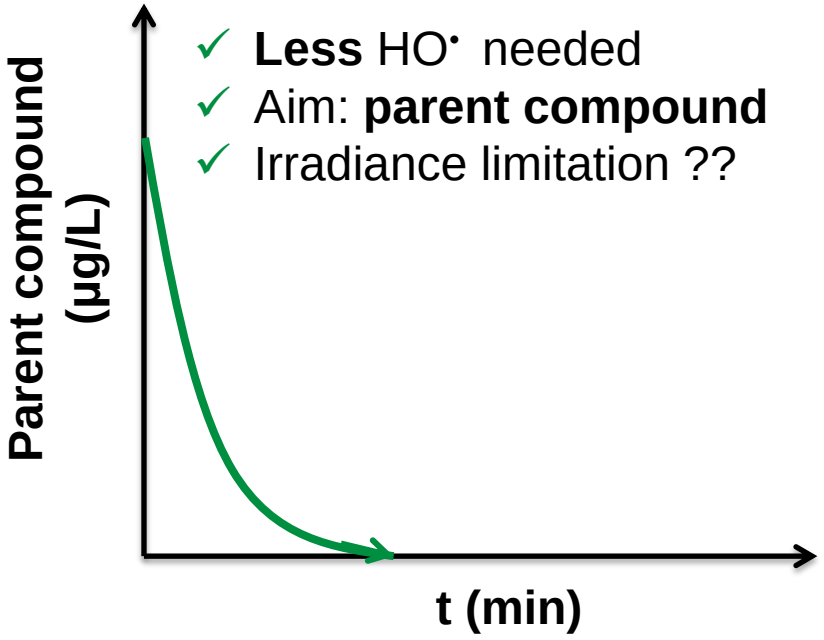
Highly polluted effluents (g/L or mg/L)



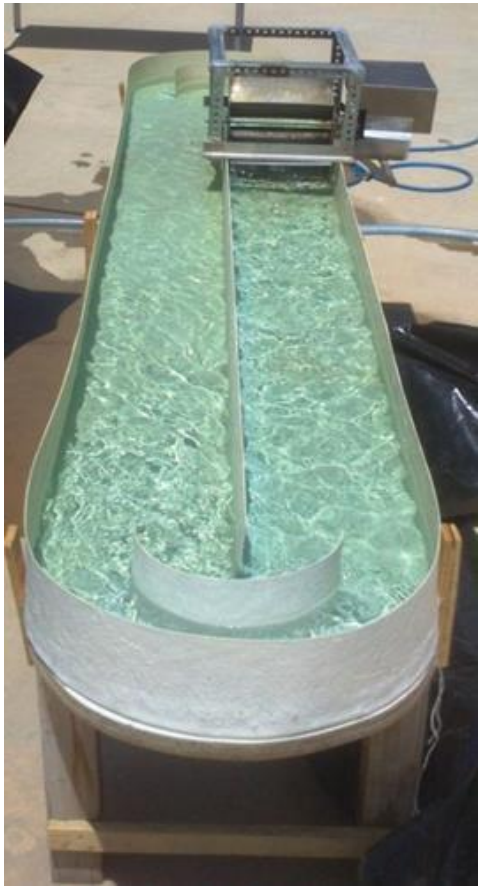
Effluents containing micropollutants (µg/L)



For micropollutant removal, **there is photosaturation,** so the process can be operated in photoreactors with wider optical lengths. **NOT possible with CPCs !!!**

J. Hazar. Mat., **279**, 322-329, 2014.
Appl. Catal. B: Environ., **178**, 210-217, 2015.

Design of the photoreactor



Extensive and non-concentrating solar photoreactors could be a good alter-native for working at high light path length, large volumes and **short treatment time with low iron concentration.** **Micropollutants!!**

Raceway Pond Reactors (RPR) liquid depth can be easily varied

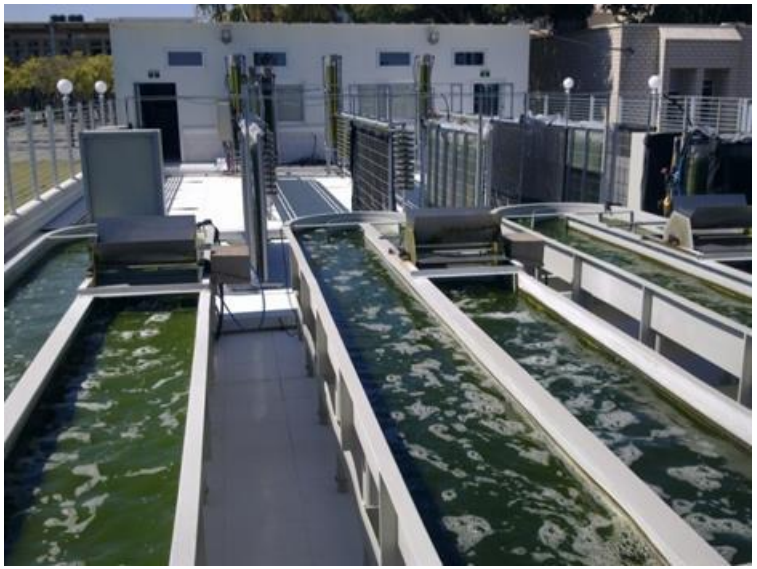
Pay attention when using open photoreactors as wastewater should be completely confined in them and requiring treatment time should be in the range of minutes, for avoiding evaporation of water

Depth	RPR 10 cm	RPR 15 cm	RPR 20 cm	CPC (5 cm)
Efficiency	0.93 mg/kJ	1.07 mg/kJ	1.08 mg/kJ	0.26 mg/kJ

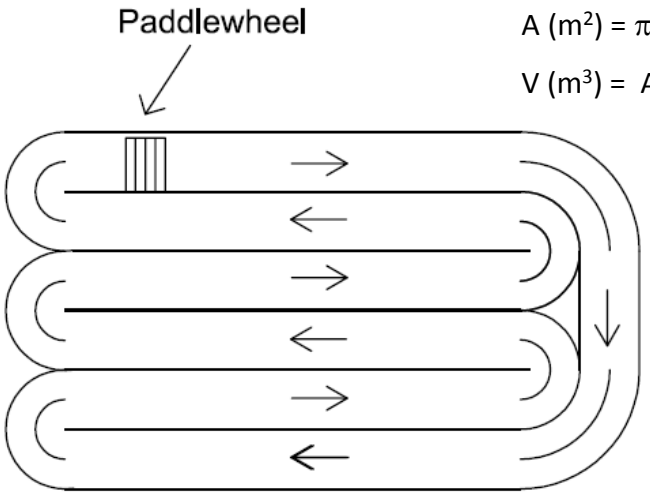
Chemosphere, **130**, 73-81, 2015
Catalysis Today, **287**, 10–14, 2017

Design of the photoreactor

In Raceway Pond Reactors (RPR) liquid depth can be easily varied

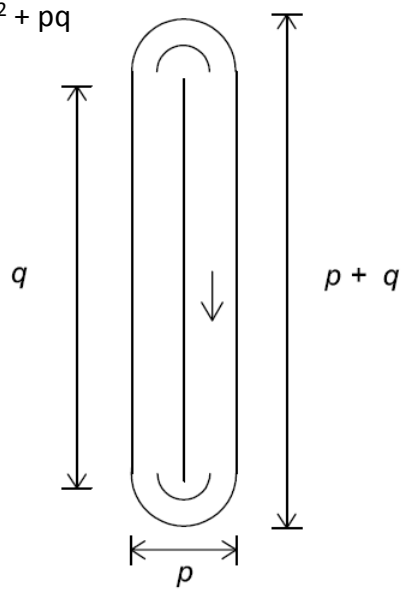


Microalgal cultures in RPR and TPBR. Almería.



$A\ (m^2) = \pi/4\ p^2 + pq$

$V\ (m^3) = A\ D$



Applied for microalgal mass culture

q ≥10 p

Low cost materials, mainly plastic liners.
Construction cost ~ **10 €/m² (CPC ~ 100 €/m²)**

Adequate experiments for CECs?

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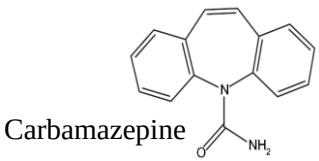
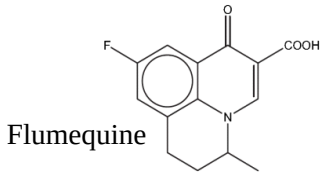
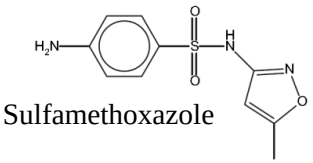
$r = kC$

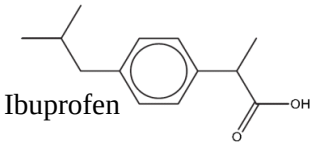
Correct C_0 for kinetic studies?

