# Photo-Fenton processes at mild conditions

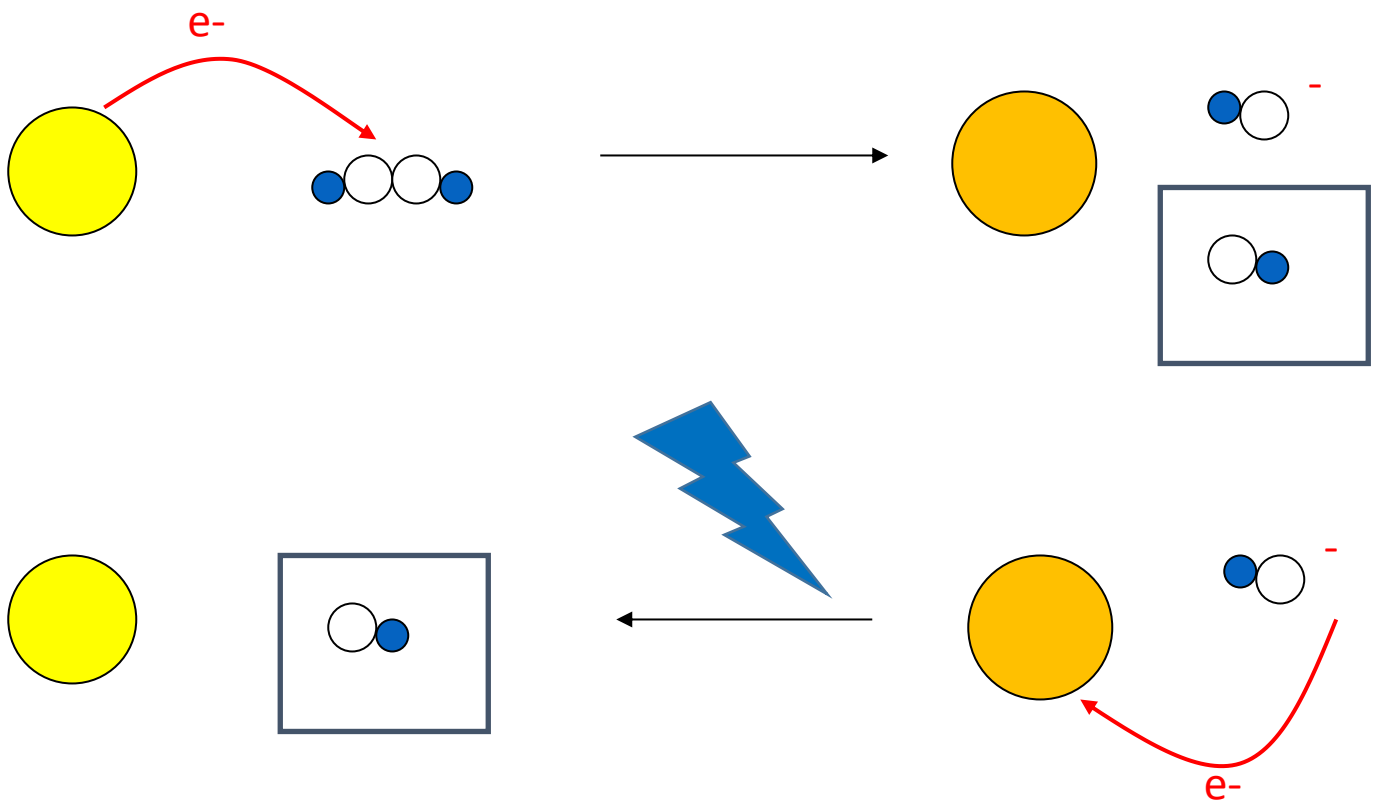
Antonio Arques

Campus de Alcoy, Universitat Politècnica de València

aarques@txp.upv.es

# Photo-Fenton process

- The most efficient AOP that can be driven under sunlight
- Iron plays a photocatalytic role, but hydrogen peroxide is consumed




$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH$$

$$Fe^{3+} + OH^- \xrightarrow{hu} Fe^{2+} + OH$$

# Photo-Fenton process

- Major concerns are the amount of iron that is required and, mainly, the acidic pH that is required (optimum pH = 2.8)
- An alternative approach is decreasing the amount of iron and working at milder pH conditions
- This is interesting when dealing with effluents with low organic loading

