Technical Workshop
INDUSTRIAL WASTEWATER TREATMENT

Industrial wastewater treatment through combined processes

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Industrial wastewater

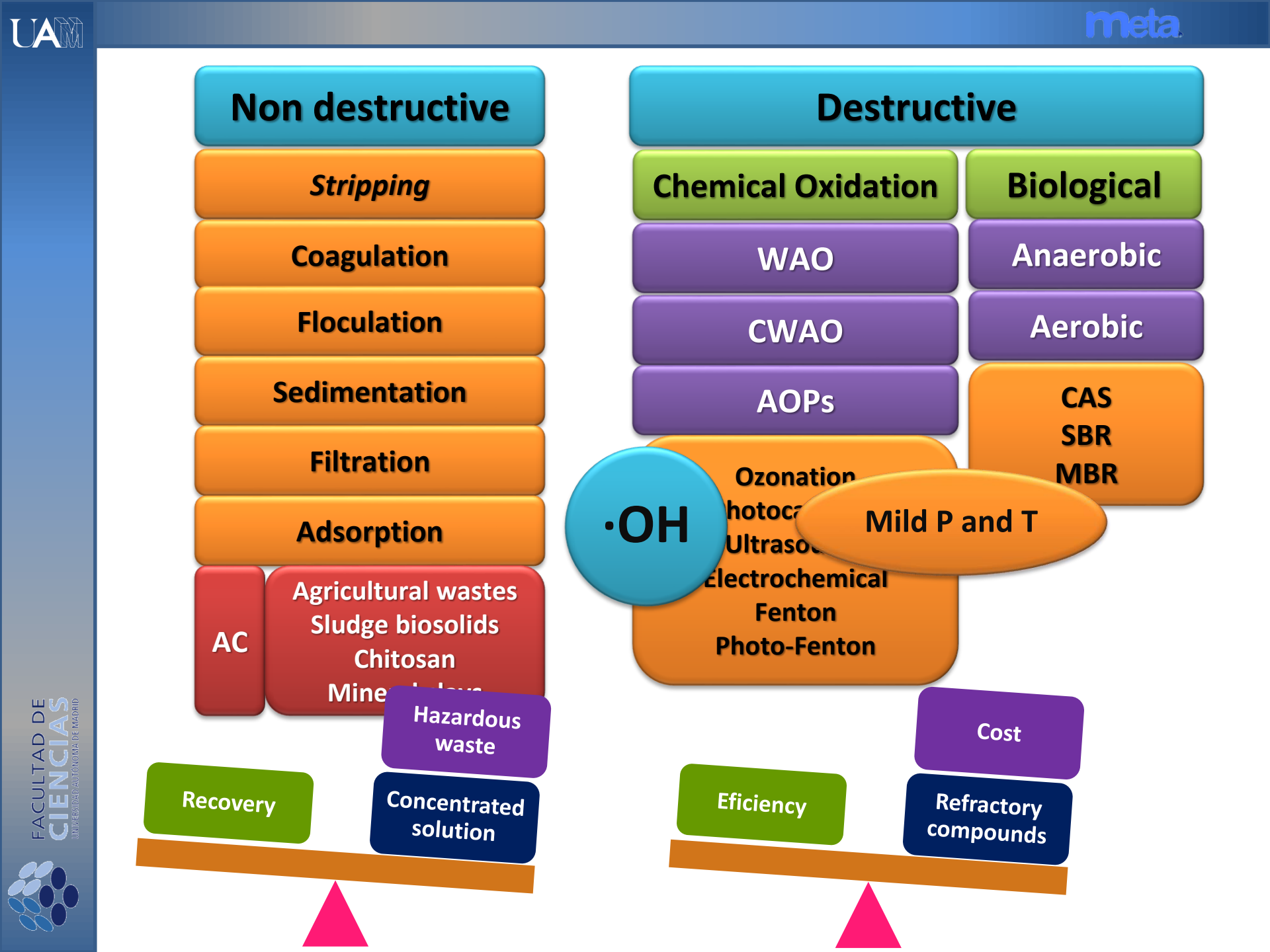
Wastewater derived from any industrial or commercial activity, not directly related to sanitary uses (washbasins, toilets, showers).

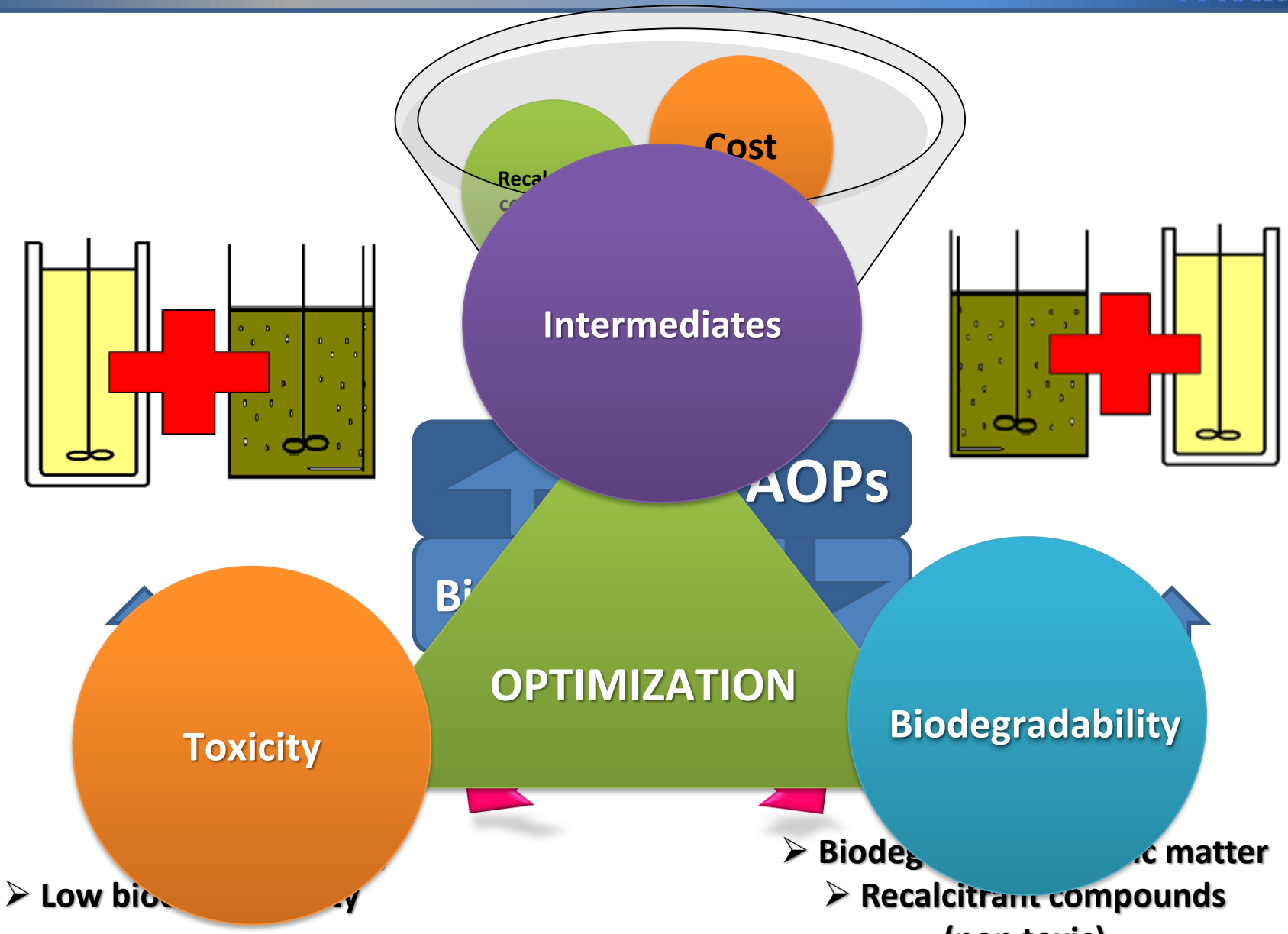
Herbicides
Pesticides

Phenols
Chlorophenols
Metals
Solvents

Drugs
Personal care products

Priority and Emerging Contaminants


Non destructive
Stripping
Coagulation
Floculation
Sedimentation
Filtration
Adsorption
AC
Agricultural wastes
Sludge biosolids
Chitosan
Hazardous waste
Recovery
Concentrated solution
Destructive
Chemical Oxidation
Biological
WAO
CWAO
AOPs
Anaerobic
Aerobic
CAS
SBR
MBR
·OH
Ozonation
Electrochemical
Fenton
Photo-Fenton
Mild P and T
Cost
Eficiency
Refractory compounds



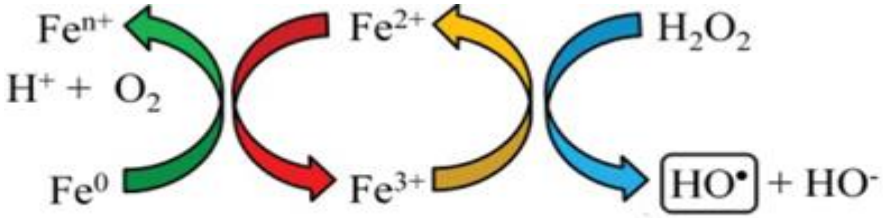
➢ Low bio… …y

➢ Biodeg… …ic matter

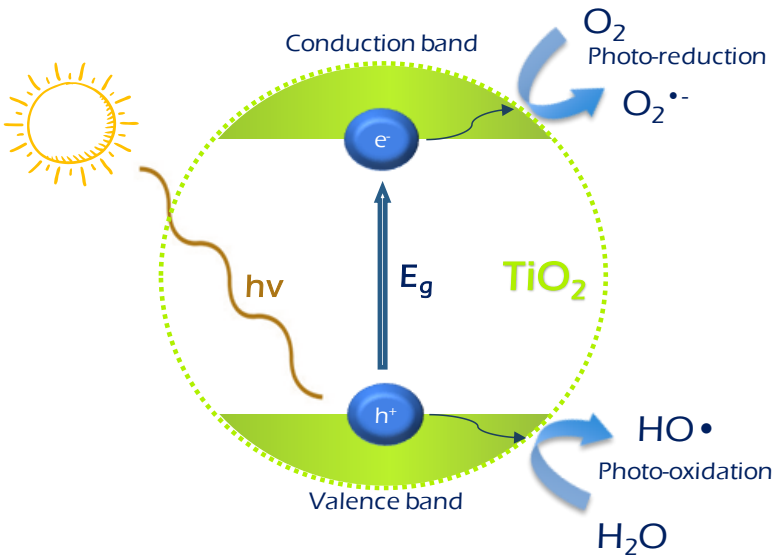
➢ Recalcitrant compounds (non toxic)

Advanced Oxidation Processes (AOPs)