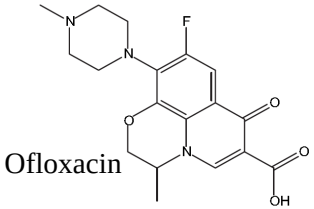
Model compounds at different "realistic" C_0 in natural water.
Fe (II), 0.1 mM, H_2O_2, 25 mg L^{-1}, natural pH

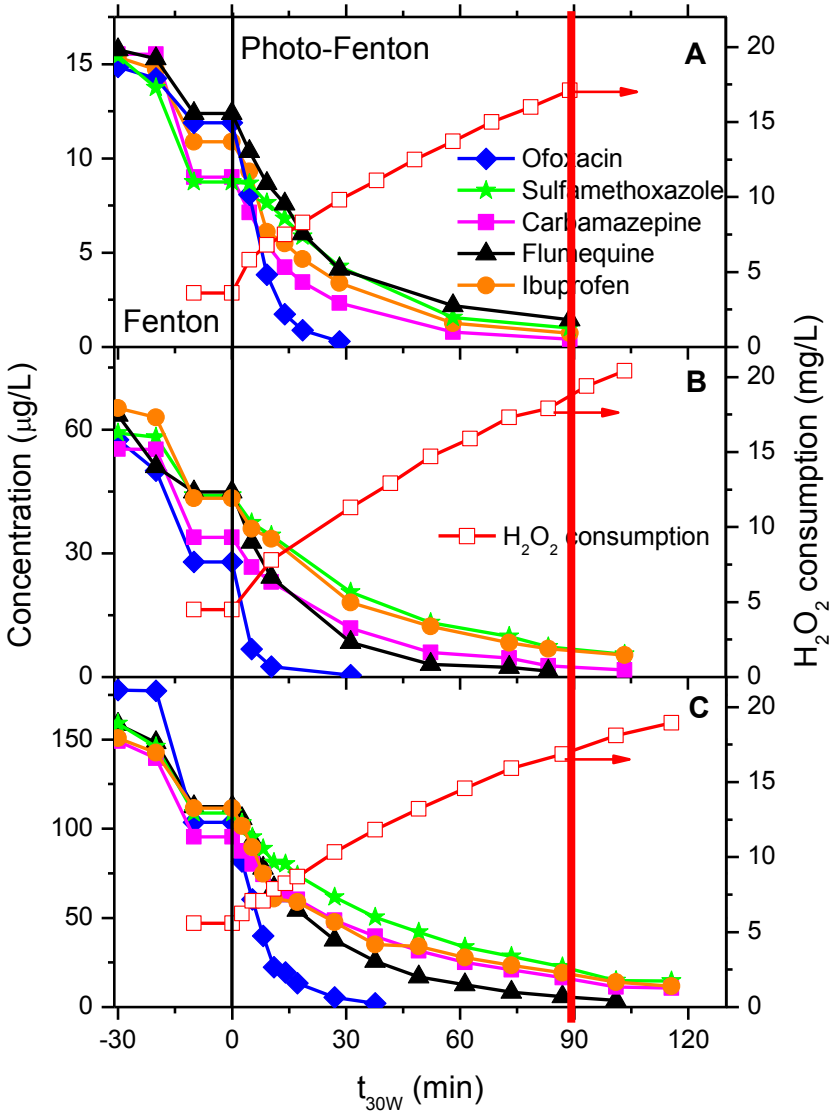






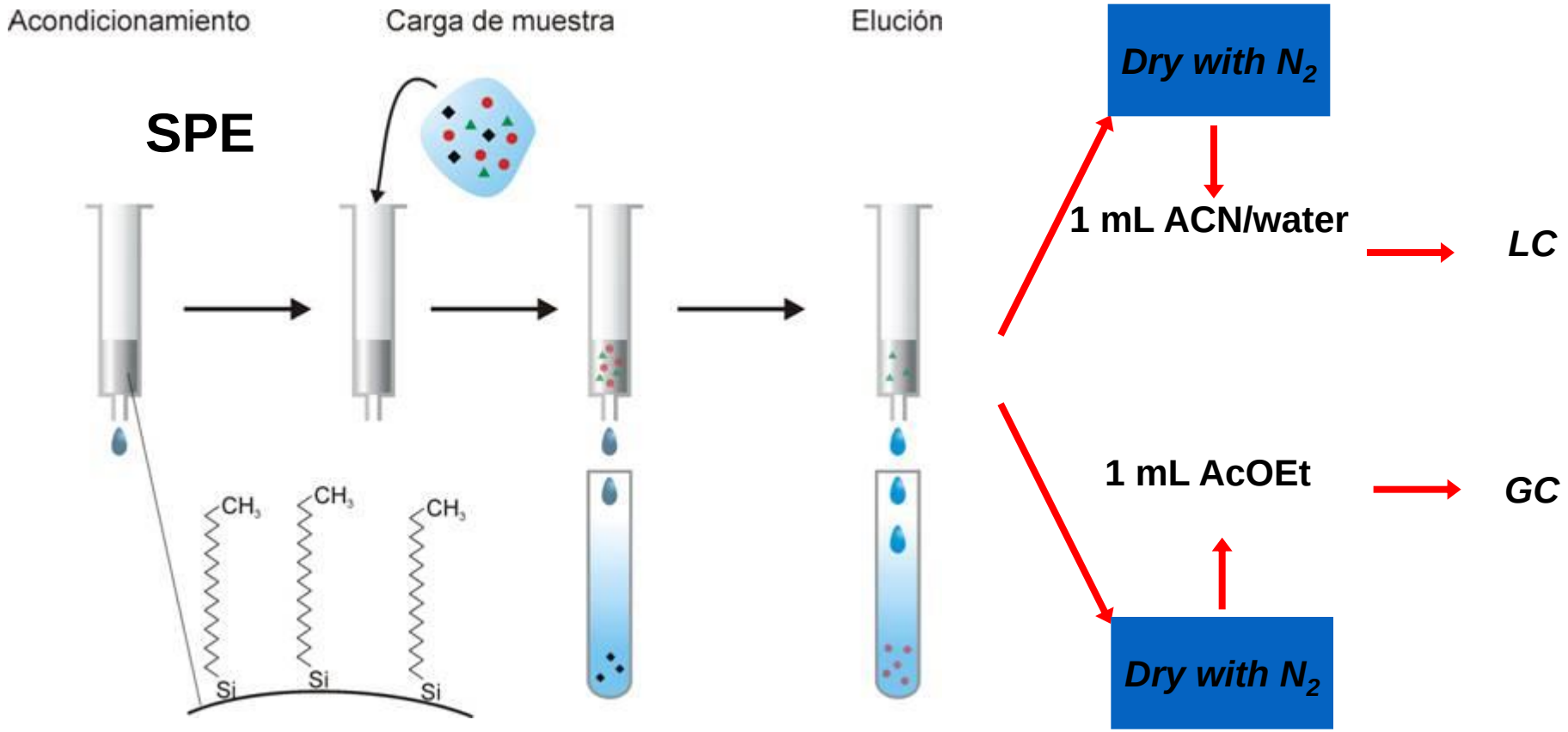






Adequate evaluation of CECs?

SOLID PHASE EXTRACTION (SPE)



Adequate evaluation of CECs?

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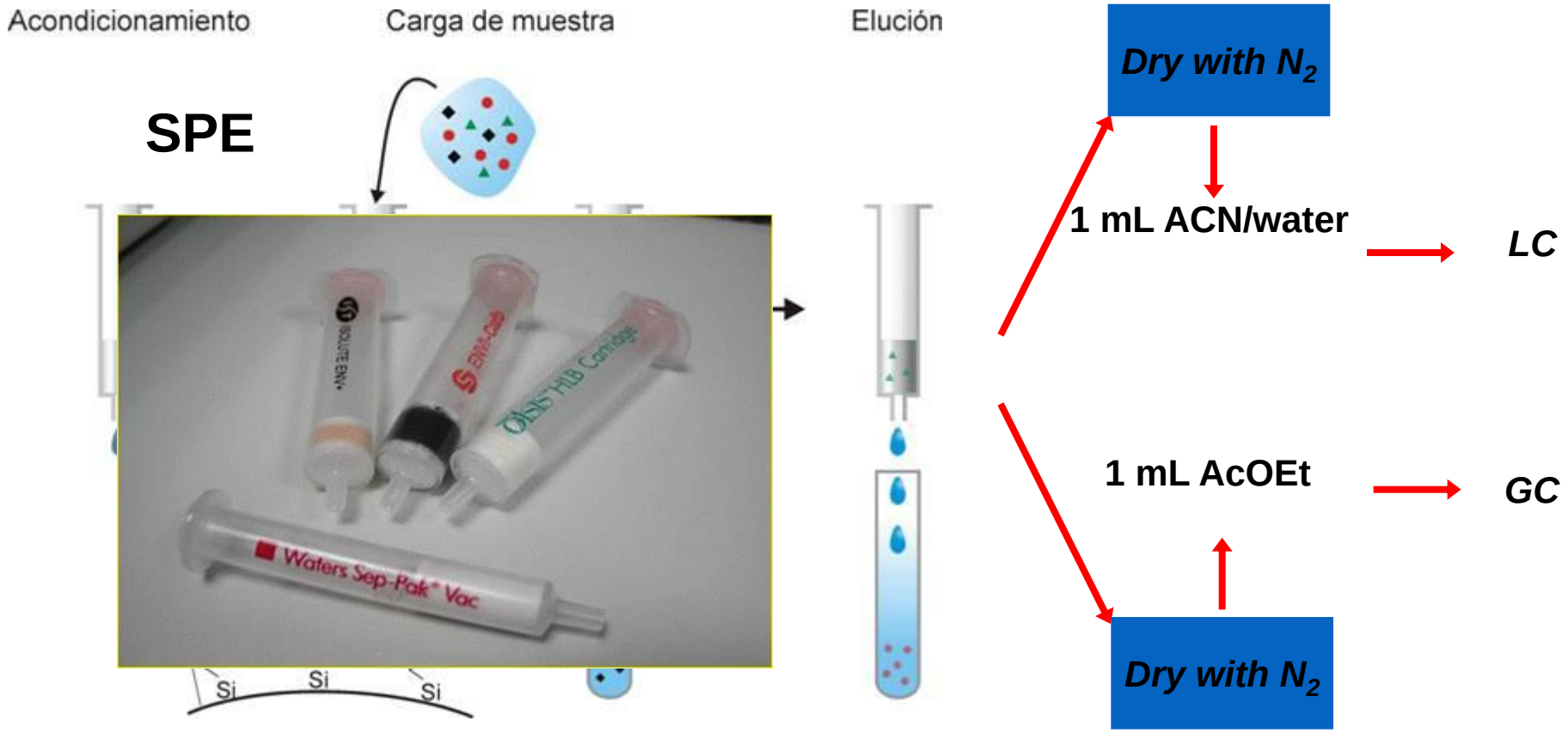

Adequate evaluation of CECs?

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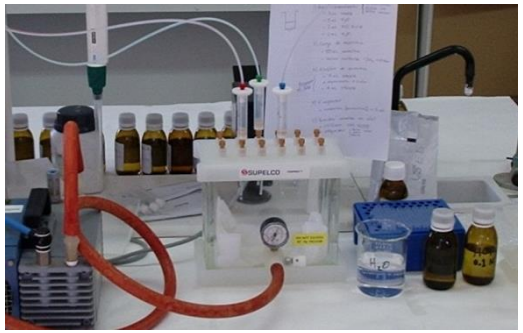
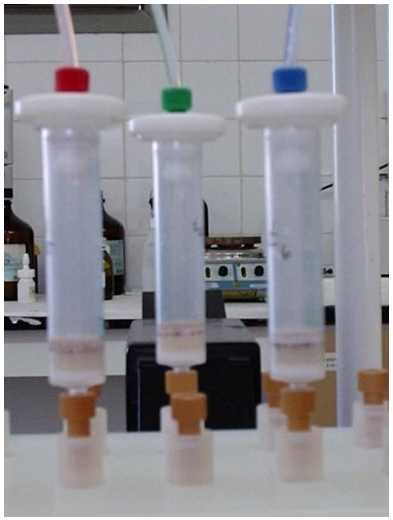
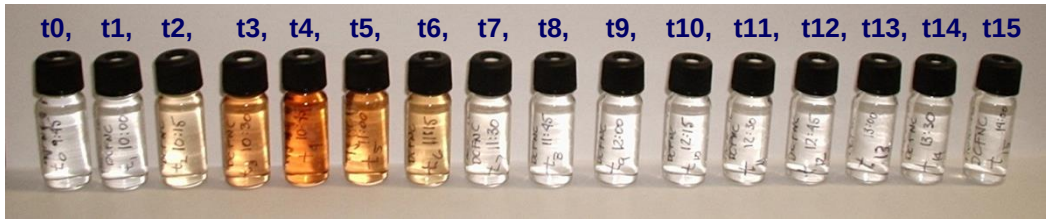
SPE





SOLID PHASE EXTRACTION (SPE)

- Before the analysis, samples were prepared by a Solid Phase Extraction.
- Stop the reaction.
- Concentrate the sample.
- Separates interferences from the sample matrix.



Adequate evaluation of CECs?

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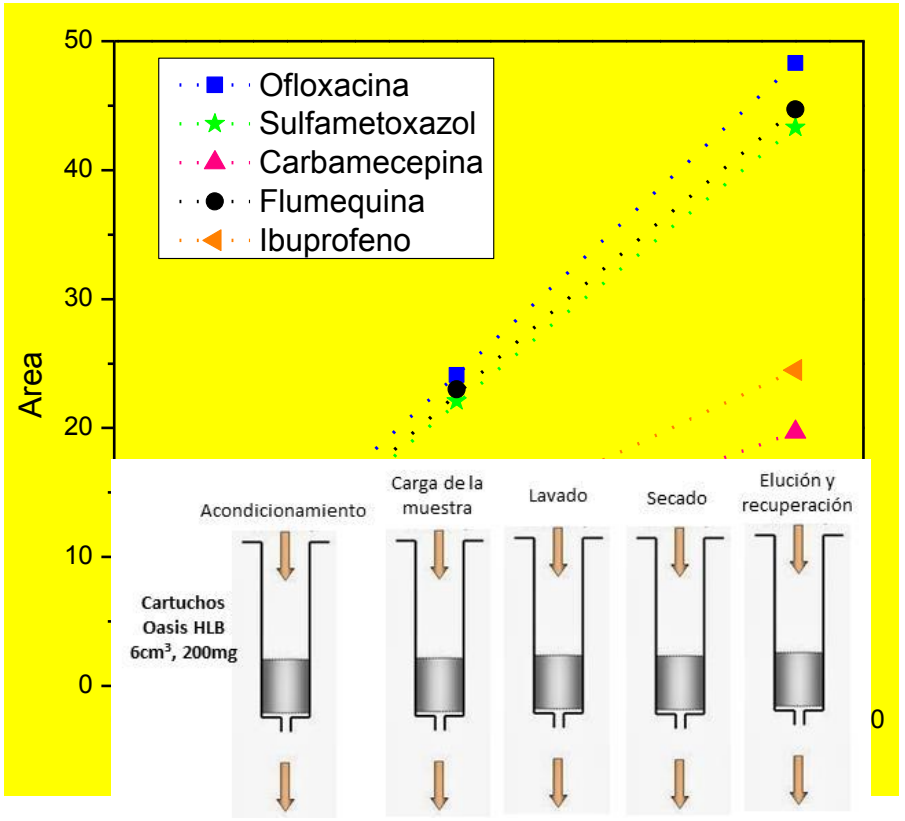
HPLC/MS/MS Qtrap 5500

>100µg/L

15µg/L

Model CECs
Carbamacepine
Ibuprofen
Flumequine
Ofloxacin
Sulphametoxazole



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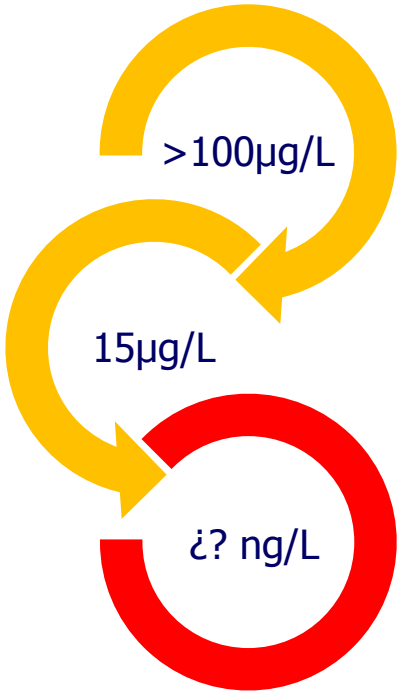
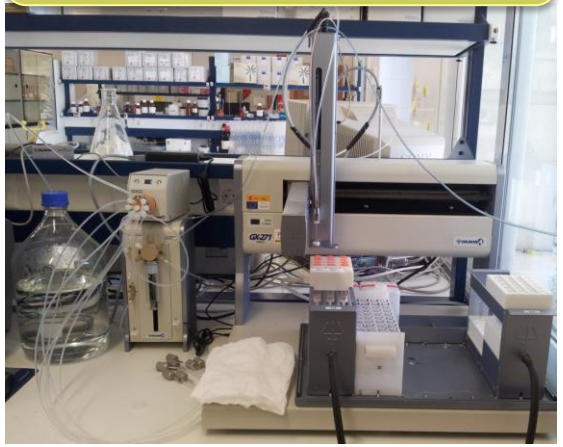
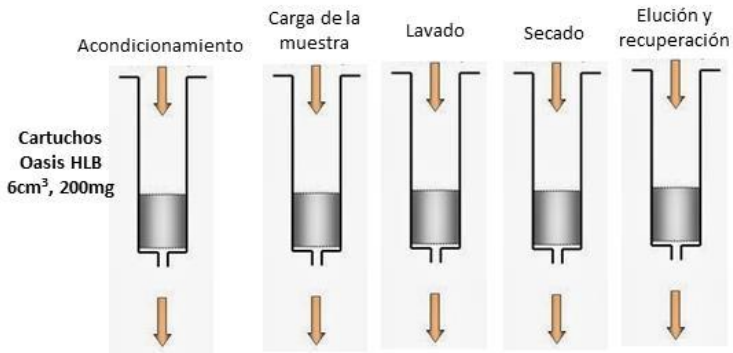


Optimised method:
micro-contaminants in MWTP effluent.

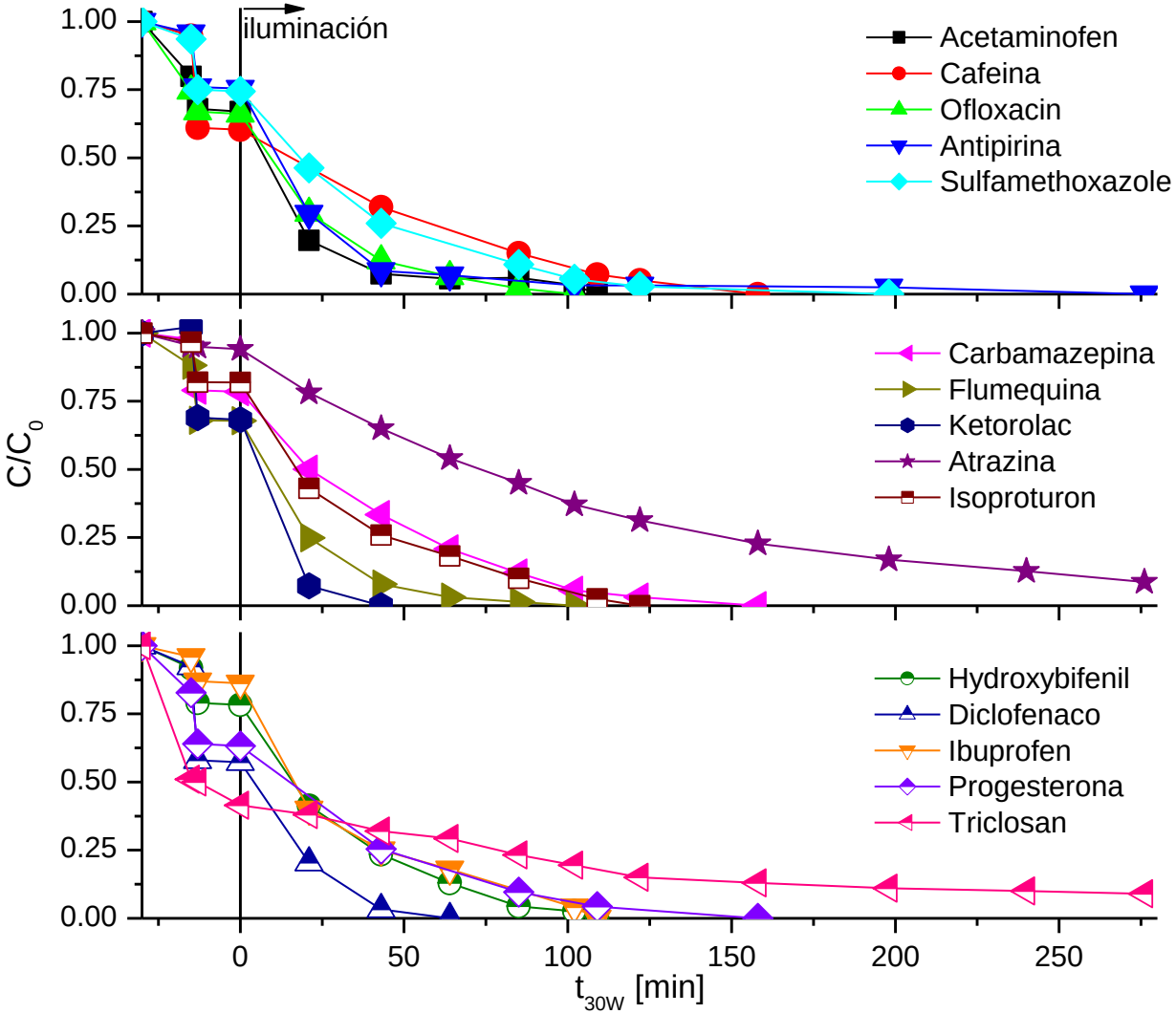
HPLC/MS/MS Qtrap 5500

SPE (automatic)





Adequate evaluation of CECs?



Degradation of 15 contaminants;

15 µg L^{-1} each in MWTP effluent evaluated by SPE and UPLC/UV-DAD.

One could study the whole process.

Conclusions later applied to MWTP effluent evaluated by LC-MS.

Adequate experiments for plants design and economical approach?

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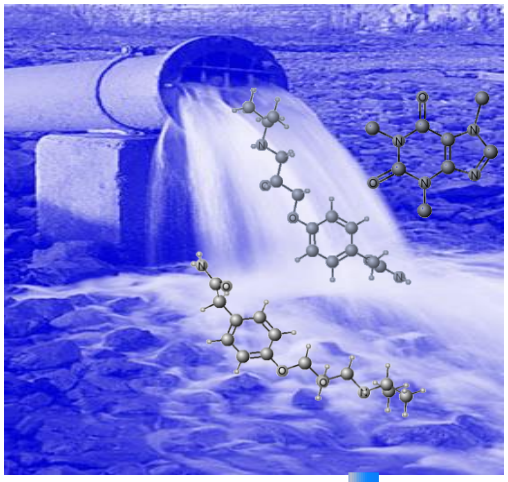

CHARACTERIZATION

(QTRAP LC-MS/MS system)

29/62 Compounds with higher contribution in MWTP Effluent

Wat. Res., **47**, 833-840, 2013.

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	12[illegible]	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	129[illegible]	7161	6
Furosemide*	2206.8	[illegible]81	7667	9
4-MAA*	2090.3	93	5684	10
Hydrochlorothiazide*	204[illegible]	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	-

Adequate experiments for plants design and economical approach?

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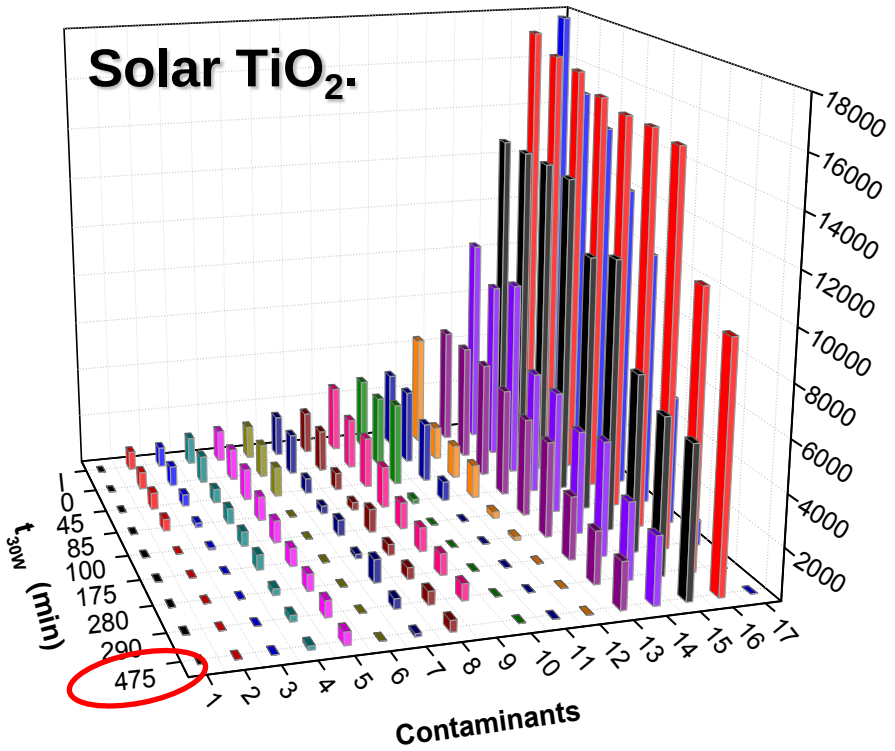
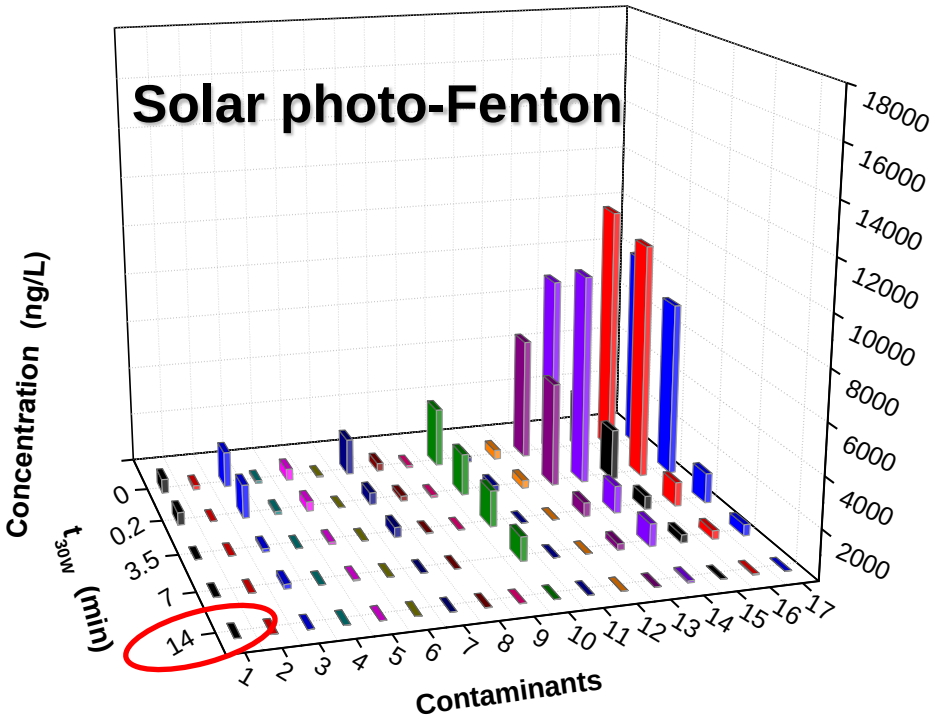


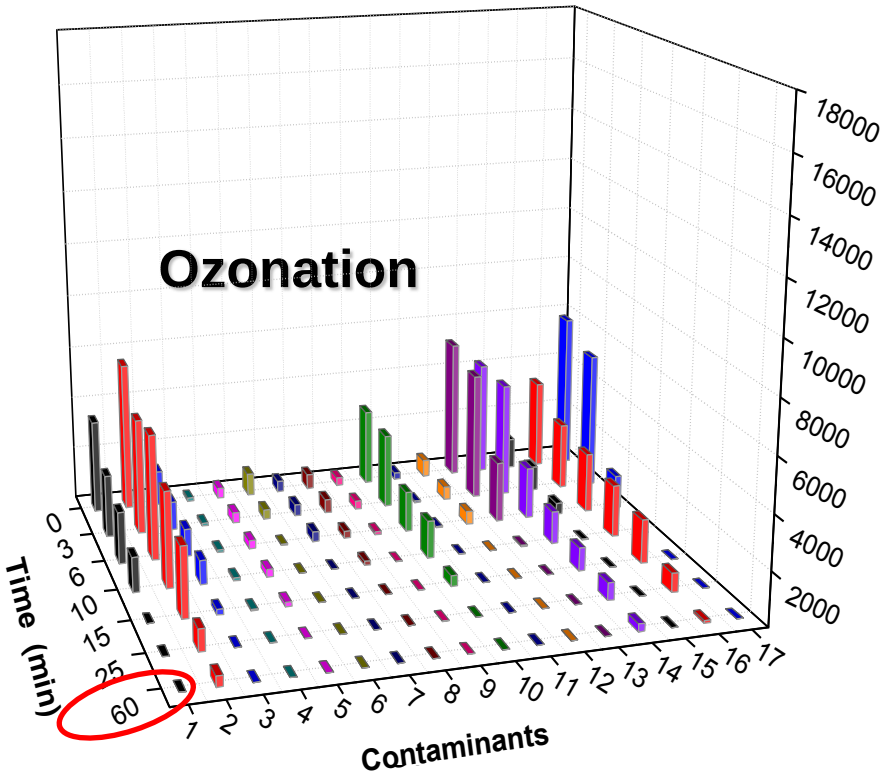


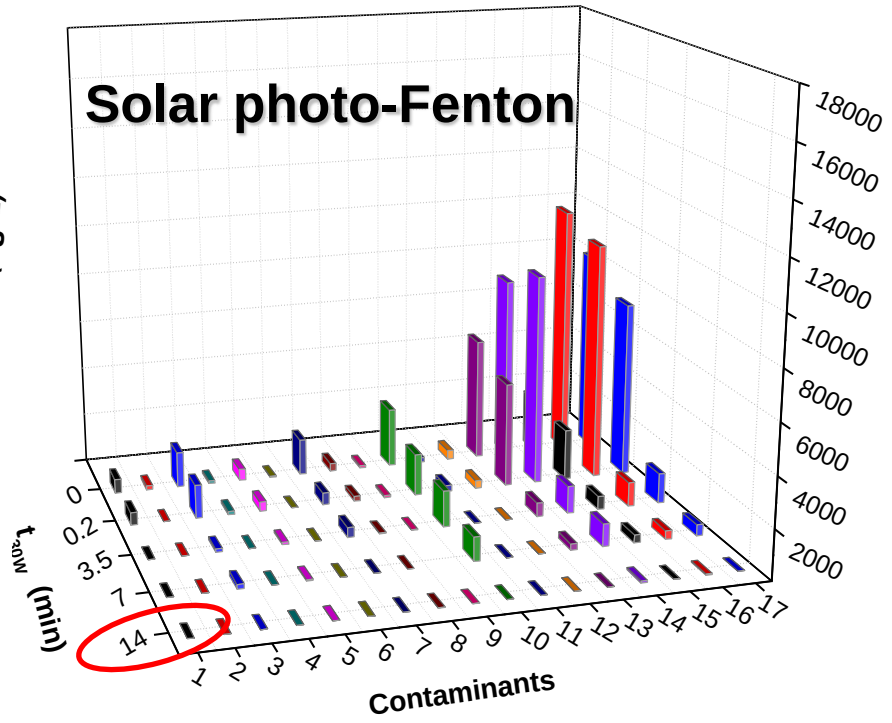
1-Bisphenol A; 2-Ibuprofen; 3-Hydrochlorothiazide;
4-Diuron; 5-Atenolol; 6-4-AA;
7-Diclofenac; 8-Ofloxacin; 9-Trimethoprim;
10-Gemfibrozil; 11-4-MAA; 12-Naproxen;
13-4-FAA; 14-∑C; 15-4-AAA; 16-Caffeine; 17-Paraxanthine

Contaminants > 1000 ng L^{-1}.
∑C = rest of contaminants at less than 1000 ng L^{-1}

Wat. Res., **47**, 833-840, 2013.
J. Hazar. Mat., **323**, 442–451, 2017.
Chem. Eng. J., **318**, 161-170, 2017.

Adequate experiments for plants design and economical approach?





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Adequate experiments for plants design and economical approach?

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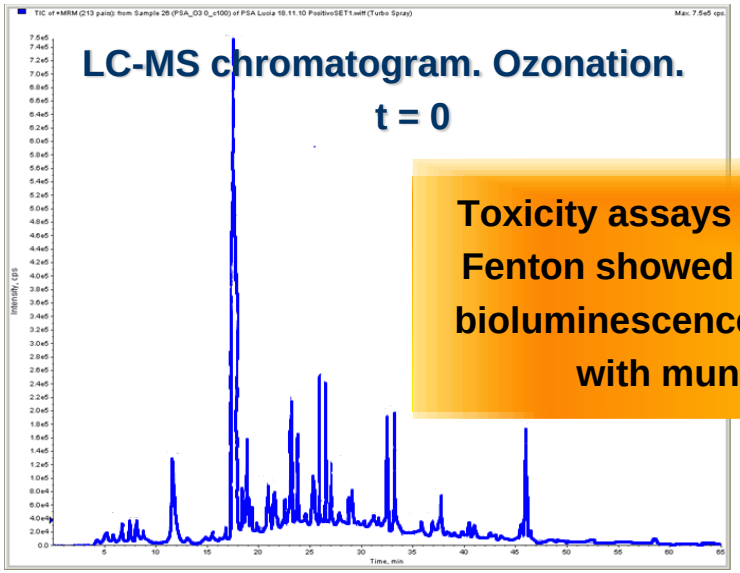
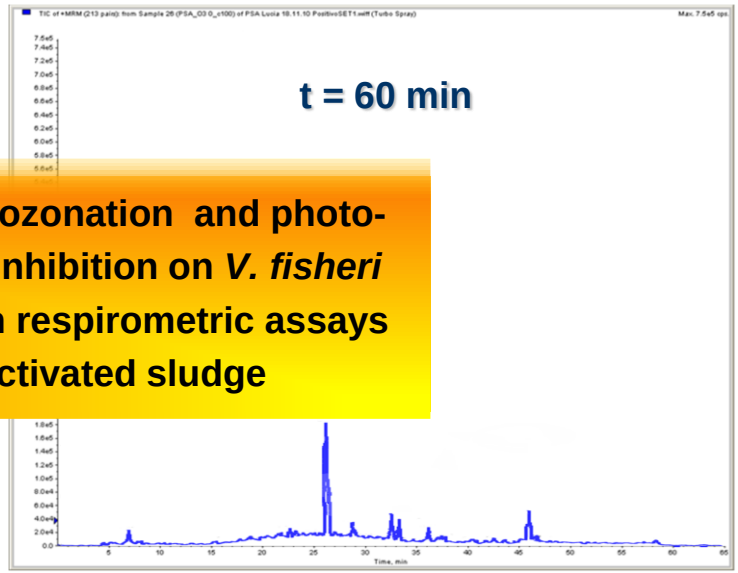
	~~Solar TiO2~~	Solar photo-Fenton		Ozonation
Treatment time, min	475	20		60
Accumulated solar Energy, kJ L^{-1}	212	2.3		-
Reagent Consumption	- -	H_2O_2 54 mg L^{-1}	Fe(II) 5 mg L^{-1}	O_3 9.5 mg L^{-1}





Toxicity assays during ozonation and photo-Fenton showed < 10% inhibition on *V. fisheri* bioluminescence and in respirometric assays with municipal activated sludge

Other concepts: Fe-complexes

Advantages of organic - iron complexes

- Maintain Fe^{3+} soluble at wider pH range, enabling direct treatment at near-neutral pH values found in many natural waters
- Better absorbers in the UV-VIS region than ferric-aqua complexes
- Possible formation of additional oxidative species from Ligands via loss of electrons.

$[Fe^{3+}L] + hv \rightarrow [Fe^{3+}L]^* \rightarrow Fe^{2+} + L^{\bullet}$ Complex photolysis

$L^{\bullet} + O_2 \rightarrow O_2^{\bullet -} + L'$ Formation of superoxide radical species

$HO_2^{\bullet} \leftrightarrow H^+ + O_2^{\bullet -}$ Superoxide/hydroperoxyl equilibrium

$Fe^{3+} + O_2^{\bullet -} \rightarrow Fe^{2+} + O_2$

$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^+$

Promotion of Fe^{3+} reduction

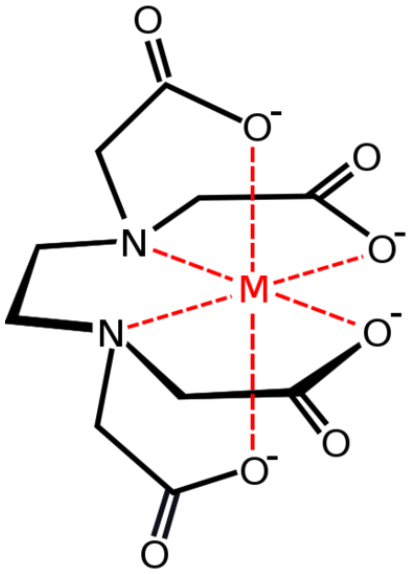
Other concepts: Fe-complexes

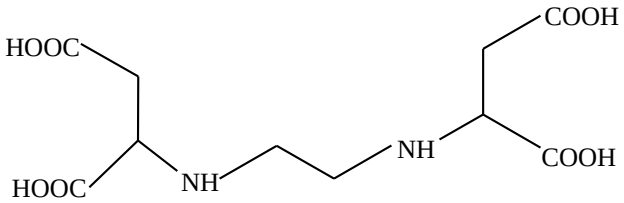
Limitations of using Fe (III)-complexes for the treatment of contaminated water at near-neutral pH

- Treatment of high concentrations of contaminants or achieving mineralization is difficult as continuing treatment requires adding more and more complexing agent. This leads to a non-sustainable process with increasing TOC instead.
- Rapid photolysis of Fe(III)-complexes doesn't allow long treatment times necessary for mineralization.
- Logistics costs would be limited, as the reused WW could be used locally at municipal wastewater treatment plants or local industries within a short radius of the production plants.

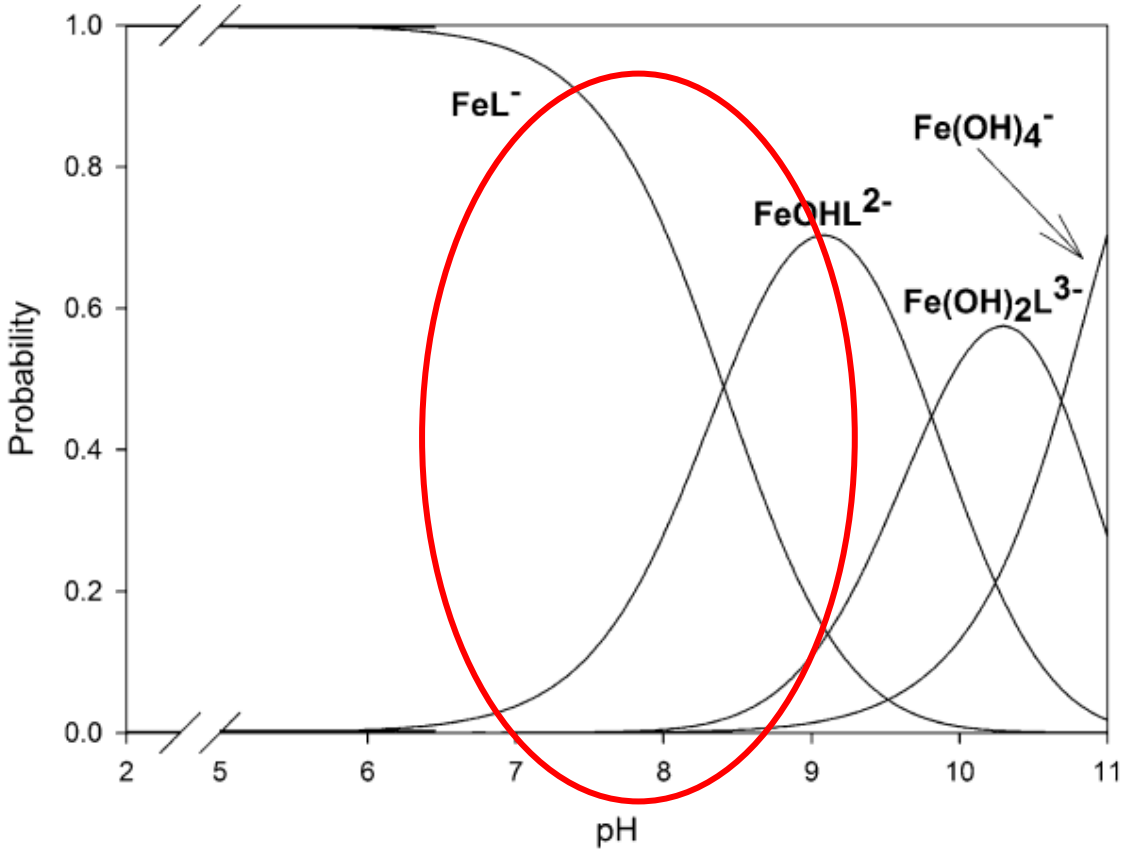
Therefore…adequate for CECs.

Other concepts: Fe-complexes





Ethylenediamine-N,N'-disuccinic acid (EDDS)

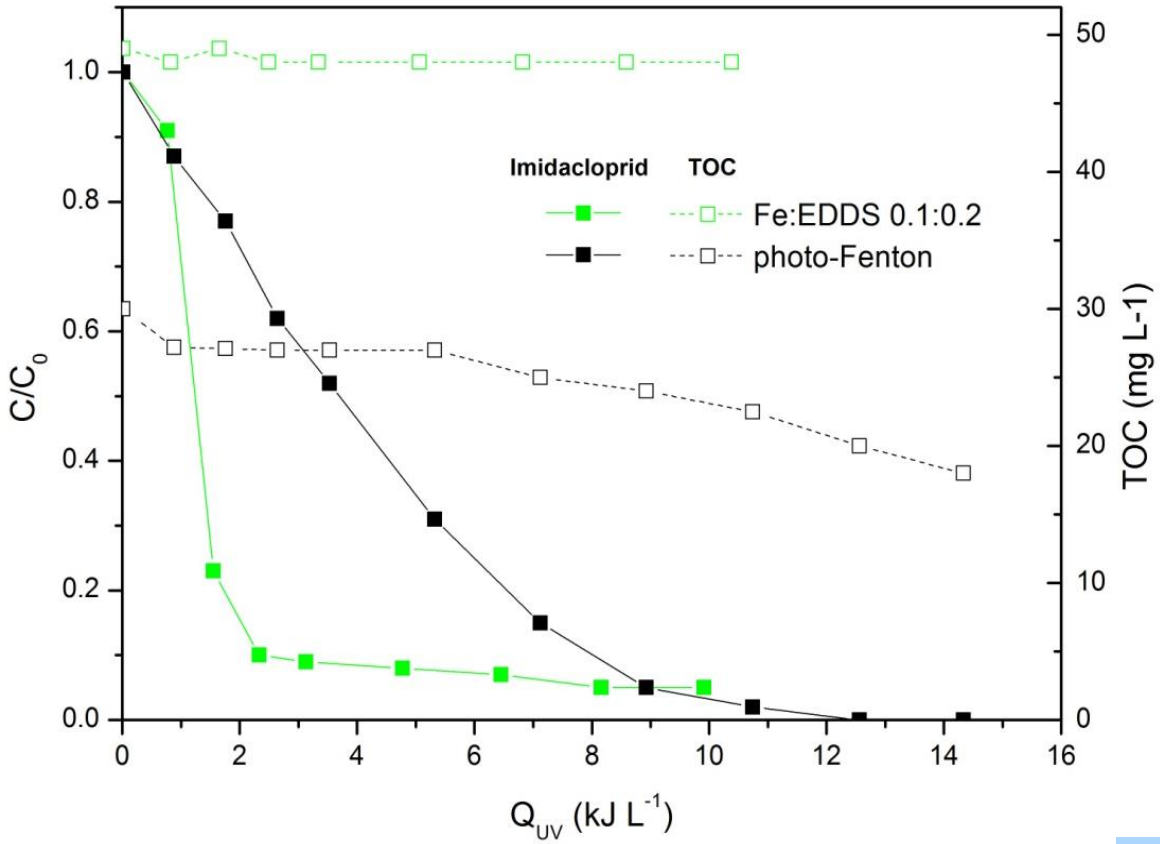


$Fe(III)\text{-}L + h\nu \rightarrow [Fe(III)\text{-}L]^* \rightarrow Fe(II) + L^{\bullet}$

J Phys Chem A **118**, 396-403, 2014.

Other concepts: Fe-complexes

Comparing Fe:EDDS at neutral pH with classical photo-Fenton at pH 3



Fe(III)-EDDS:

(+) Rapid degradation of contaminant.

(-) Constant TOC (total loss of activity following the break-up of the Fe(III)-EDDS complex).

Classical pF:

Slower degradation, but reliable (Fe dissolved) for longer time.

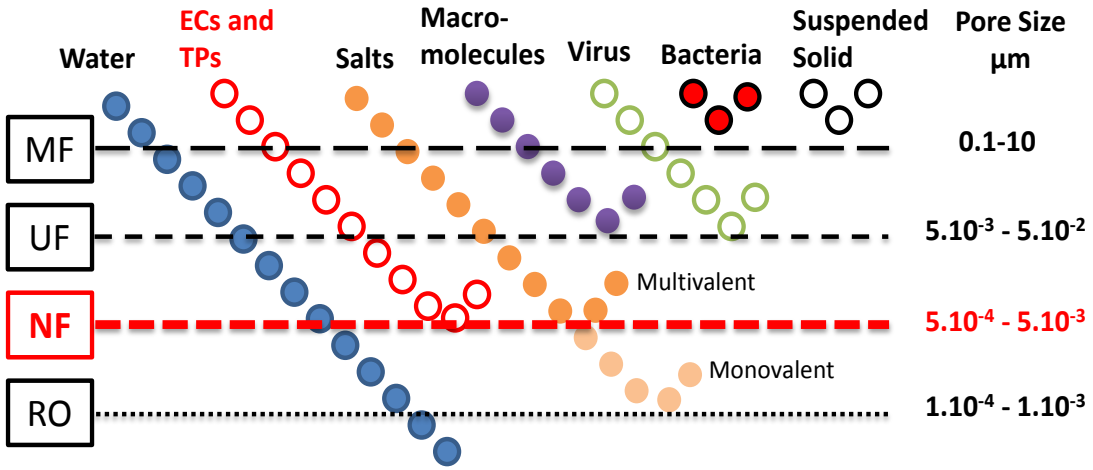
(+) TOC eventually starts to decrease.

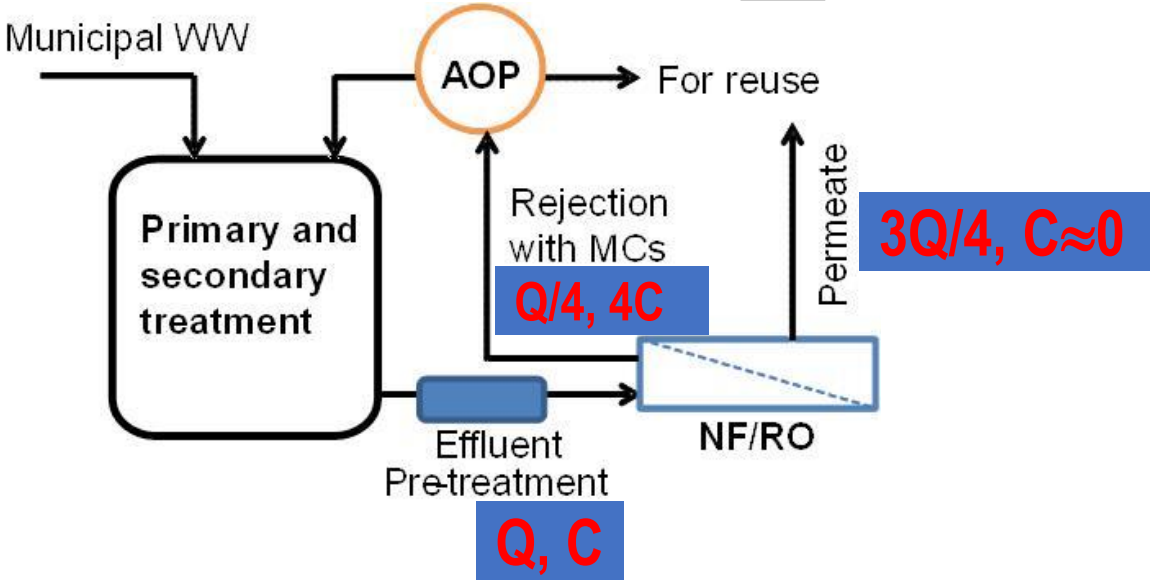
J. Photochem. Photobiol. A: Chem. ***303***, 1-7, 2015.

Combination with other technologies

AOPs PhD School

Combination NF/AOPs





$$r = kC$$

Combination with other technologies

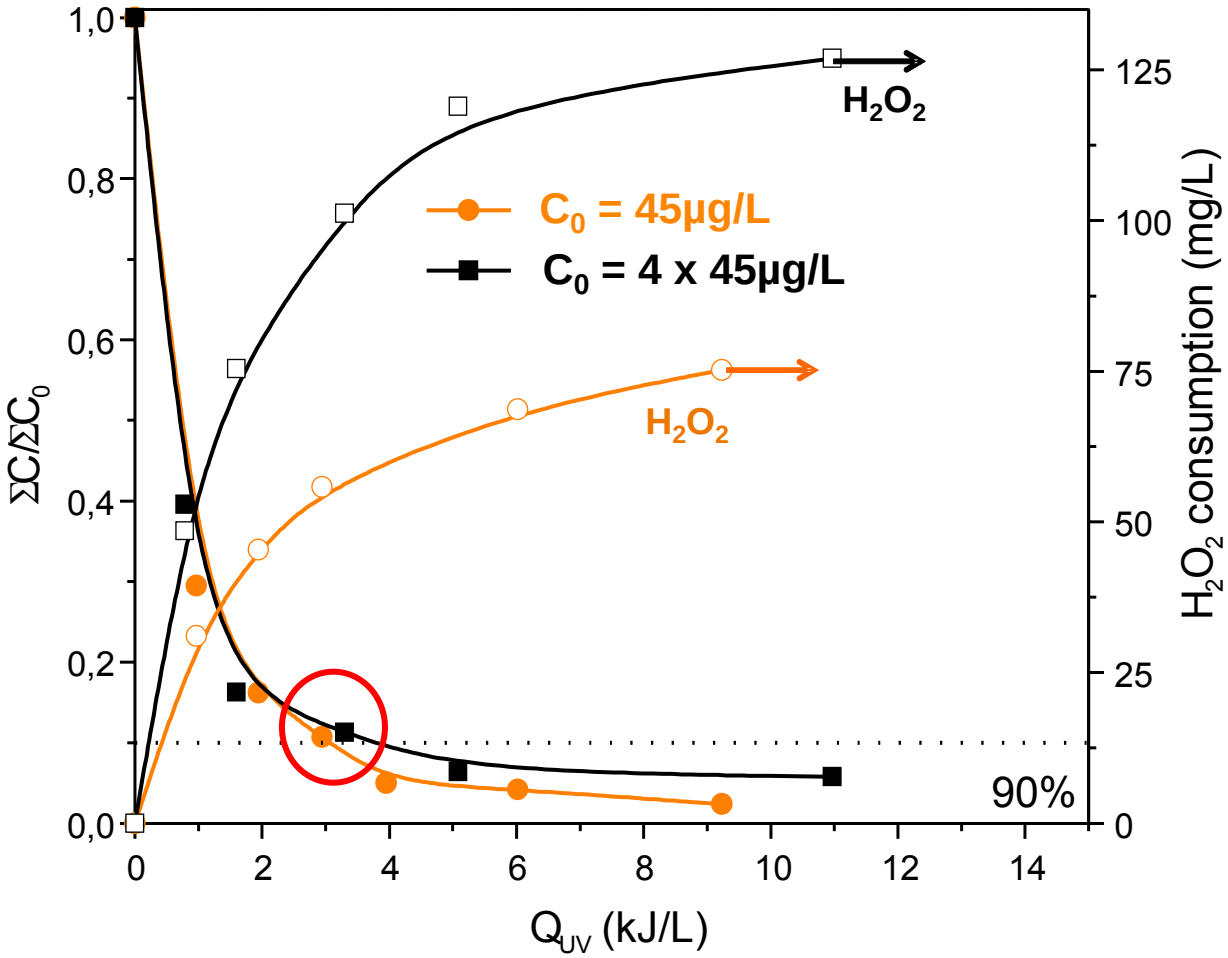
AOPs PhD School

	CF=1 C_o (ng L^{-1})		CF=4 $C_{o,c}$ (ng L^{-1})	
Caffeine	19980	20480	54550	53746
Carbamazepine	7460	5670	28615	15395
Naproxen	4740	4359	11350	8365
4-AAA	4234	4324	21585	16750
4-FAA	2126	2380	6035	12175
Norfloxacin	3118	1418	16590	5315
Antipyrin	1277	1228	4174	5802
Sulfamethoxazole	905	835	3325	3674
Ofloxacin	1107	603	4279	2348
Ciprofloxacin	327	562	1487	1452
Atenolol	594	525	2411	2162
Erithromycin	363	391	1214	1423
Azithromycin	144	391	648	1276
Fenofibric acid	223	309	789	741
Sulfapirydine	270	238	836	792
Ranitidine	294	218	1080	959
Trimetroprim	211	211	720	350
Sum of micro-contaminants < 200 ng L^{-1}	1164	839	3500	3208
Total	48537	44981	163188	135933

LC-Qtrap-5500-MS/MS

Combination with other technologies

Combination NF/AOPs



$r = kC$

Combination with other technologies

AOPs PhD School

Combination NF/AOPs

	CF	1	4
Solar photo-Fenton at pH = 3	H_2O_2 consumed (gm^{-3})	17.0	4.4
	Q_{uv} (kJ L^{-1})	22.5	5.1
	t(min) / CPC surface	90/100	120/22.6
Solar photo-Fenton like Fe (III)-EDDS complex	H_2O_2 consumed (gm^{-3})	24.9	6.2
	Q_{uv} (kJ L^{-1})	2.7	0.6
	t(min) / CPC surface	14/15	10/3.3

Operational requirements for attaining *95% of pharmaceuticals degradation* present in NF concentrates (CF=4) when solar photo-Fenton (pH = 3) and photo-Fenton like Fe(III)-EDDS complex were applied. CF=1, no NF, only AOP.

Catalysis Today **252**, 61-69, 2015.

Economic assessment

Solar photo-Fenton treatment of 1000 m^3/day MWTP effluent. Elimination of CEC **>90%**

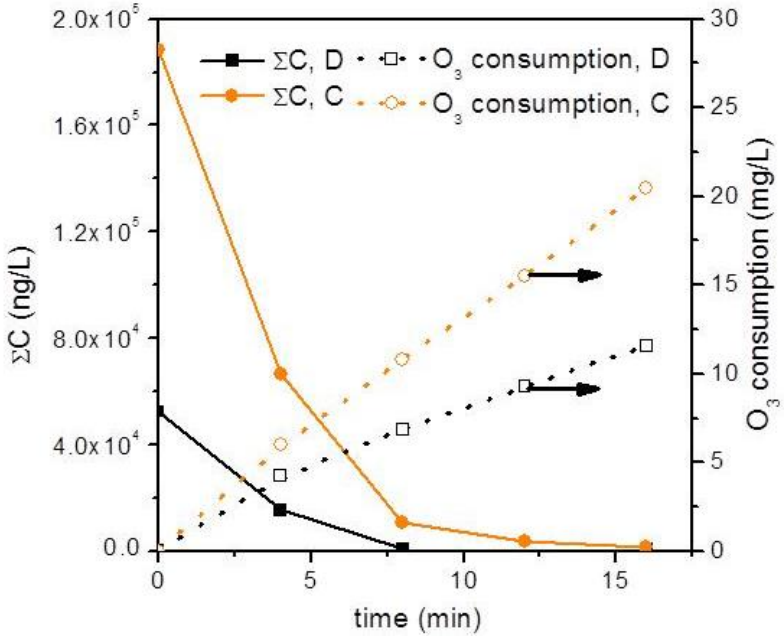
	Classic photo-Fenton, pH 3		Fe-EDDS, circumneutral pH	
	D	**C**	**D**	**C**
S_{CPC} (m^2)	4,300	2,300	3,600	1,200
Amortization Costs, €/year				
AC_{CPC}	102,000	70,100	90,900	47,000
AC_{mbm}	---	40,600	---	40,600
Operation costs, €/year				
Reagents	34,300	13,200	292,700	145,900
Electricity	30,100	25,200	20,100	22,700
Maintenance and personnel	28,200	27,600	23,500	20,300
Total OC	92,600	66,000	336,300	188,900
Total costs				
TC, €/year	194,600	176,700	427,200	276,500
TC, €/m^3	**0.53**	**0.48**	**1.17**	**0.76**

Chem. Eng. J., **318**, 161-170, 2017.
Chem. Eng. J., **310**, 514-524, 2017.

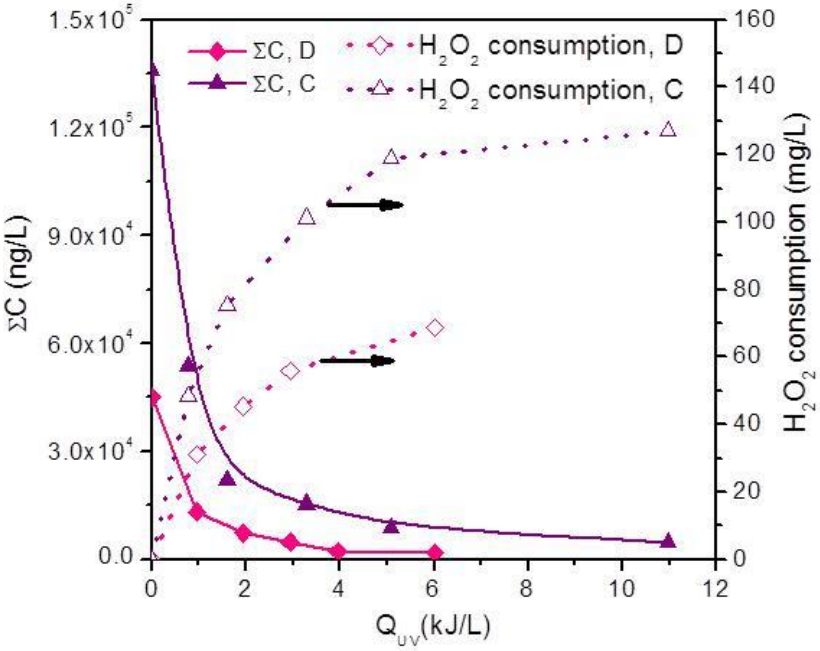
Economic assessment

AOPs PhD School

Ozonation



Fe(III):EDDS



	Solar photo-Fenton		Ozonation	
	D	C	D	C
Time, min	---	---	6.7	7.4
Fe(III), mM	0.1	0.2	---	---
H_2O_2, mg/L	55.8	105.4	---	---
Q_{UV}, kJ/L	2.9	3.8	---	---
O_3, mg/L	---	---	6.1	10.1
H_2SO_4, mg/L	110	65	---	---
EDDS, mL/L	0.2	0.1	---	---

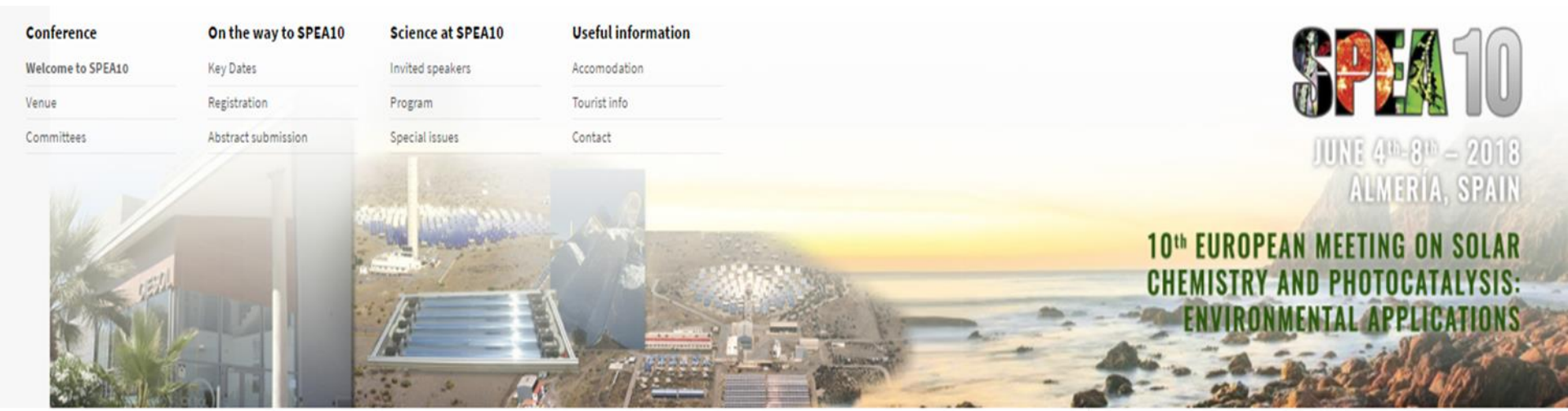
Economic assessment

Treatment of 1000 m^3/day
MWTP effluent.
Elimination of CEC **>90%**

	Solar photo-Fenton				Ozonation			
	D		C		D		C	
	€	€/m^3	€	€/m^3	€	€/m^3	€	€/m^3
AC	90900	0.25	47000	0.13	59400	0.16	25500	0.07
AC_{mbm}			40600	0.11			40600	0.11
OC	336200	0.92	188800	0.52	231900	0.64	88000	0.24
TC	427100	**1.17**	276400	**0.76**	291300	**0.80**	154100	**0.42**
TC (€/m^3), *excluding NF membrane system*				**0. 65**				**0.31**

	Solar photo-Fenton			Ozonation		
	€/m^3	€/m^3	€/m^3	€/m^3	€/m^3	€/m^3
Flow (m^3/day)	**D**	**C**	***excluding NF membrane system***	**D**	**C**	***excluding NF membrane system***
500	1.31	0.86	0.71	0.85	0.49	0.34
1,000	1.17	0.76	0.65	0.80	0.42	0.31
2,000	1.08	0.68	0.60	0.76	0.37	0.29
3,000	1.04	0.64	0.57	0.74	0.35	0.27
5,000	1.00	0.61	0.55	0.72	0.32	0.26
10,000	0.96	0.57	0.53	0.70	0.29	0.25

Environ. Sci.: Water Res. Technol. **2**, 511–520, 2016.



Welcome to SPEA10 in Almería (SPAIN)

June 4th-8th – 2018

Palacio de Exposiciones y Congresos Cabo de Gata Ciudad de Almería.

Welcome

On behalf of the Organizing and Scientific Committees, it is our great pleasure to welcome you to the **10th European meeting on Solar Chemistry and Photocatalysis: Environmental Applications (SPEA)**, held in Almería, Spain, on June 4th – 8th 2018.

Launched in 2000 and 2002 in Saint-Avold, France, the European meeting series SPEA progressively gained over the last years its renown among the most relevant meetings in solar chemistry and photocatalysis by travelling around Europe. Hosted in Barcelona (2004), Gran Canaria (2006), Palermo (2008), Prague (2010), Oporto (2012), Thessaloniki (2014), Strasbourg in (2016) SPEA will take place in Almería in 2018.

Updates

November 30, 2017. Online registration and abstract submission open.

23 June, 2017

January 31, 2018. Abstract submission deadline

23 June, 2017

March 15, 2018. Notification of abstract acceptance

23 June, 2017

Sponsors

3rd Iberoamerican Conference on
Advanced Oxidation Technologies (III Cipoa)
2nd Colombian Conference On Advanced
Oxidation Processes
(II Ccpaox)

November 14 – 17, 2017
Medellín (Guatapé), Colombia

CIPOA 2017

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https://cipoa2017. com/

Category	Before or on September 12th		After September 12th	
	COP	USD	COP	USD
Undergraduate students	$ 210.000	$ 81	$ 300.000	$ 115
Postgraduate students	$ 560.000	$ 215	$ 800.000	$ 308
Professors	$ 805.000	$ 310	$ 1.150.000	$ 442
Other professionals	$ 875.000	$ 337	$ 1.250.000	$ 481

Discount rates:
Members of AOPs School (Students) – 15%
Members of AOPs School (Professors) – 10%

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Phone +57 (4) 2198926

cipoa2017.com

Thank you very much for your attention
Questions?

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