# Towards photo-Fenton at milder conditions

- The pH = 2.8 required for photo-Fenton is mainly due to the presence of photo-active $Fe(OH)^{2+}$ species
- Changes in the coordination sphere of iron results in a variation of the mechanism
- At higher pH values formation of photochemically non-active iron oxides or hydroxides occurs, thus decreasing the efficiency of photo-Fenton
- Formation of such species should be prevented

# Approaches for photo-Fenton at mild pH condition?

# Approaches for photo-Fenton at mild pH condition

- Low iron concentrations
- Use of complexing agents
- “In situ” generation of iron salts
- Heterogeneization
- Use of other metals
- Taking advantage of the simple matrix

# Iron at low concentrations

Neutral pH
5 mg/L of EPs

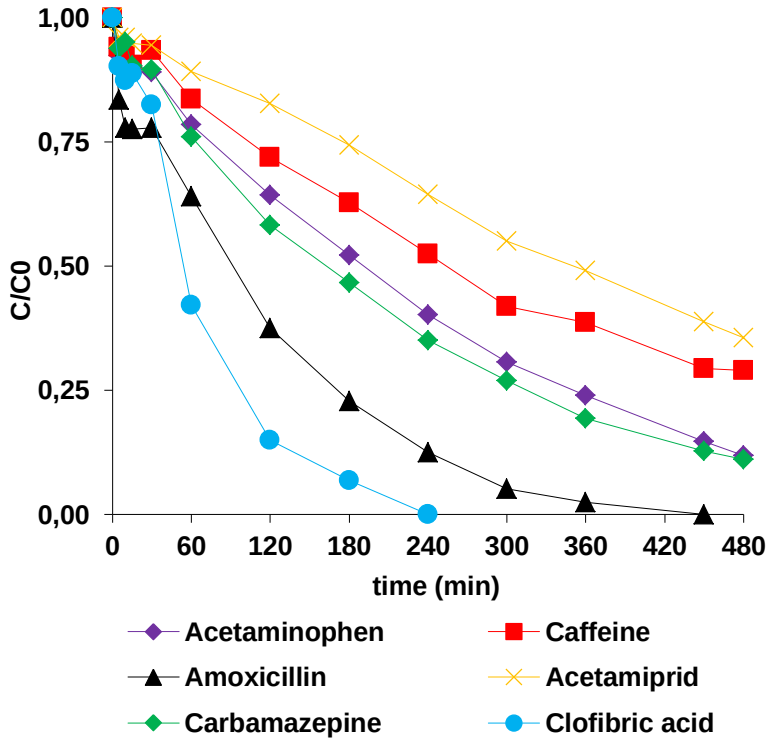
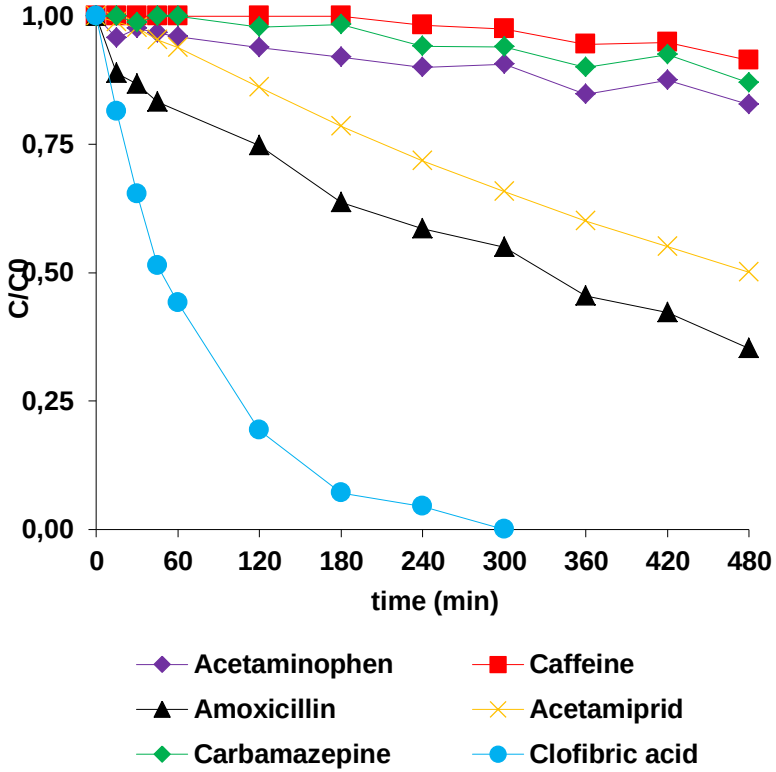



**Photo-Fenton**

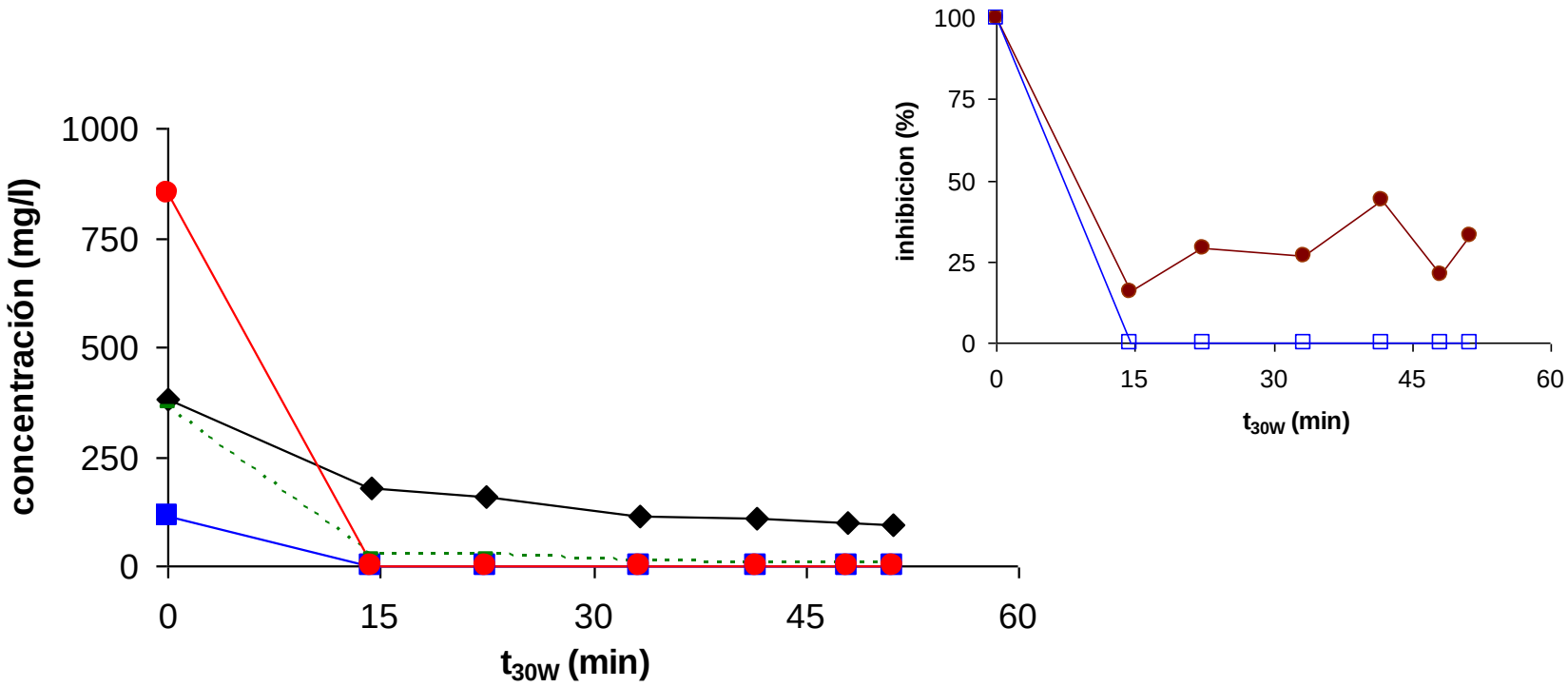



**Photolysis**

# Use of other metals

- Some other metals can drive (photo)-Fenton like processes
- Their behaviour might differ from that of iron (e.g. copper)
- Their high toxicity might be a major drawback
- They should only employed:
  - Supported onto different structures
  - When they are already present in the effluent

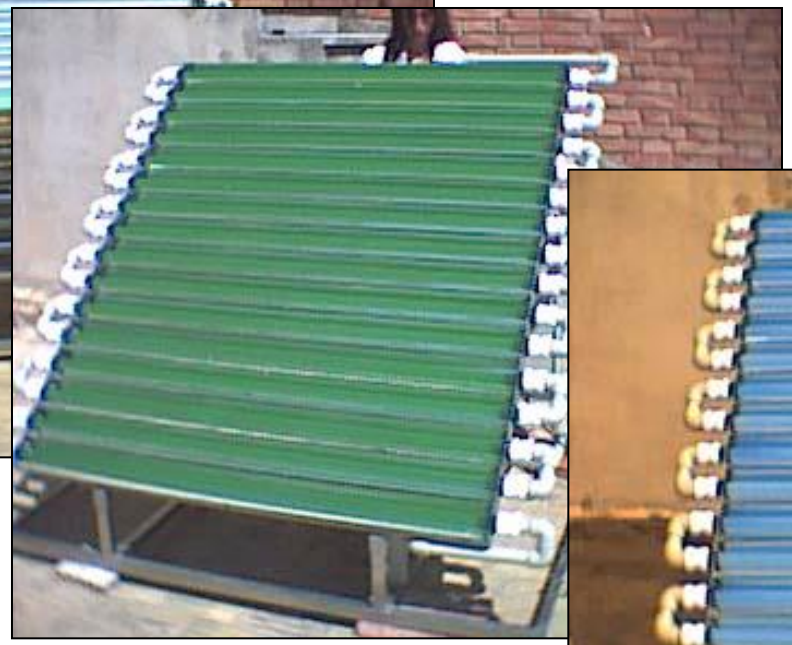
# Use of other metals




Total $CN^-$ (● ), free $CN^-$ (■), DOC (◆) and Cu (▲). Toxicity determined by inhibición de la luminiscencia por vibrio *fischeri* (● ), Inhibición de la respiración de fangos activos ( □ ).

# Use of other metals

t= 0; Toxicity = 75%



t= 3h, Toxicity = 37%

t= 6h, Toxicity = 13%

# Heterogeneization

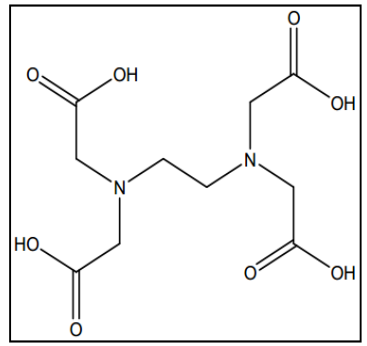
# Heterogeneization

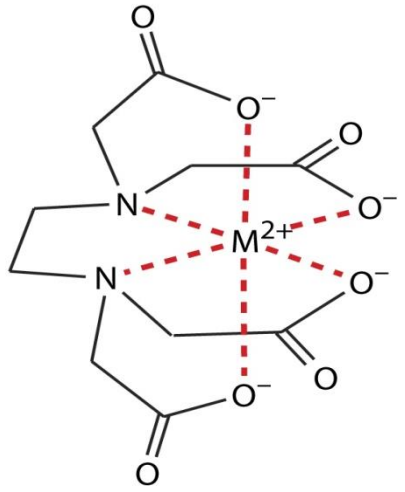
- Iron can be supported onto different structures:
  - Membranes
  - Zeolites or other clays
  - Photochemically active inorganic  iron-containig species
  - Complexation with macromolecules
  - ZVI
- The processes are generally slower because of diffusion control
- In most cases iron leached from the solid structures are the real key species

# Use of complexing agents

**COMPLEX FORMATION**

| | | |
|---|---|---|
| **Oxalate**<br>**Citrate**<br>**Chitosane**<br>**EDTA**<br>**EDDS** | **Humic acids,**<br>**Fulvic acids** | **SBO** |



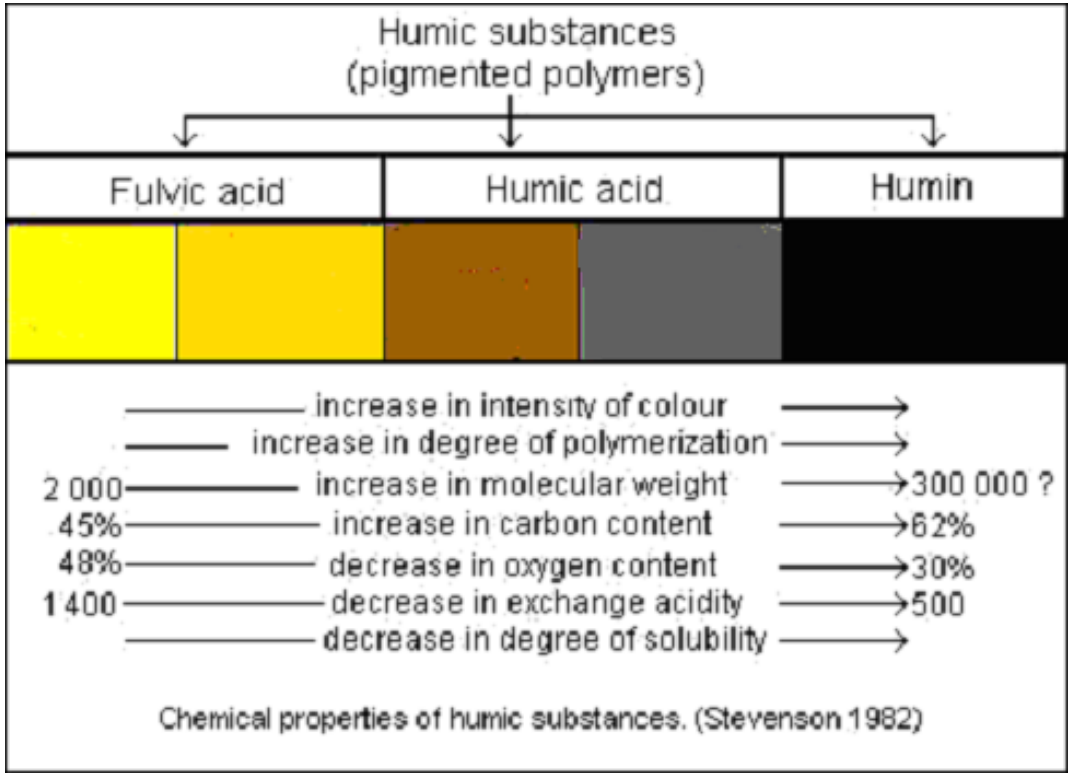




Carboxy and phenoxy groups are prefered

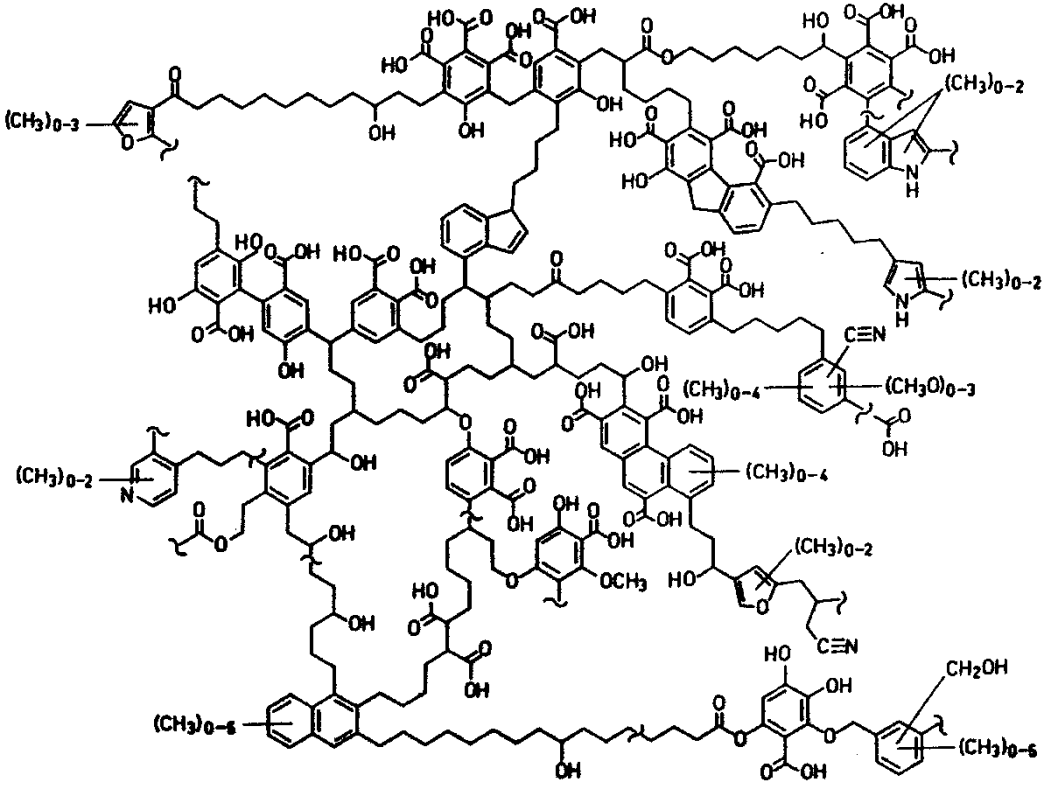
# Humic substances

- They are commonly found in water released from animal or vegetal debrisses
- They are photochemically active
- Humic substances constitute a major pathway for the abiotic removal of xenobiotics in the environment

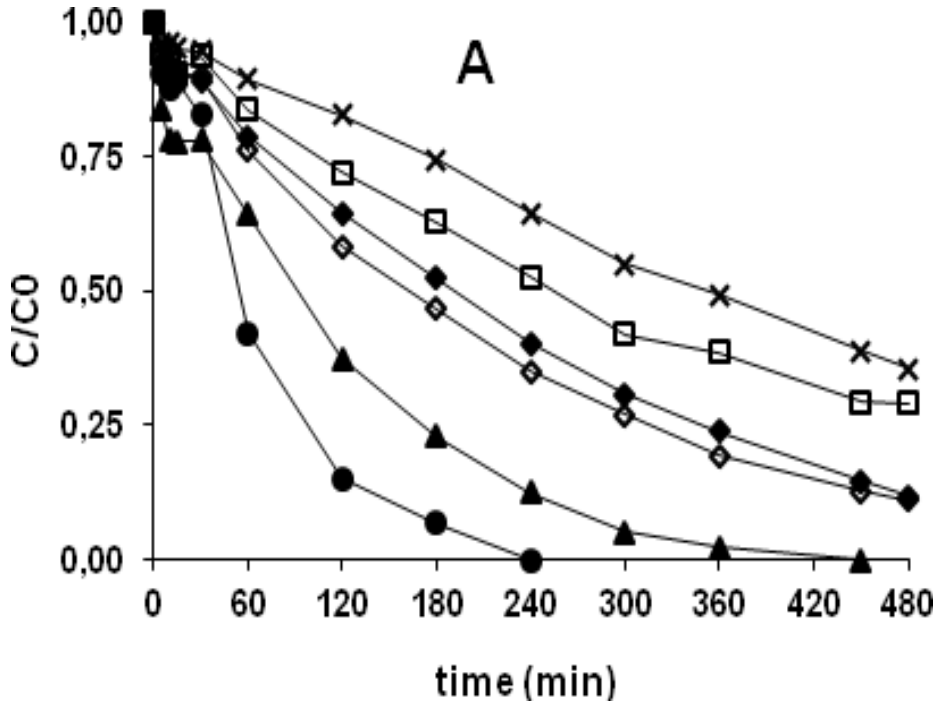
# Humic substances

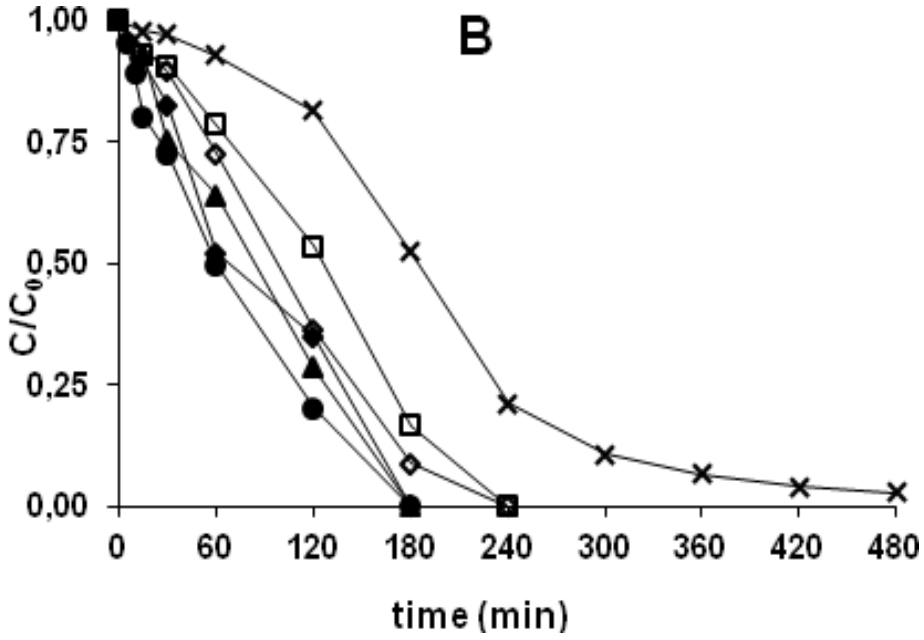


Chemical properties of humic substances. (Stevenson 1982)



# Humic substances

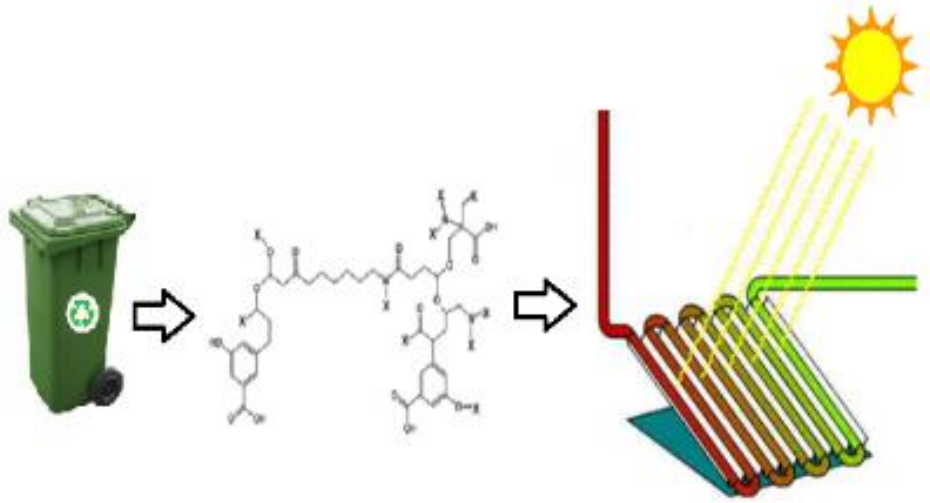



Removal of emerging pollutants at neutral photo-Fenton in the presence of humic substances

# Soluble bio-organic substances (SBOs)

- The use of SBOs might be a sustainable alternative as a waste is valorized to be employed in water detoxification
- Constituted by macromolecules (67 to 463 kg $mol^{-1}$) with similar characteristics as humic substances
- Similar photophysical/photochemical behaviour is expectable



# Soluble bio-organic substances (SBOs)

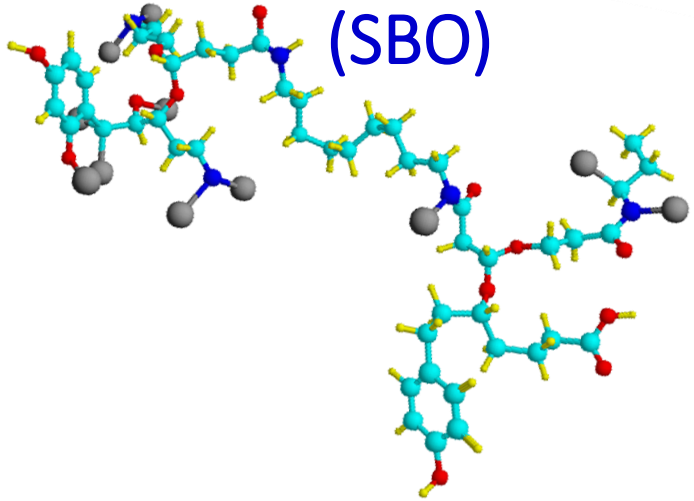
Organic fraction

Pre-treatments
-Anaerobic digestion
-Aerobic biodegradation

Urban wastes

Biomass

Soluble Bio-Organics (SBO)



- Digestion at basic conditions
- Centrifugation to remove the non-soluble fraction
- Ultrafiltration of supernatant
- Drying of the retentate

# Composition of SBOs

| | A (FORSUD) | B (CVDFT110) | C (CVT230) |
|---|---|---|---|
| Volatile solids (%, w/w) | 84.6 | 72.7 | 72.1 |
| Carbon (%, w/w) | 45.1 | 35.5 | 38.2 |
| Nitrogen (%, w/w) | 7.8 | 4.3 | 4.0 |
| Si (%, w/w) | 0.36 | 0.92 | 2.55 |
| