

# **LESSON 4**

**12/02/2020**

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# Plant layouts

## Removal of emerging pollutants



### Biological treatment

It involves the oxidation of biodegradable compounds and their conversion mainly into: biomass, carbon dioxide and water. In addition, nitrogen and phosphorus removal can occur.

### Advanced oxidation processes:

UVC/H<sub>2</sub>O<sub>2</sub>

O<sub>3</sub>

O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>

O<sub>3</sub>/UVC

O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UVC

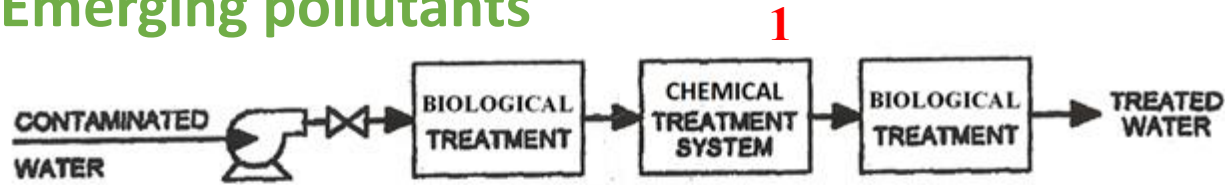
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These processes lead to the chemical oxidation of the biorecalcitrant compounds and their conversion first into biodegradable compounds and then into carbon dioxide and water (mineralization).

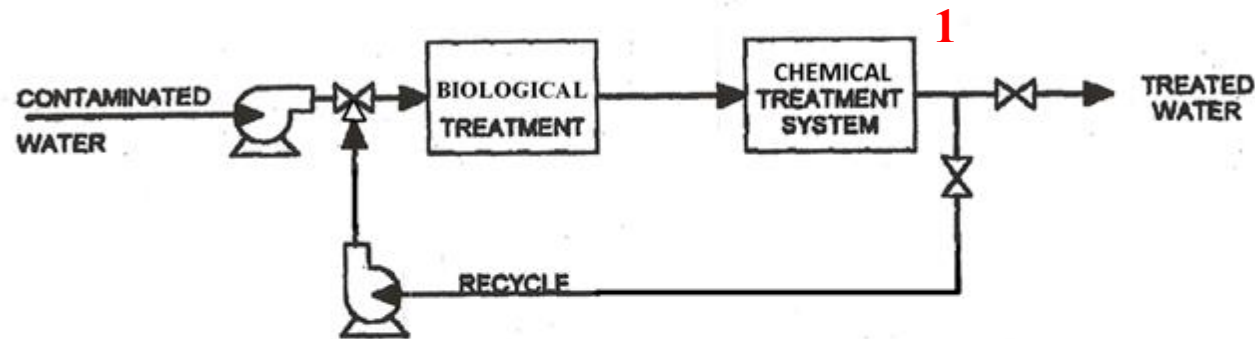
**Getting to mineralization with these processes is too expensive (ozone, hydrogen peroxide ... they are expensive!)**

# Plant layouts

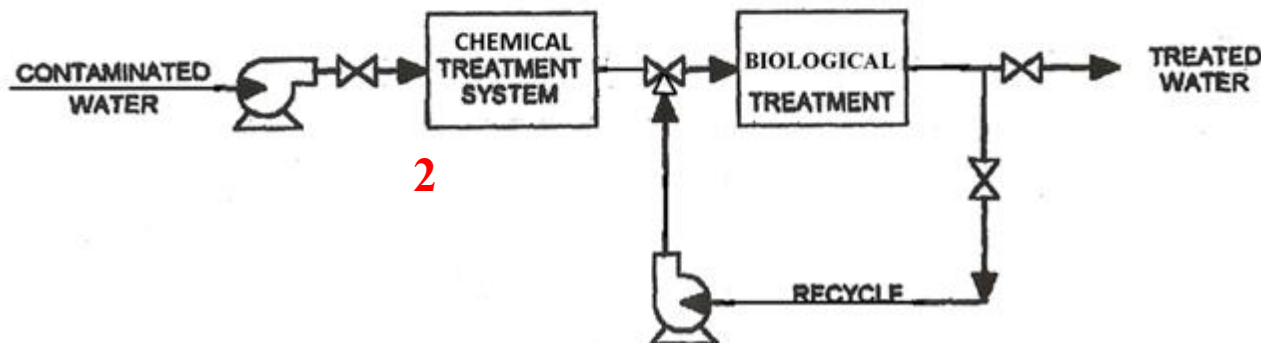
## Emerging pollutants



1) We oxidize non-biodegradable or recalcitrant compounds until we obtain biodegradable by-products



## Emerging and toxic\* pollutants



2) We oxidize the compounds toxic for microorganisms before the sewage to be treated reaches biological treatments

# Advanced oxidation processes: ecofriendly solutions

## Advanced oxidation processes:

UVC/H<sub>2</sub>O<sub>2</sub>

O<sub>3</sub>

O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>

O<sub>3</sub>/UVC

O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/UVC

....

The processes we have studied so far require the use of ozone, hydrogen peroxide and UVC radiation. We consume reagents whose production requires a great deal of energy and resources.

In addition to changing the plant layouts, we can adopt other more "eco-sustainable" advanced oxidation processes. These processes should be characterized by a low consumption of reagents and by the use of renewable energy sources.

An example are photocatalytic processes

photo-: they use a radiation... specifically, the solar radiation;

-catalytic: they need a catalyst.



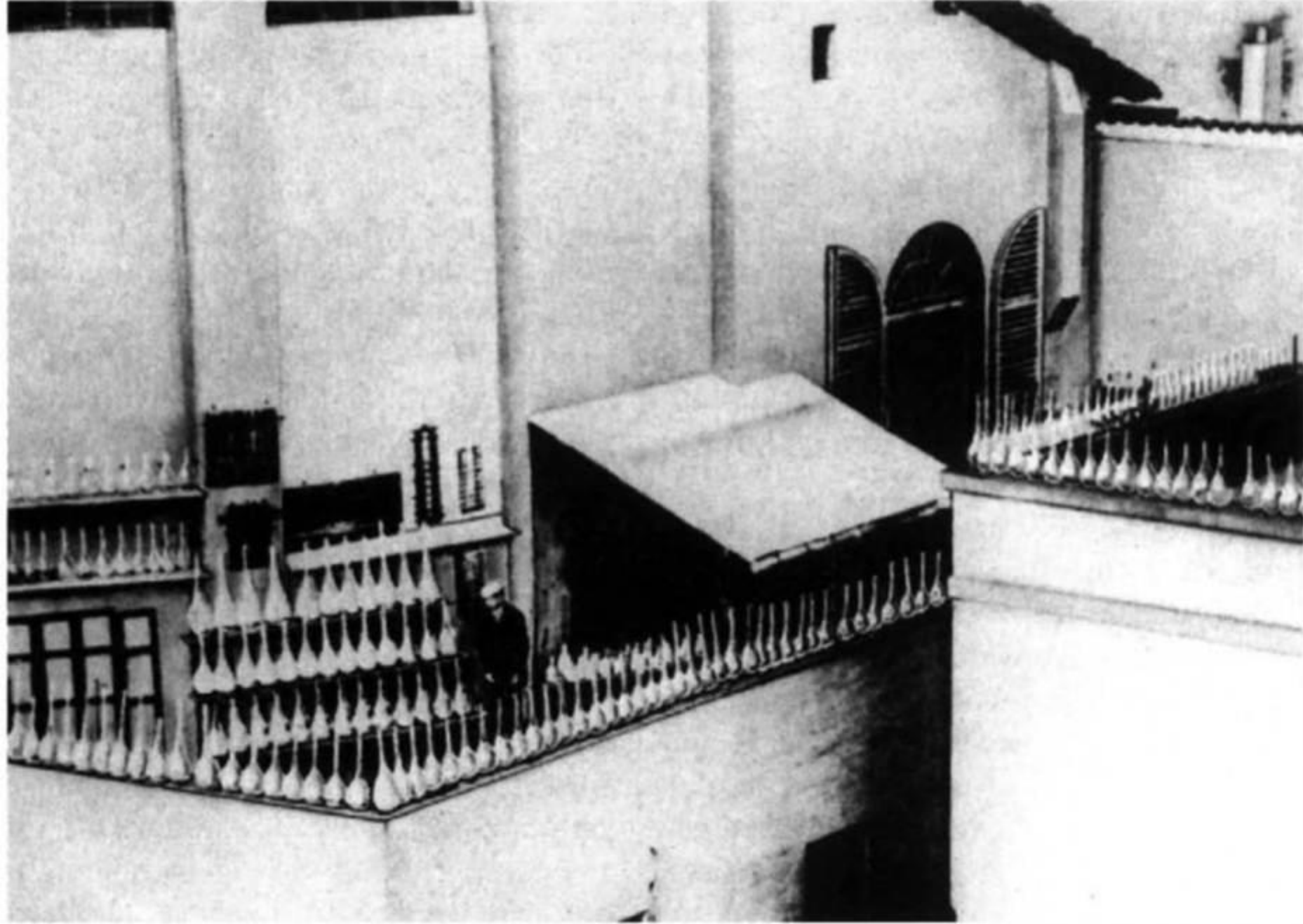


Photo courtesy of the University of Bologna



*G. Ciamician*

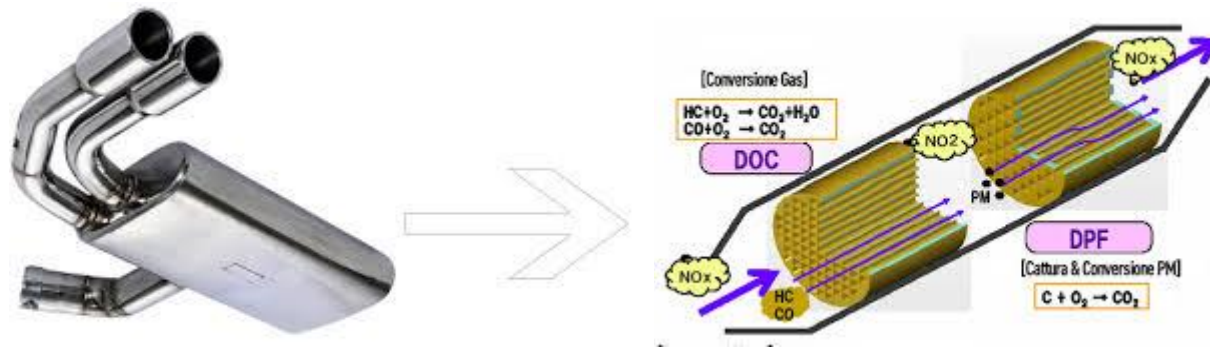
"On the arid lands there will spring up industrial colonies without smoke and without smokestacks; forests of glass tubes will extend over the plains and glass buildings will rise everywhere; inside of these will take place the photochemical processes that hitherto have been the guarded secret of the plants, but that will have been mastered by human industry which will know how to make them bear even more abundant fruit than nature, for nature is not in a hurry and mankind is."

Giacomo Luigi Ciamician  
Science 36, 385-394 (1912)

# Catalysts

Catalysts are compounds that participate in reactions, accelerating them, without wearing out.

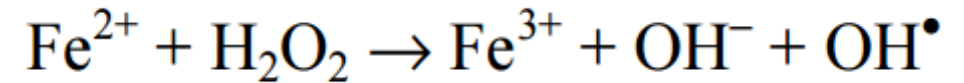
For example, how many times have you changed the catalytic converter? NEVER!



The catalysts used in this field are formed of noble metals (generally platinum and rhodium) dispersed on a ceramic support, formed by cerium oxide and zirconium oxide. They promote the simultaneous oxidation of unburnt fuel and carbon monoxide to carbon dioxide and water, and the reduction of nitrogen oxides to nitrogen and water.

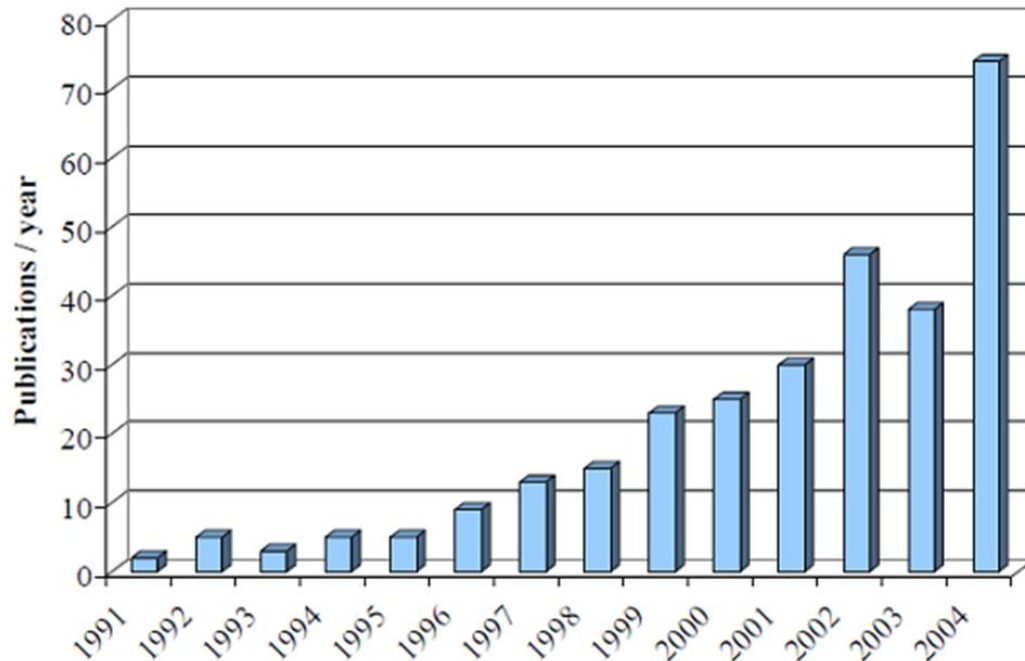
# Foto-Fenton

It is a young process that has its roots in a reaction discovered (accidentally) in 1894 by Henry John Horstman Fenton:



Fenton reacton

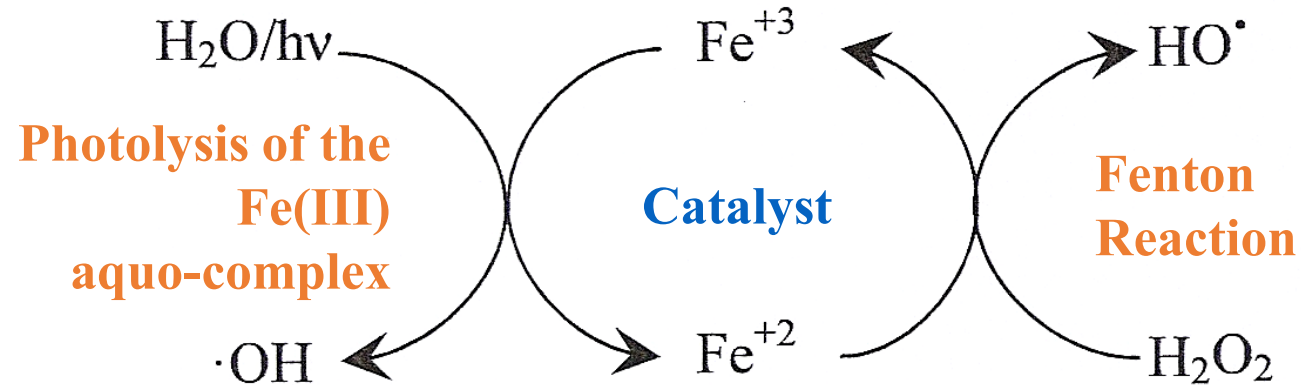
**Has a consequence, we obtain:  
High consumption of Fe(II) e H<sub>2</sub>O<sub>2</sub>  
High production of sludge (Fe(II) and Fe(III) hydroxides)**



Number of publications on photo-Fenton in peer-reviewed journals (source: [www.scopus.com](http://www.scopus.com), November 2005)



# Photo-Fenton



**Fe(II) is a catalyst because it is not consumed!**

**The process uses a renewable energy source: solar radiation.**

We need to understand:

What is the Fe (III) aqueo-complex;

Which is the optimal pH of the process;

How does the Fe (III) aqueo-complex photolyses.

# Fe(III) complexes

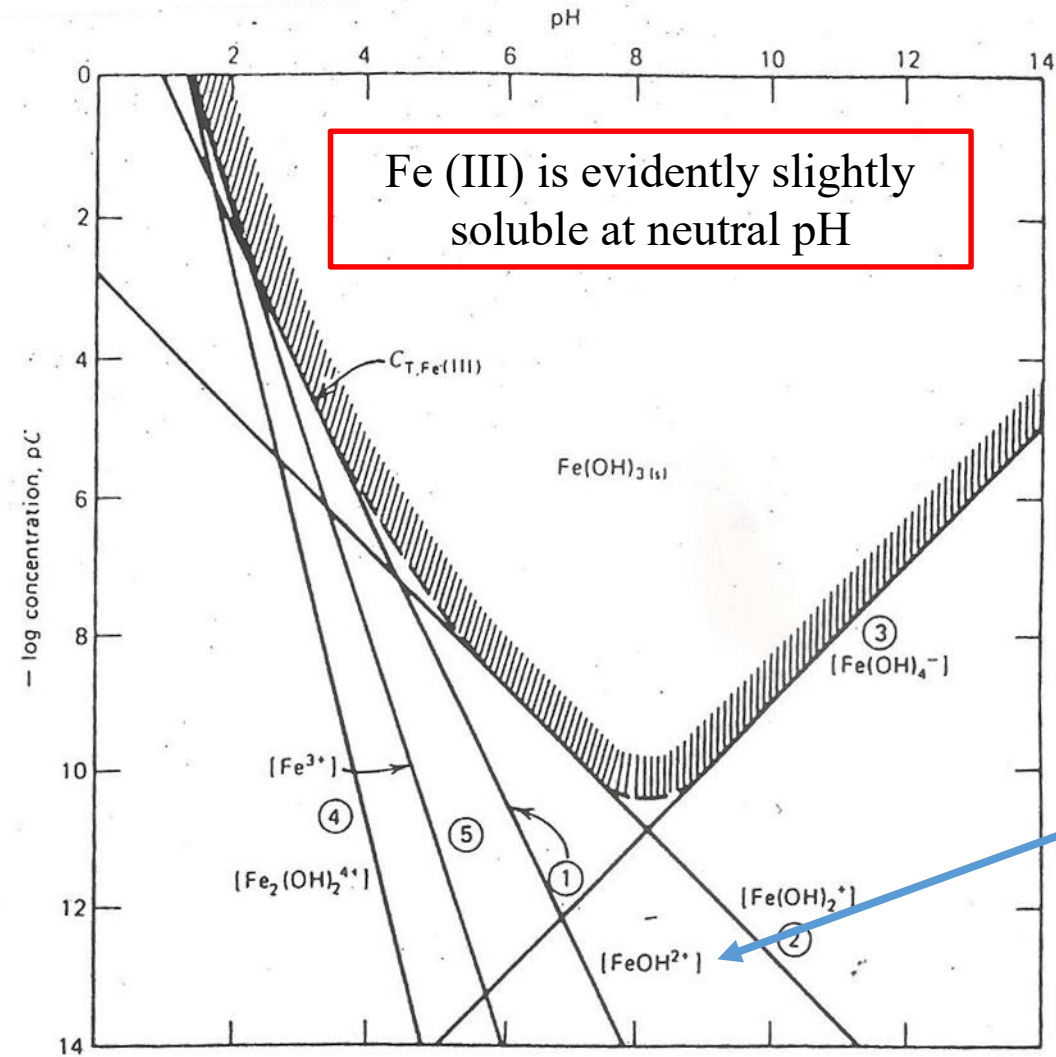
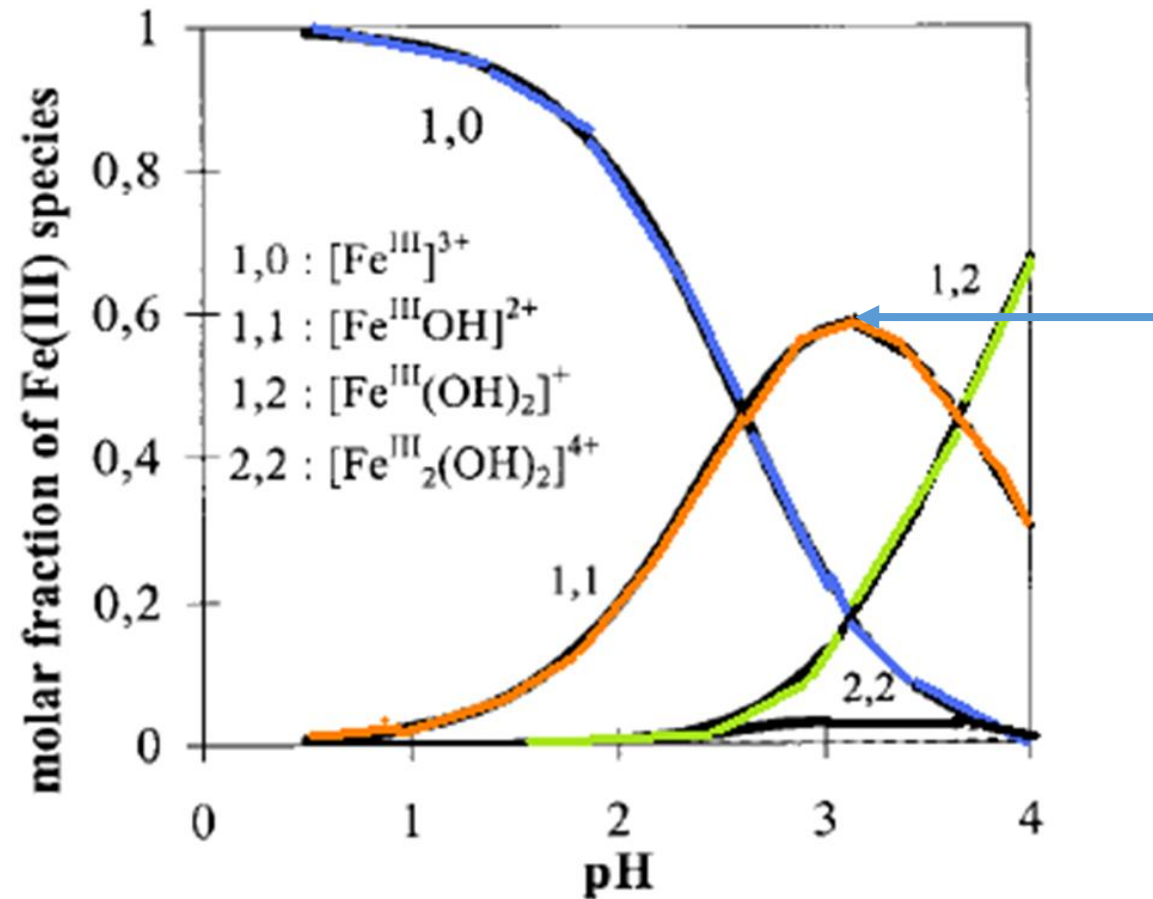


Figure 19-6. Equilibrium concentration of hydroxo iron(III) complexes in a solution in contact with freshly precipitated  $\text{Fe(OH)}_3(\text{s})$  at 25°C. (From Ref. 18-1.)

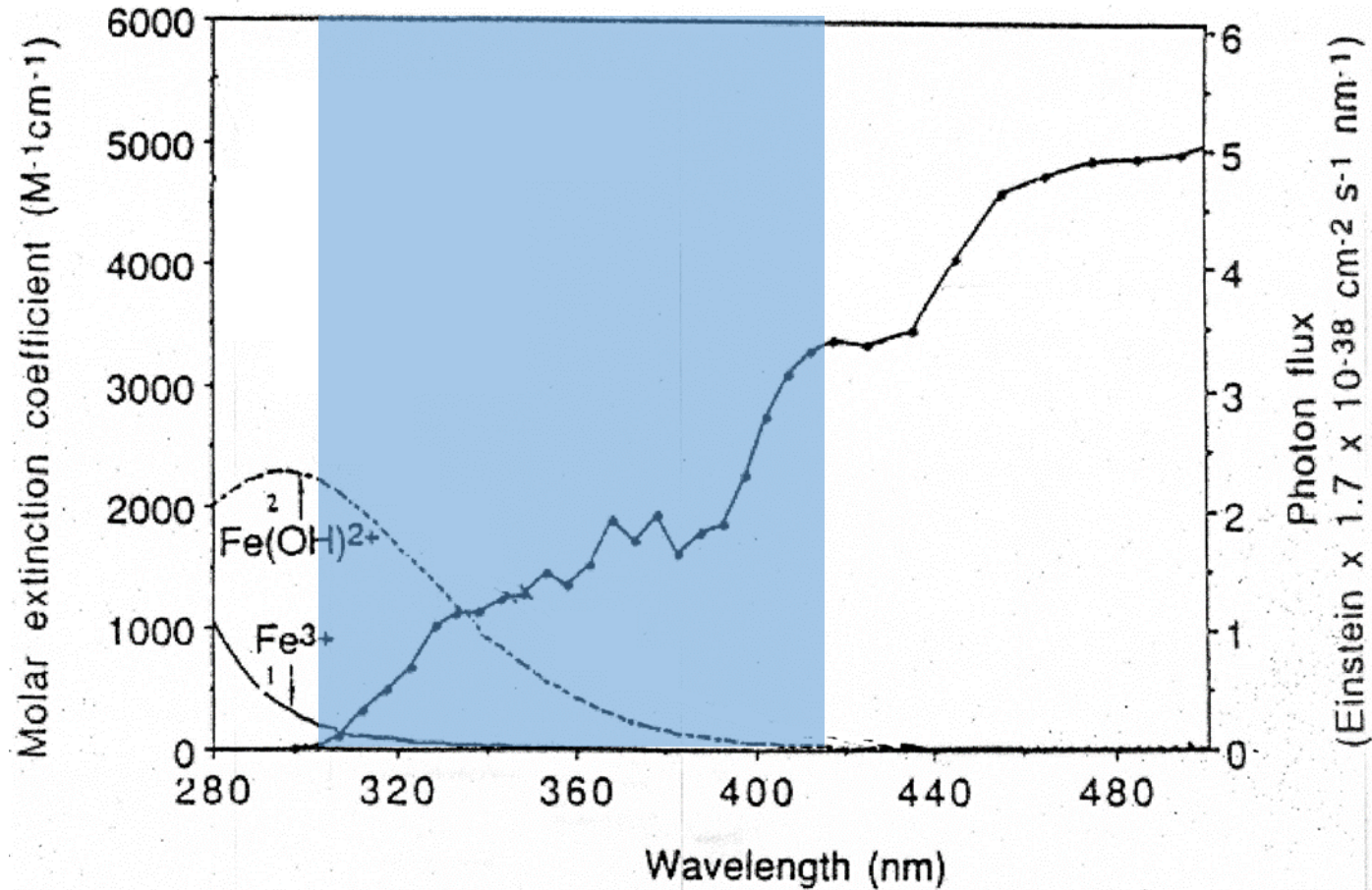
# Fe(III) complexes



the maximum concentration of the monoquo-complex of Fe (III) is at pH = 3

Fig. 1. Speciation of  $\text{Fe}^{\text{III}}$  species in acidic aqueous solution ( $[\text{Fe}^{\text{III}}] = 1 \times 10^{-3} \text{ mol l}^{-1}$ , the dashed lines denote region supersaturated with respect to amorphous  $[\text{Fe}^{\text{III}}(\text{OH})_3]$ ,  $I = 0.1 \text{ M NaClO}_4$ ,  $25^\circ\text{C}$ ).

# Fe(III) monoquo-complex photolysis



# Foto-Fenton

## **advantages:**

- 1) It uses dissolved Fe(II) ions as catalysts;
- 2) It uses the UV solar visible radiation.

## **disadvantages:**

- 1) The process need the consumption of acid to lower the pH at the optimal values (2,8-3,0);
- 2) At the end of the process, basses have to be added to rise the pH at neutral values;
- 3) It is necessary to recover all the iron that precipitates during 2<sup>nd</sup> phase and make sure that not too much dissolved iron is discharged;
- 4) The process requires the use of hydrogen peroxide.



# Titanium dioxide

## Advantages:

- 1) It uses  $\text{TiO}_2$  (it is cheap) as catalyst;
- 2) Titanium dioxide is sedimentable solid: it can be easily and economically recovered at the end of the treatment;
- 3) The process exploits UV-visible radiation;
- 4) The process does not require the addition of reagents: titanium dioxide is very effective at neutral pH and does not require the use of other oxidizing species. The oxygen dissolved in water is enough!.

## Disadvantages:

There are none! But...

titanium dioxide absorbs only a small part of the solar energy that arrives daily on earth (3-5%). In addition, a large part of the absorbed solar energy is released in the form of heat (the hole-electron recombination reaction is predominant). Il mondo scientifico sta facendo di tutto per migliorare l'efficienza di tale catalizzatore.

Currently titanium dioxide is not widely used for water purification. Titanium dioxide is widely used as a photocatalyst in other applications: air purification.

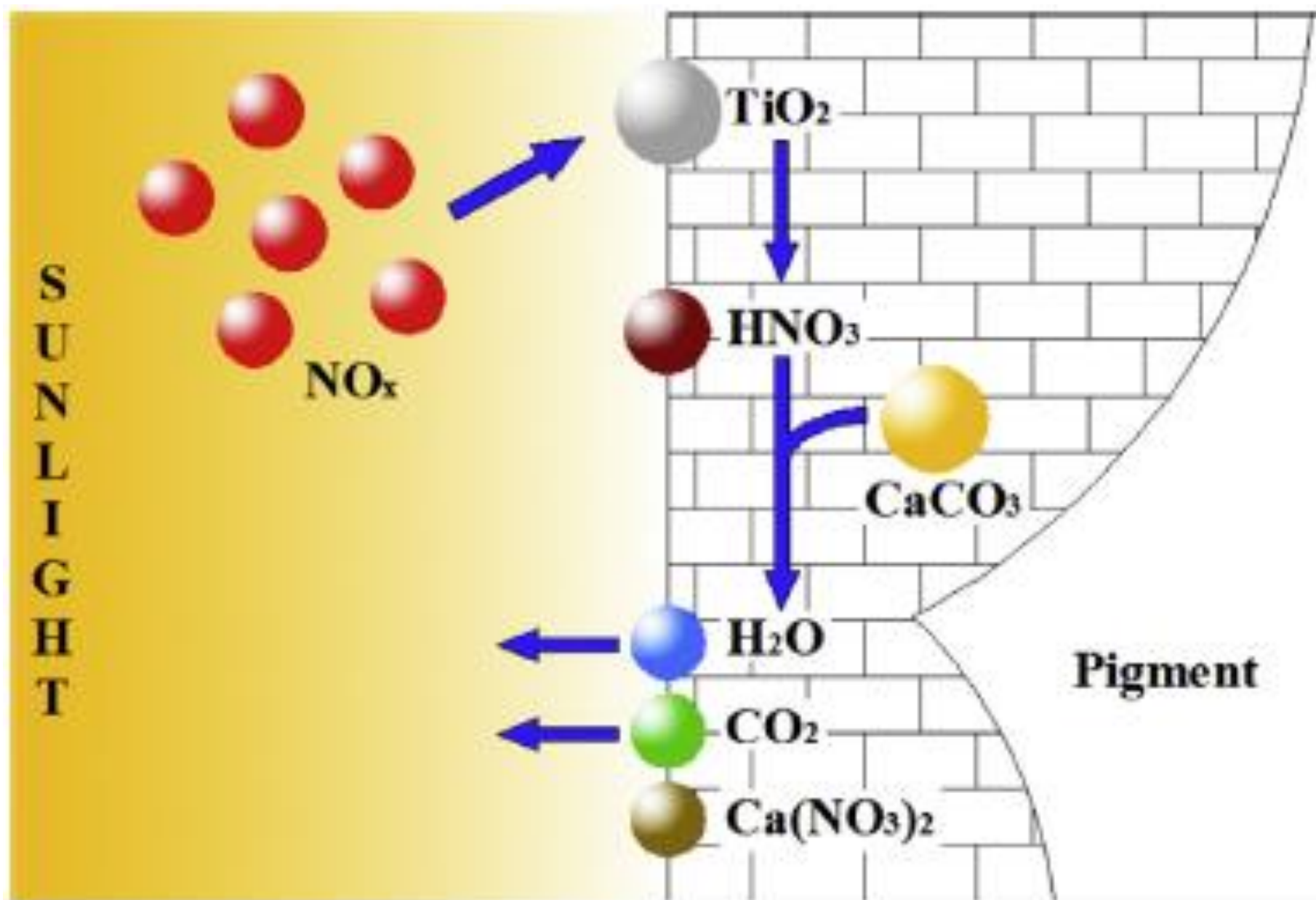


Dives in Misericordia Church in Rome (left); Cité de la Musique et des Beaux-Arts in Chambéry (right).

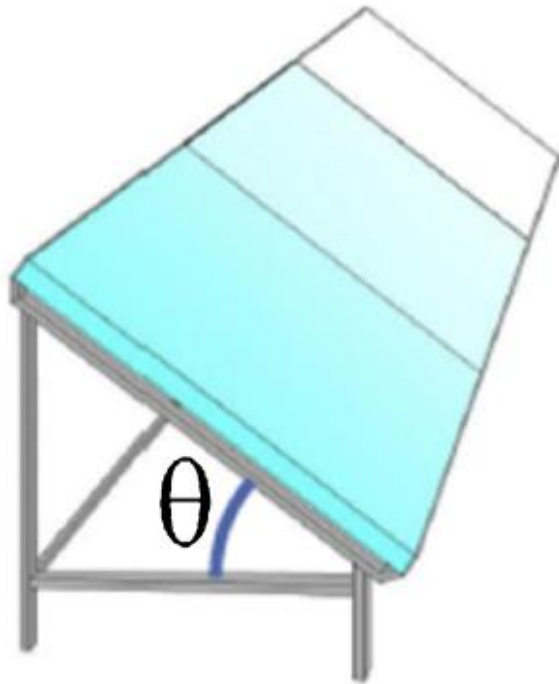
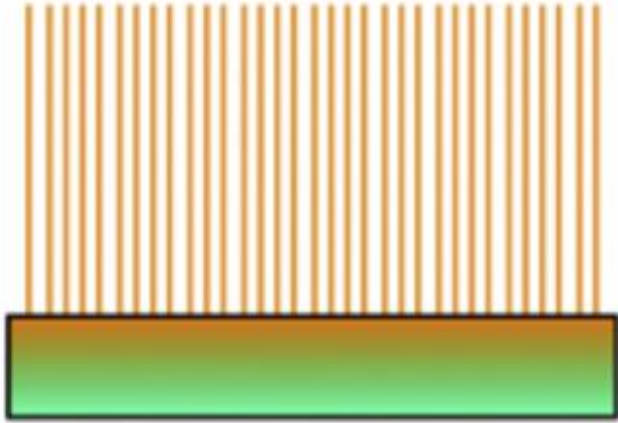




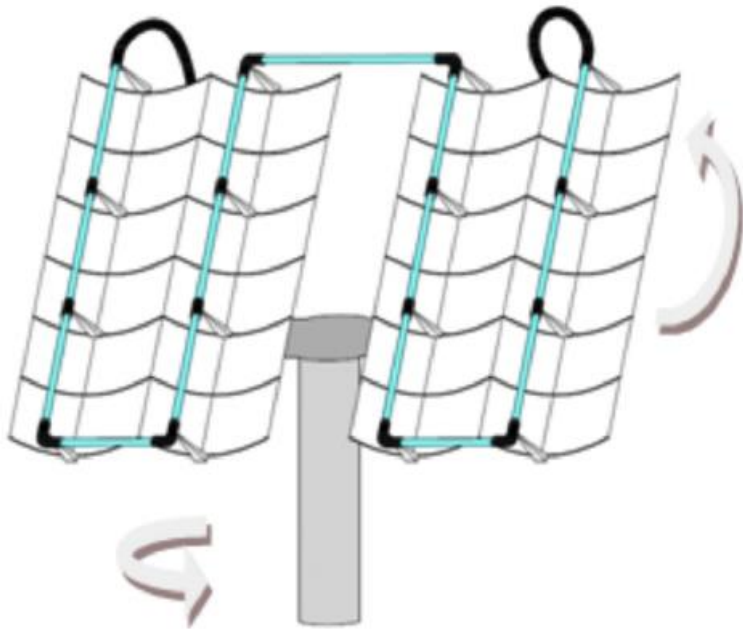
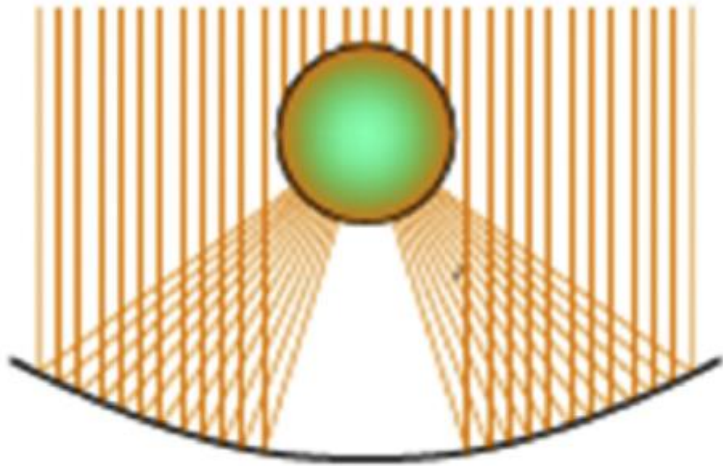
(a) Cowboy Stadium (Dallas, U.S.), (b) Tokyo University (Japan), (c) Kajigaya Station (Japan), (d) YAS Marina Circuit (UAE). Manufacturer: Taiyo Kogyo Corporation.



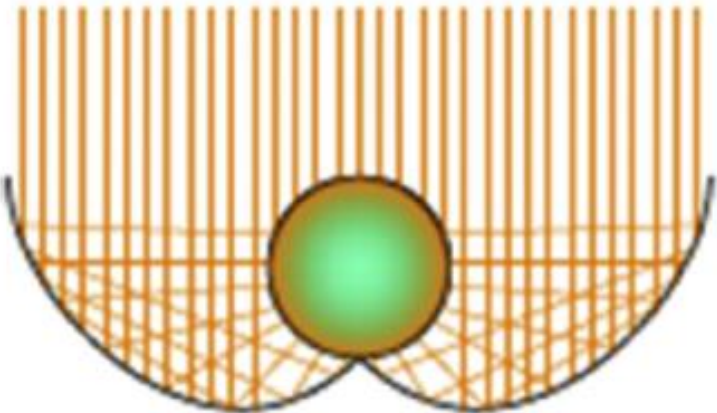
# Non-concentrating collectors (NCC)

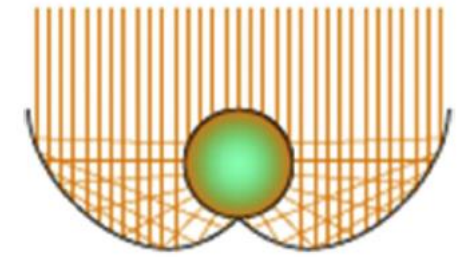
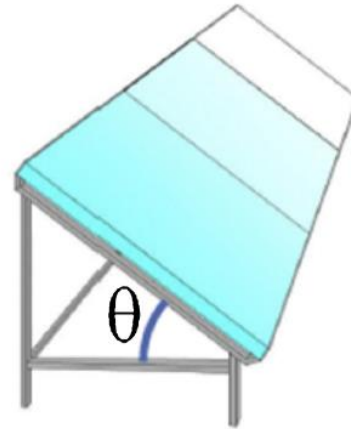
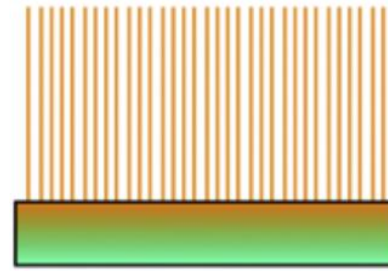
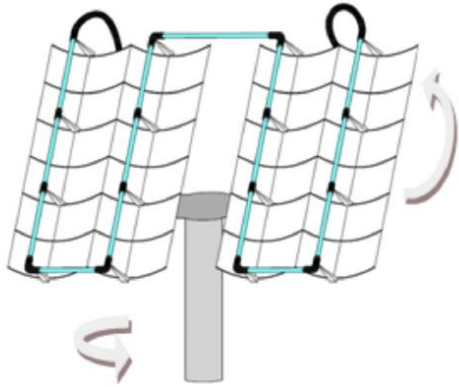
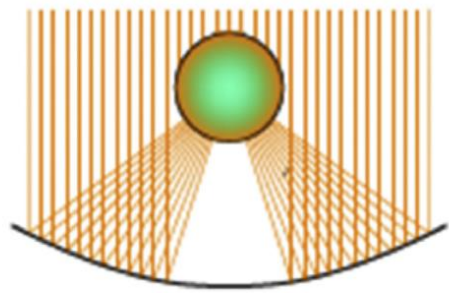


# Parabolic trough collectors (PTC)



# Compound parabolic collectors (CPC)





PTC		NCC		CPC	
Smaller reactor volumes	Higher costs (sun tracking)	No optical losses and high optical efficiencies	Large reactor volumes	Smaller reactor volumes	Moderate capital cost
Higher flow rates	Direct solar beams	Low costs (no reflective surfaces)	Pressure limitations	Higher flow rates	Moderate heat generation
Better mass transfer	Optical losses	Simple design (no tracking parts)	Low mass transfer (Laminar flow)	Better mass transfer (turbulent flow)	Difficult to scale up
Low catalyst load	Overheating	Direct and diffuse solar beams	Reactant evaporation (if open)	Direct and diffuse solar radiation	-
Smaller reactor area	Low efficiency	No heating	-	Low catalyst load	-

## The collector area per mass ( $A_{CM}$ )

$$A_{CM} = \frac{10^3 \cdot A_r \cdot t \cdot \overline{E}_s}{M \cdot V_t \cdot t_o \cdot E_s^o \cdot (C_i - C_f)}$$

“batch”

$$A_{CM} = \frac{10^3 \cdot A_r \cdot \overline{E}_s}{M \cdot F \cdot t_o \cdot E_s^o \cdot (C_i - C_f)}$$

“through-flow”

$A_{CM}$ : the collector area required to reduce a unit of substrate mass in the reactor system in a reference time of 1 h ( $t_0$ ) and incident solar irradiance of  $1000 \text{ W m}^{-2}$  ( $E_s^0$ ) based on the AM1.5 standard solar spectrum on a horizontal surface.

$A_r$  is the real collector area,  $M$  is the molar mass of the substrate ( $\text{g mol}^{-1}$ ),  $V_t$  is the volume of treated solution (L),  $E_s$  ( $\text{W m}^{-2}$ ) is the average direct solar irradiance during reaction time  $t$ ,  $F$  ( $\text{m}^3 \text{ h}^{-1}$ ) is the flow rate, and  $C_i$  and  $C_f$  are the starting and final substrate concentrations ( $\text{mol L}^{-1}$ ), respectively.

# Photo-Fenton

	Substance	$[C]_0$ (mg/L)	Removal (%)	$V_t$ (L)	$V_l$ (L)	$S$ (m <sup>2</sup> )	[Fe] (mM)	Fe source	$[H_2O_2]$ (mM)	pH	Solvent	Collector geometry	$A_{CM}$ (m <sup>2</sup> )	Refs.
1a	Direct Black 38	100	80	3	0.05	0.1	0.1	FeSO <sub>4</sub>	5	2	Syntetic wastewater	CPC	$4.09 \times 10^2$	[171]
1b	Direct Black 38	100	90	3	0.05	0.1	1	FeSO <sub>4</sub>	50 (in 2 portions)	2	Syntetic wastewater	CPC	$3.64 \times 10^2$	
1c	Direct Black 38	100	60	3	0.05	0.1	1	FeSO <sub>4</sub>	50 (in 2 portions)	2	Real wastewater	CPC	$5.60 \times 10^2$	
2a	Phenols (from olive mill wastewaters)	3000	97	30	22.4	3.08	1	FeSO <sub>4</sub>	588	2.8	Real wastewater	CPC	$5.75 \times 10^{2^{***}}$	[159]
2b	Phenols (from olive mill wastewaters)	2800	79	30	22.4	3.08	5	FeSO <sub>4</sub>	147	2.8	Real wastewater	CPC	$4.91 \times 10^{2^{***}}$	
2c	Phenols (from olive mill wastewaters)	2700	88	19	-	1	5	FeSO <sub>4</sub>	147	2.8	Real wastewater	FFR	$7.95 \times 10^{2^{***}}$	
3	Mixture of 10 commercial pesticides	100	88	250	108	9	1	FeSO <sub>4</sub>	1 (in 5 portions)	2.8	Desalinated water	CPC	$1.35 \times 10^{3^{***}}$	[174]
4a	4-Chlorophenol	216	100	4	2	0.42	0.75	FeSO <sub>4</sub>	45	2.8	Distilled water	Pool	$1.74 \times 10^{2^{**}}$	[208]
4b	4-Chlorophenol	216	100	12	12	0.42	0.75	FeSO <sub>4</sub>	45	2.8	Distilled water	Pool	75 <sup>**</sup>	
4c	4-Chlorophenol	216	100	20	20	0.42	0.75	FeSO <sub>4</sub>	45	2.8	Distilled water	Pool	52 <sup>**</sup>	
5a	Imidacloprid	52	100	40	22	3	0.05	FeSO <sub>4</sub>	15 (maintained constant)	2.8	Desalinated water	CPC	$5.54 \times 10^{2^*}$	[207]
5b		28	98										$1.74 \times 10^{2^*}$	
6a	Diethyl phthalate	58	100	40	22	3	0.305	Fe(ClO <sub>4</sub> ) <sub>3</sub>	0	-	Desalinated water	CPC	$4.10 \times 10^{2^{***}}$	[175]
6b		38	85										$1.36 \times 10^{3^{***}}$	
7a	Grape juice (WG)	1185	93	40	22	3	55	FeSO <sub>4</sub>	12	3	Milli-Q water	CPC	$3.89 \times 10^{2^*}$	[209]
7b	Red wine (WV)	1185	46				55						$8.07 \times 10^{2^*}$	
7c	WG and WV (50:50)	1165	90				20						$1.53 \times 10^{2^*}$	
7d	WG and WV (50:50)	1165	84				20						$1.64 \times 10^{2^*}$	
7e	WG and WV (50:50) without ethanol	1165	96				20						$1.25 \times 10^{2^*}$	



# Titanium Dioxide

	Substance	[C] <sub>0</sub> (mg/L)	Removal (%)	V <sub>r</sub> (L)	V <sub>i</sub> (L)	S (m <sup>2</sup> )	[TiO <sub>2</sub> ] (mg/l)	Form	pH	Solvent	Collector geometry	A <sub>CM</sub> (m <sup>2</sup> )	Refs.
1a	Methyl-oxydemeton	50	70	25	15.1	2.15	200	Slurry (degussa P-25)	-	Water (milli Q grade)	CPC	1.16 × 10 <sup>6</sup>	[201]
1b	Methidathion	50	100	25	15.1	2.15	200	Slurry (degussa P-25)	-	Water (milli Q grade)	CPC	4.06 × 10 <sup>5</sup>	
1c	Carbaryl	50	100	25	15.1	2.15	200	Slurry (degussa P-25)	-	Water (milli Q grade)	CPC	1.62 × 10 <sup>6</sup>	
1d	Dimethoate	50	100	25	15.1	2.15	200	Slurry (degussa P-25)	-	Water (milli Q grade)	CPC	8.54 × 10 <sup>5</sup>	
2a	Progesterone	0.1	100	10	0.96	0.3	335	Immobilized (HP on glass spheres)	-	Syntetic water	CPC	8.93 × 10 <sup>5</sup>	[202]
2b	Triclosan	0.1	100	10	0.96	0.3	335	Immobilized (HP on glass spheres)	-	Syntetic water	CPC	4.46 × 10 <sup>5</sup>	
2c	Hydroxybiphenyl	0.1	100	10	0.96	0.3	336	Immobilized (HP on glass spheres)	-	Syntetic water	CPC	2.23 × 10 <sup>6</sup>	
2d	Diclofenac	0.1	100	10	0.96	0.3	337	Immobilized (HP on glass spheres)	-	Syntetic water	CPC	2.23 × 10 <sup>6</sup>	
2e	Ibuprofen	0.1	100	10	0.96	0.3	338	Immobilized (HP on glass spheres)	-	syntetic water	CPC	2.90 × 10 <sup>6</sup>	
2f	Ofloxacin	0.1	100	10	0.96	0.3	339	Immobilized (HP on glass spheres)	-	Syntetic water	CPC	4.46 × 10 <sup>5</sup>	
2g	Caffeine	0.1	100	10	0.96	0.3	340	Immobilized (HP on glass spheres)	-	Syntetic water	CPC	1.78 × 10 <sup>6</sup>	
2h	Acetaminophen	0.1	100	10	0.96	0.3	341	Immobilized (HP on glass spheres)	-	Syntetic water	CPC	1.78 × 10 <sup>6</sup>	
2i	Sulfamethoxazole	0.1	100	10	0.96	0.3	342	Immobilized (HP on glass spheres)	-	Syntetic water	CPC	4.91 × 10 <sup>6</sup>	
2j	Antipyrine	0.1	70	10	0.96	0.3	343	Immobilized (HP on glass spheres)	-	Syntetic water	CPC	8.29 × 10 <sup>6</sup>	
2k	Flumequine	0.1	100	10	0.96	0.3	344	Immobilized (HP on glass spheres)	-	Syntetic water	CPC	1.34 × 10 <sup>6</sup>	
2l	Isoproturon	0.1	100	10	0.96	0.3	345	Immobilized (HP on glass spheres)	-	Syntetic water	CPC	5.35 × 10 <sup>6</sup>	
2m	Ketorolac	0.1	100	10	0.96	0.3	346	Immobilized (HP on glass spheres)	-	Syntetic water	CPC	5.36 × 10 <sup>6</sup>	
2n	Carbamazepine	0.1	100	10	0.96	0.3	347	Immobilized (HP on glass spheres)	-	Syntetic water	CPC	5.36 × 10 <sup>6</sup>	
2o	Atrazine	0.1	80	10	0.96	0.3	335	Immobilized (HP on glass spheres)	-	Syntetic water	CPC	7.25 × 10 <sup>6</sup>	
3a	Cyanides	50	100	247	108	8.9	200	Slurry (100% anatase HP)	10	Desalinated water	CPC	2.09 × 10 <sup>5</sup>	[162]
3b	Cyanides	50	88	975	675	100	200	Slurry (100% anatase HP)	10	Raw water	CPC	5.44 × 10 <sup>5</sup>	
4a	2,4-Dichlorophenoxyacetic acid	28	100	247	108	8.9	200	Slurry (degussa P-25)	-	Desalinated water	CPC	8.20 × 10 <sup>5</sup>	[203]
5a	Oxalic acid	900	85	10	5.4	0.72	200	Slurry (>99% anatase Aldrich)	-	Water	CPC	2.10 × 10 <sup>5</sup>	[176]
5b	Oxalic acid	900	70	10	0.67	0.72	200	Slurry (>99% anatase Aldrich)	-	Water	PTC	2.54 × 10 <sup>5</sup>	
5c	Oxalic acid	900	70	10	8	0.72	200	Slurry (>99% anatase Aldrich)	-	Water	Flat tubular	2.54 × 10 <sup>5</sup>	
5d	Carbaryl	50.3	77	10	5.4	0.72	500	Slurry (>99% anatase Aldrich)	-	Water	CPC	4.10 × 10 <sup>5</sup>	
5e	Carbaryl	50.3	68	10	0.67	0.72	500	Slurry (>99% anatase Aldrich)	-	Water	PTC	4.70 × 10 <sup>5</sup>	
5f	Carbaryl	50.3	55	10	8	0.72	500	Slurry (>99% anatase Aldrich)	-	Water	Flat tubular	5.92 × 10 <sup>5</sup>	
6	Oxytetracycline	15	100	15	2.94	0.91	500	Slurry (degussa P-25)	-	Water	CPC	8.47 × 10 <sup>5</sup>	[204]
7	Humic acid (sodium salt)	10	90	50	16	1	20 (g/m <sup>2</sup> )	Immobilized (degussa P-25 on 1049 AHLSTROM paper)	-	Deionized water	CPC	6.17 × 10 <sup>6</sup>	[205]
8	Yellow cibacron FN-2R	70	95	50	16	1	20 (g/m <sup>2</sup> )	Immobilized (degussa P-25 on 1049 AHLSTROM paper)	-	Well water	FFR	2.56 × 10 <sup>5</sup>	[142]
9a	2,4-Dichlorophenol	8	100	15	6.5	1.4	1500	Slurry (degussa P-25)	-	Tap water	CPC	1.20 × 10 <sup>6</sup>	[206]
9b	2,4-Dichlorophenol	22	100	15	6.5	1.4	1500	Slurry (degussa P-25)	-	Tap water	CPC	9.85 × 10 <sup>5</sup>	
10	Mix 10 commercial pesticides	100	30	250	108	9	200	Slurry (degussa P-25)	-	Desalinated water	CPC	1.59 × 10 <sup>6</sup>	[174]
11a	Imidacloprid	52	100	40	22	3	200	Slurry (degussa P-25)	-	Desalinated water	CPC	4.58 × 10 <sup>5</sup>	[207]
11b		28	98									3.19 × 10 <sup>6</sup>	

**The reactor surfaces are very large especially when working with titanium dioxide!**

**Furthermore, we are neglecting a very important thing...**



**WHAT?**

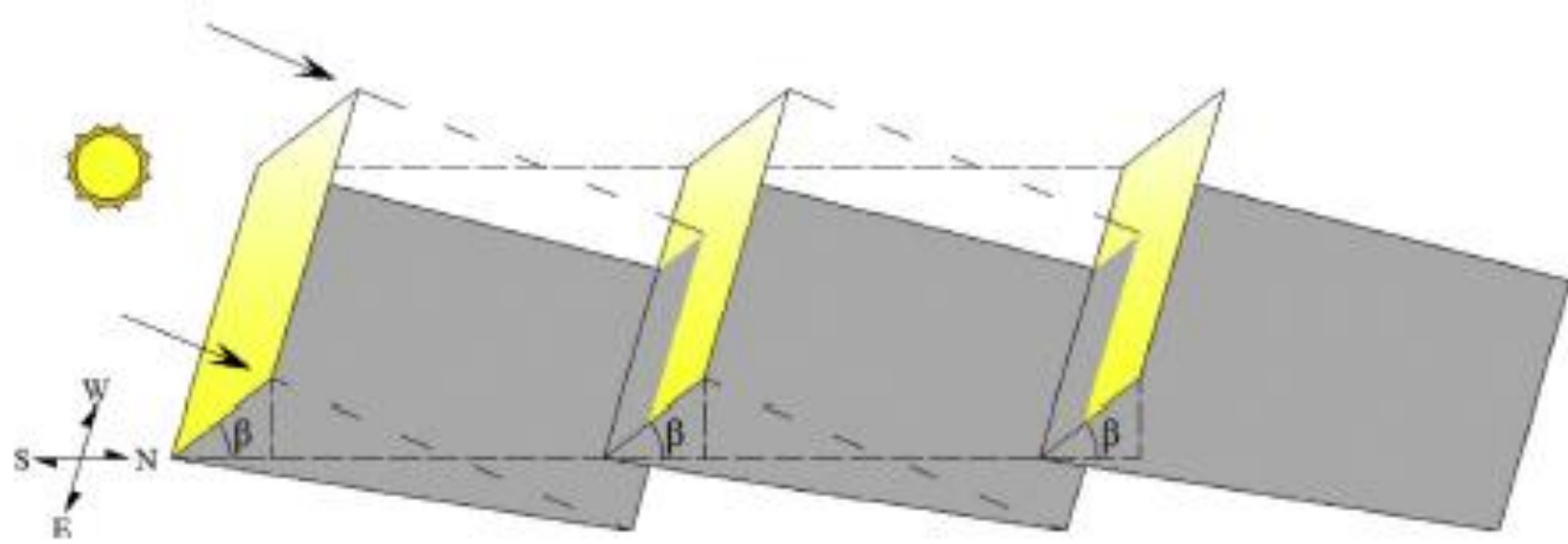


Fig. 13. Shading by collectors in a solar field.