Fenton oxidation

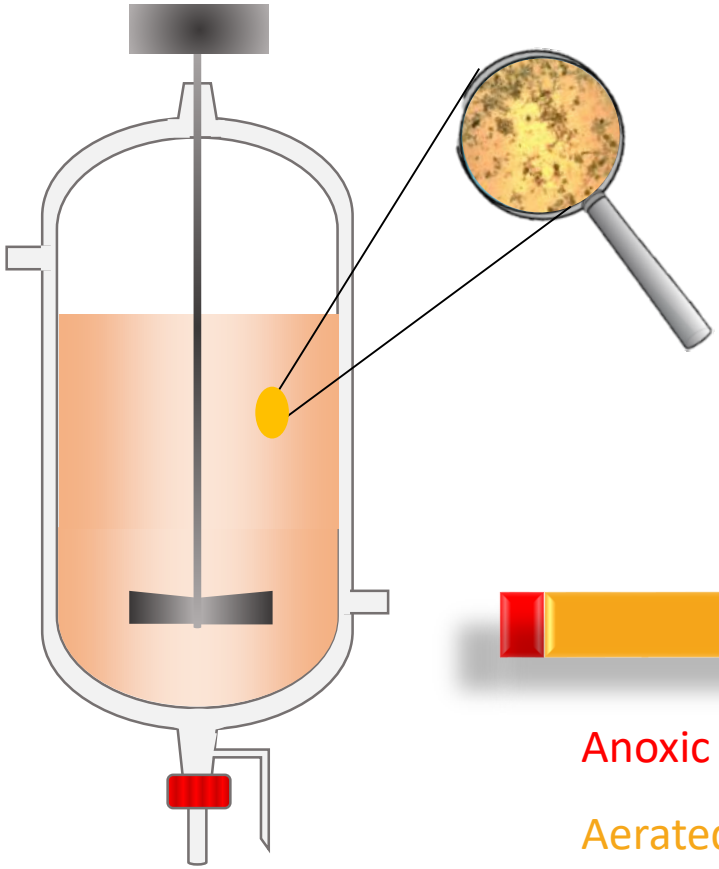


Photocatalysis



High cost ➡ AOPs as treatment to enhance biodegradability and reduce toxicity

Biological Oxidation (SBR)



- ✓ OLR 0.15-0.3 kg COD kg^{-1} SSV d^{-1}
- ✓ Biomass concentration: 2-4 g VSS L^{-1}
- ✓ Cellular retention time: 25 d
- ✓ Hydraulic residence time: 6 d
- ✓ Cycle: 6-8 h

Anoxic filling (0.5 h)

Aerated reaction (4.75-7 h)

Settle and draw (0.5-0.75 h)

THIAMETHOXAM (TMX)

Second generation
Neonicotinoids

Broad spectrum insecticidal activity

Widespread use and good stability

Bee population declination

Source of water contamination

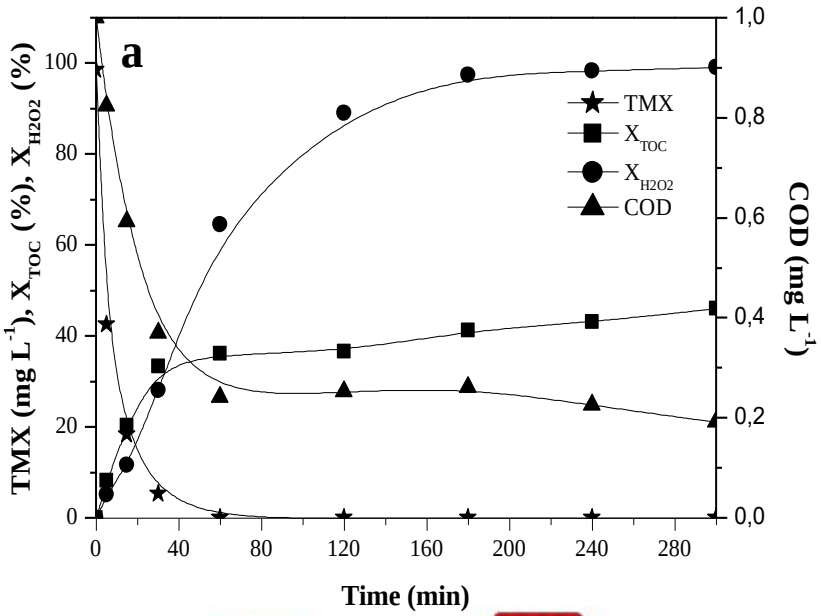
High toxicity microorganism

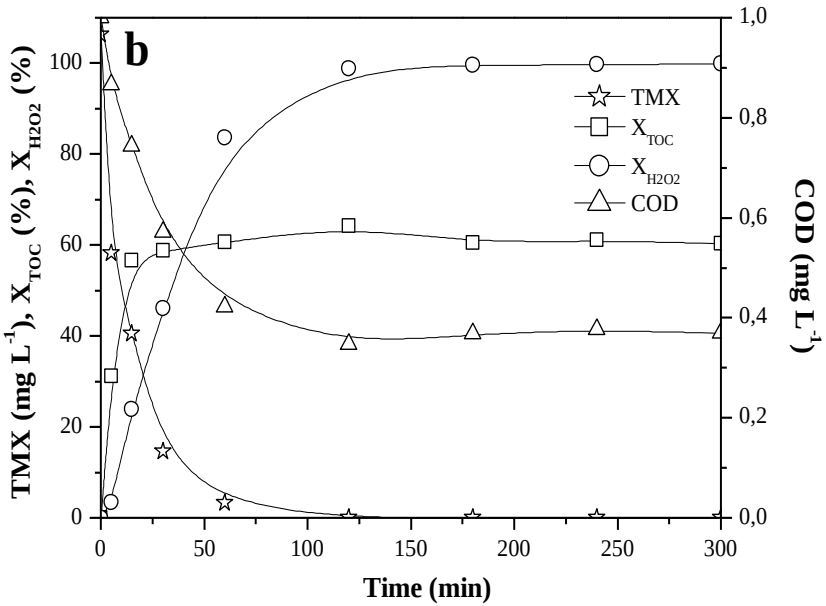
Bio-recalcitrant

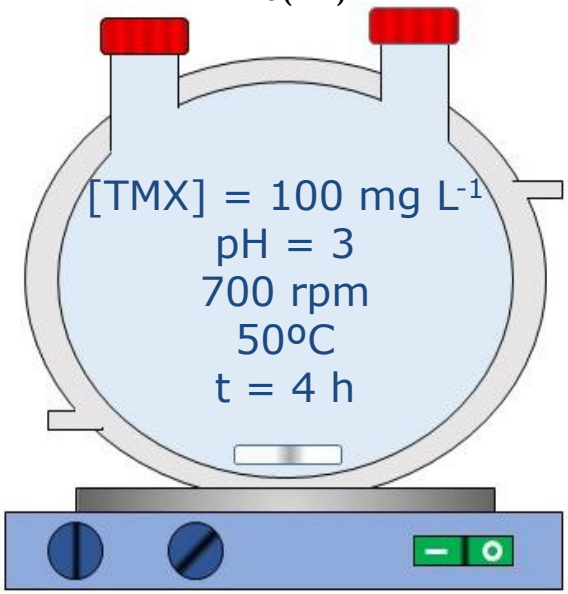
European Union expands ban of three neonicotinoid pesticides (2018)

Imidacloprid, *clothianidin* and *thiamethoxam*

FENTON OXIDATION





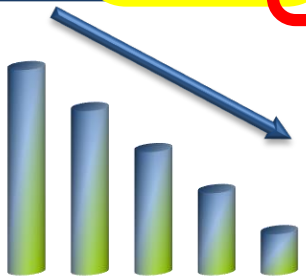


Time course of TMX concentration, COD removal, H_2O_2 and TOC conversion in the Fenton-like oxidation of pure TMX (a) and its commercial formulation (b) with a stoichiometric H_2O_2 dose.

Fenton Oxidation

TMX, TOC conversion and COD removal (%) upon Fenton oxidation at different H_2O_2 doses

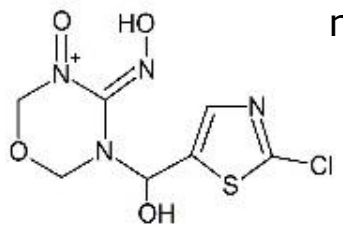
H_2O_2 (%)	TMX (commercial)				TMX (pure)			
	$X_{H_2O_2}$	X_{TMX}	X_{TOC}	X_{COD}	$X_{H_2O_2}$	X_{TMX}	X_{TOC}	X_{COD}
100	> 99	> 99	60.5	63.2	> 99	> 99	49.09	69.47
75	> 99	> 99	60.0	59.7	> 99	> 99	45.58	66.71
50	> 99	> 99	52.6	52.5	> 99	> 99	42.26	69.13
25	> 99	76.25	49.9	43.9				



(%) H_2O_2 dose

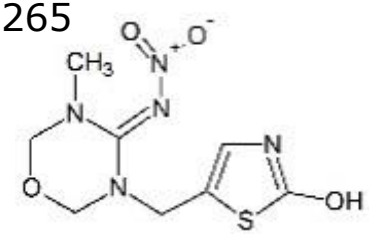
50-100 %
≈ COD-TOC removal

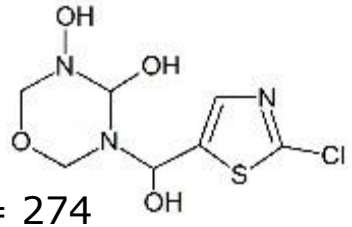
Identified by-products for Thiamethoxam oxidation



m/z = 278

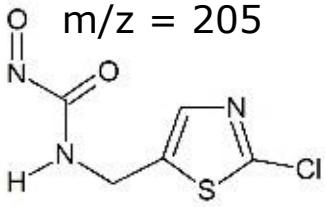
m/z = 265





m/z = 274

m/z = 247



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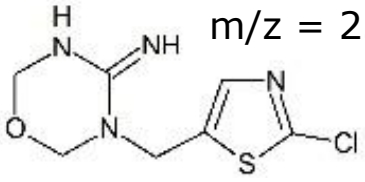

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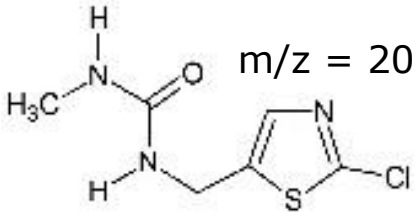

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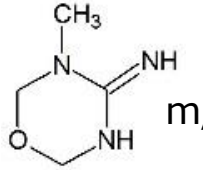

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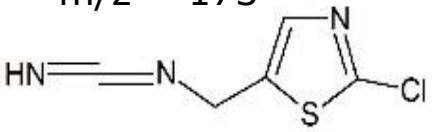

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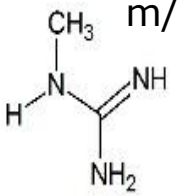

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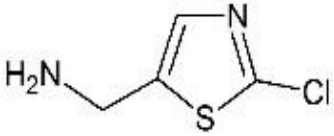

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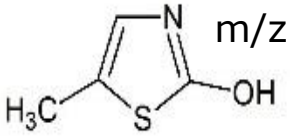

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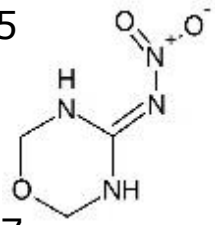

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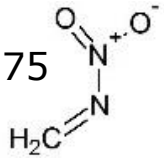
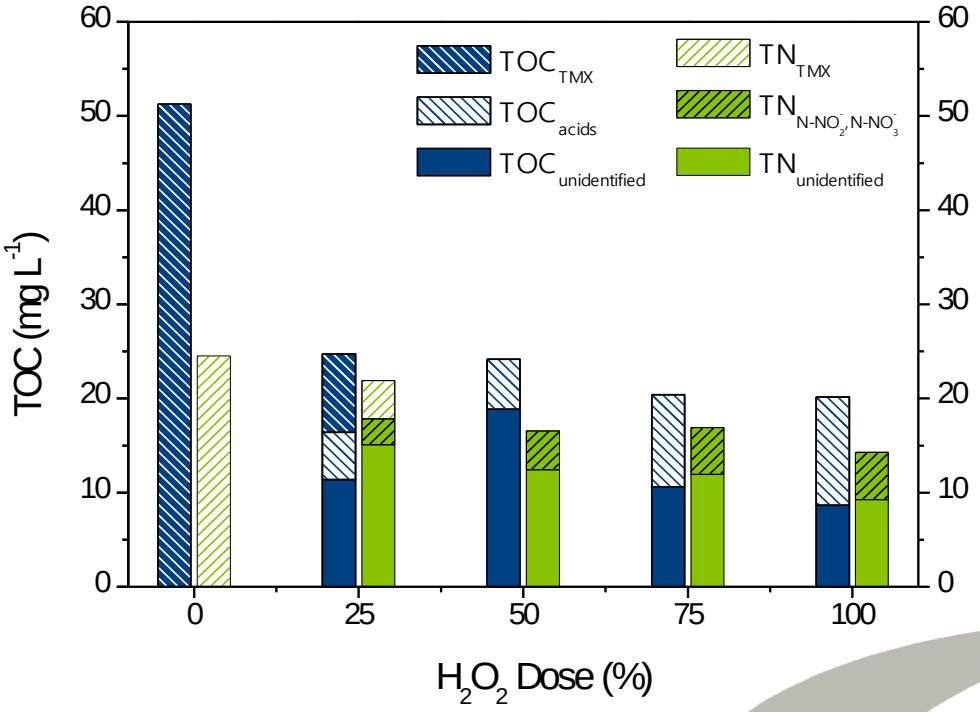
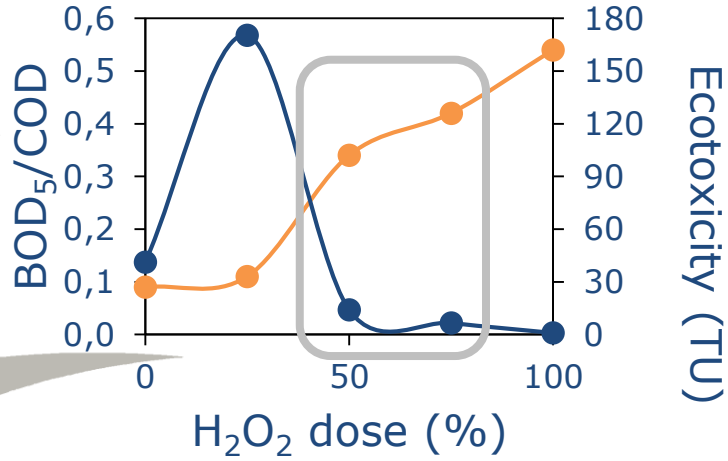


m/z = 75

Effluent characterization (commercial TMX)



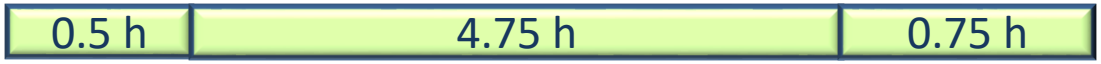
Measured and unidentified TN and TOC balance closure from Fenton oxidation.

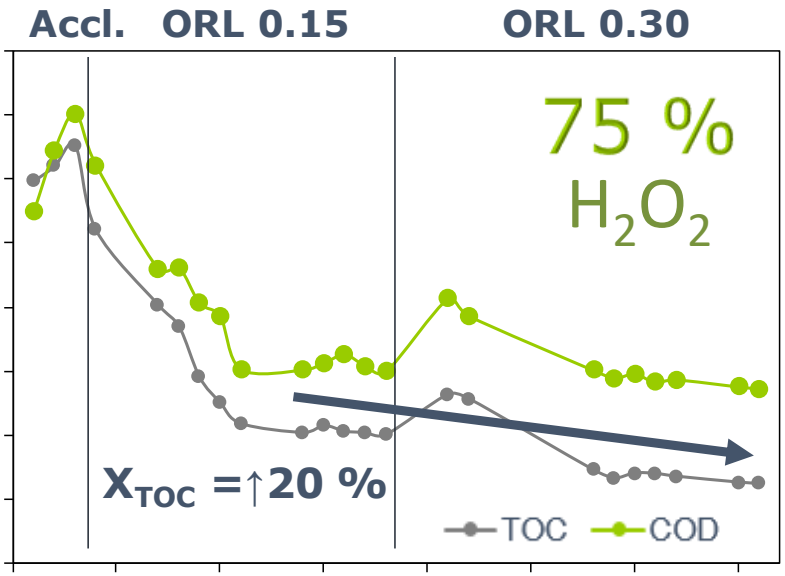


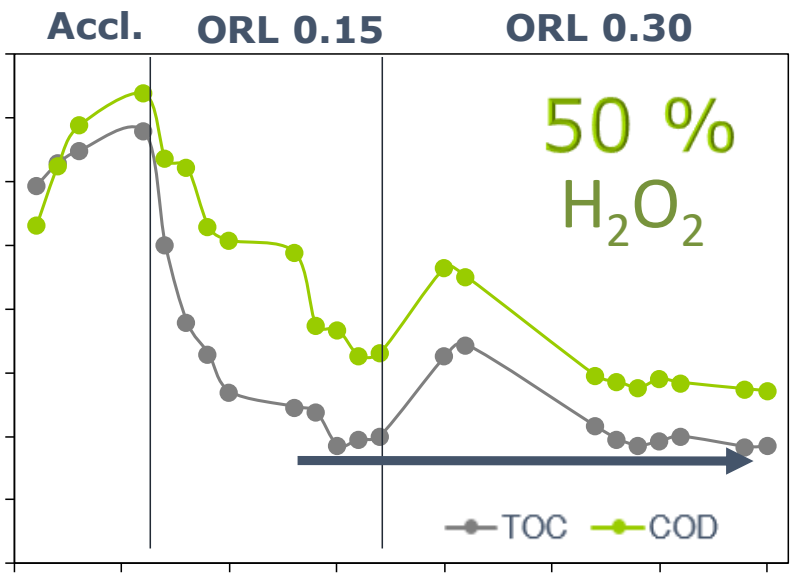
Variation of Ecotoxicity (TU) and BOD_5/COD ratio.

Effluents from Fenton oxidation with H_2O_2 doses of **50%** and **75%** from stoichiometric were selected for a subsequent biological treatment

Biological oxidation

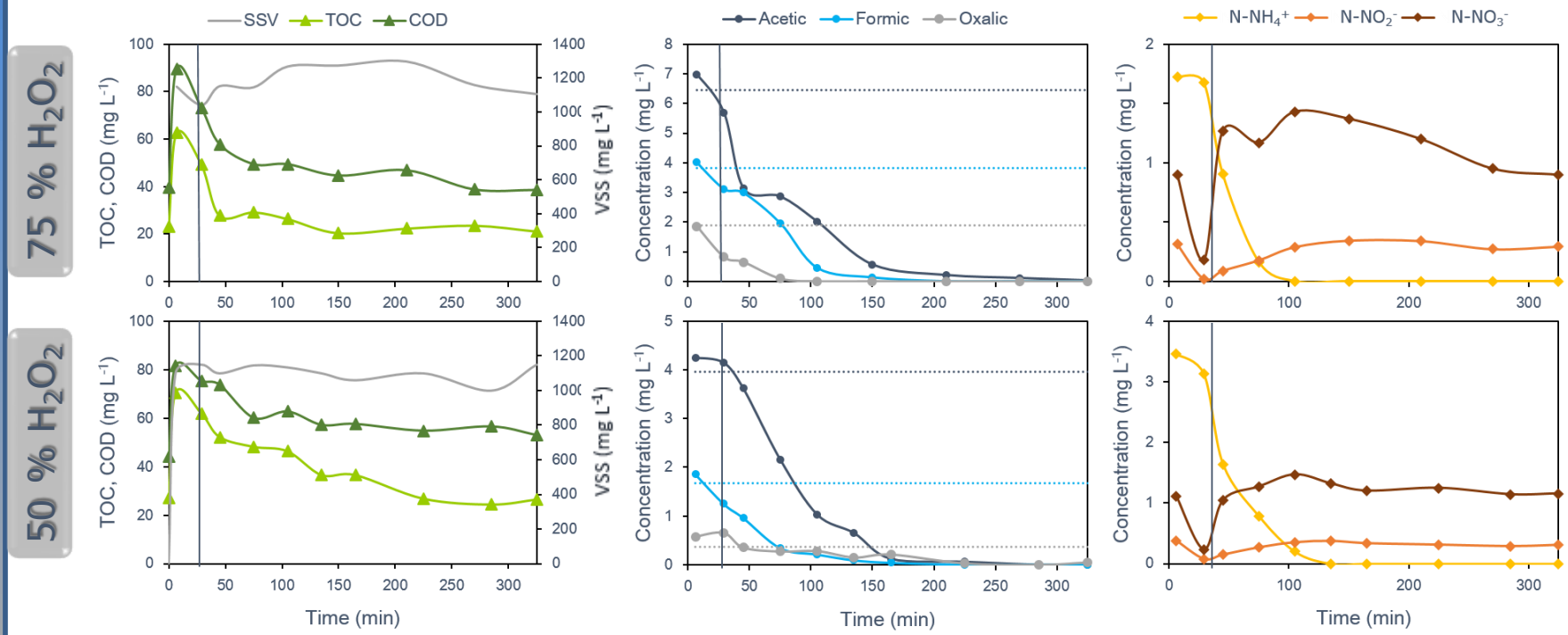






OLR: 0.15-0.3 $kg_{COD}\ kg^{-1}_{VSS}\ d^{-1}$

Biological oxidation



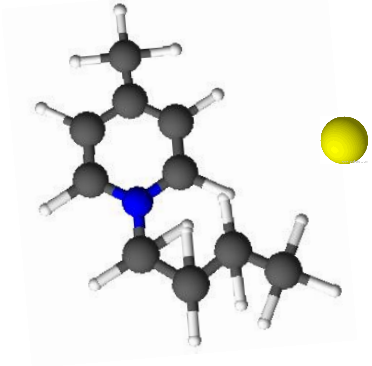
Time-course over a 6-h SBR cycle.

Coupling Fenton and biological oxidation is an adequate alternative for TMX removal, according to the TOC conversion and COD removal above 80% for the combined treatment.

IONIC LIQUIDS (ILs)

- Negligible vapor pressure
- High solvent capacity
- Non – flammability
- Thermal stability

"Design" products

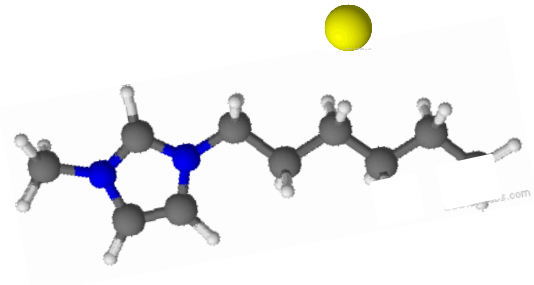


1-butyl-4-methylpyridinium

BmpyrCl

"GREEN" compounds

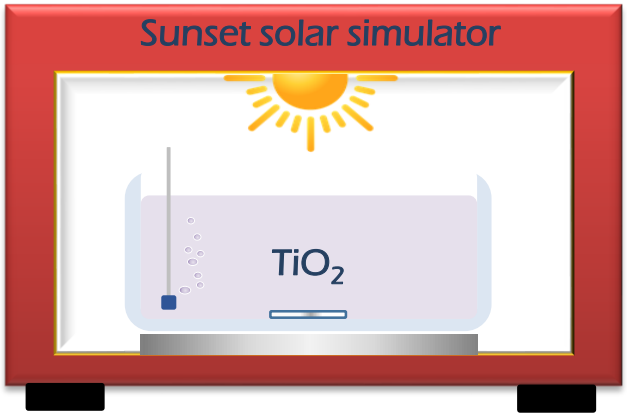
Alternative to VOCs



1-hexyl-3-methylimidazolium

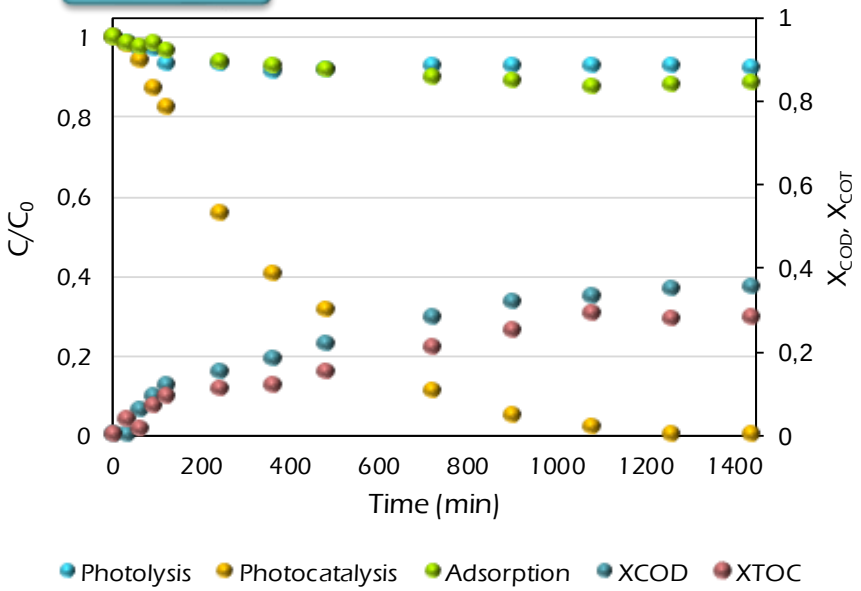
HmimCl

Solar photocatalysis

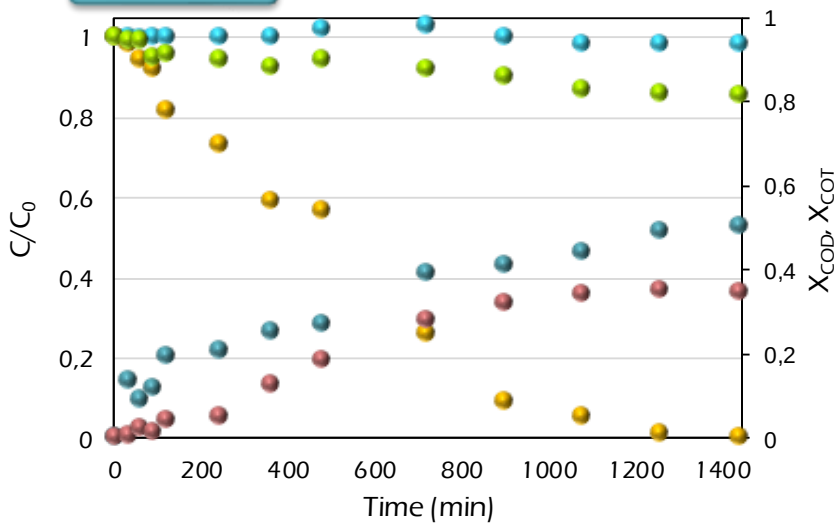


[IL] = 0.35 g L^{-1}
[TiO_2] = 0.25 g L^{-1}
24 h
Xe lamp = 600 W m^{-2}
35 ºC

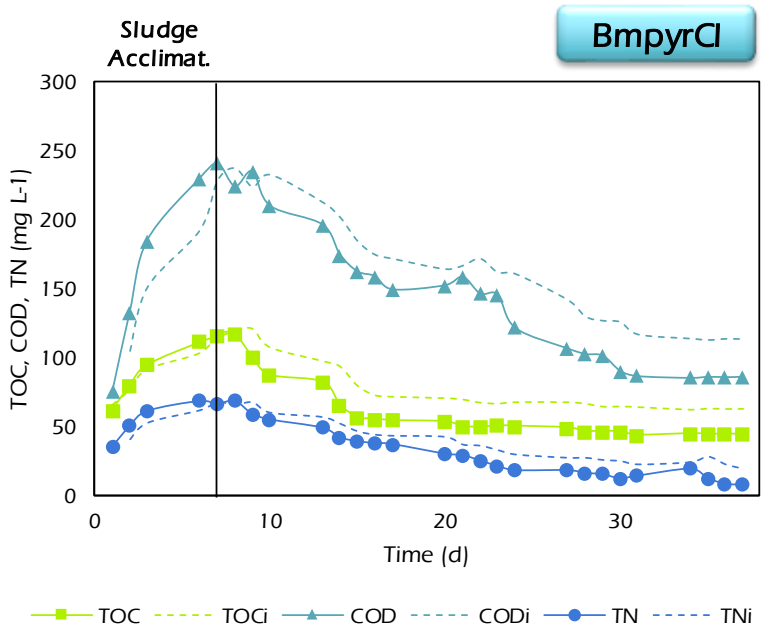
BmpyrCl

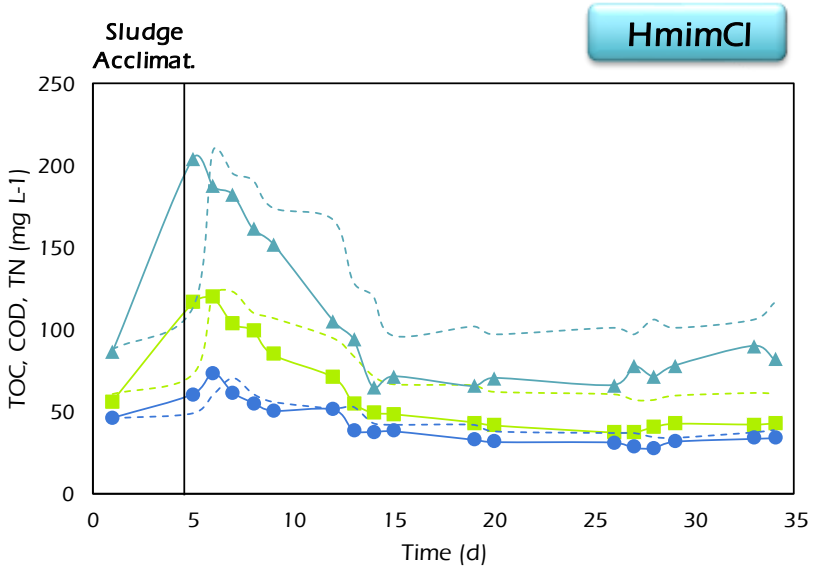


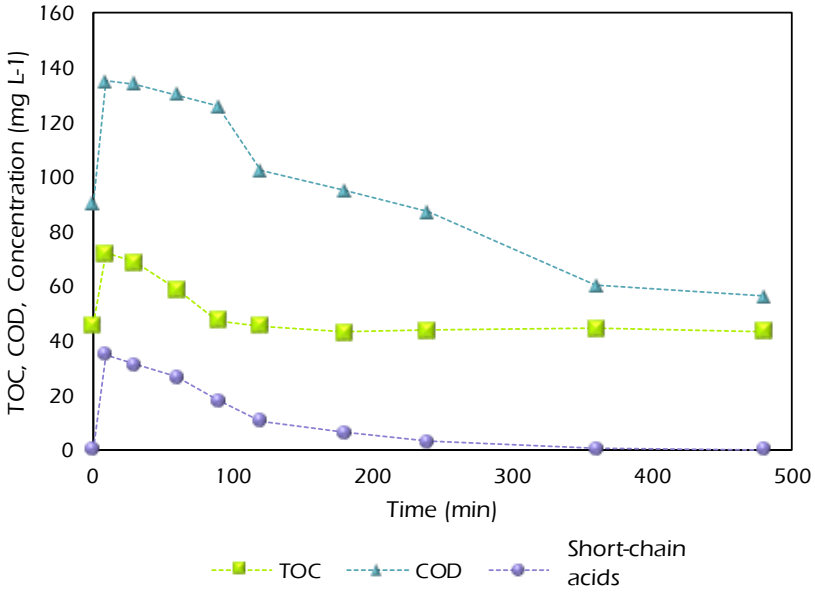
HmimCl

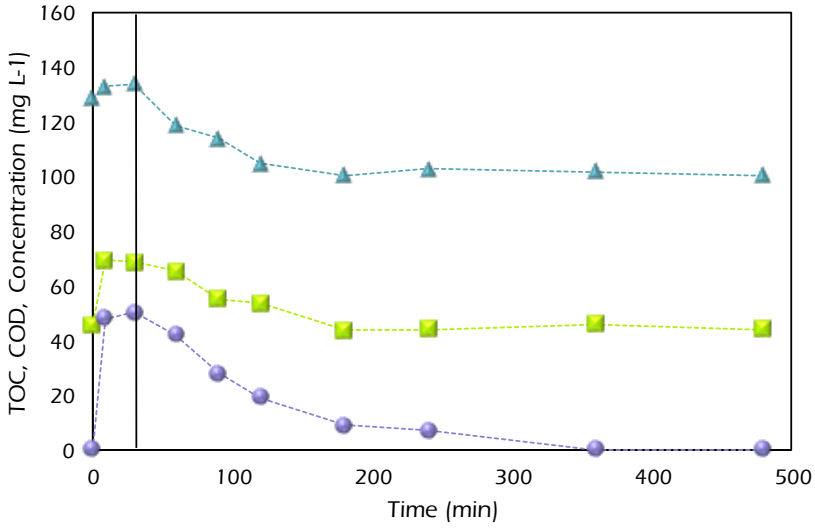


Biological oxidation









Conclusions

- Fenton oxidation and solar photocatalysis generated effluents with low ecotoxicity values and high biodegradability index.

- Working at 75 and 50% of the stoichiometric dose of H_2O_2 in Fenton oxidation gave rise to suitable effluents for the combined treatment.

- Coupling Fenton/solar photocatalysis and biological oxidation is an adequate alternative for TMX or ILs removal, according to TOC conversion and COD removal values, higher than 80% for the combined treatment.

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THANK YOU

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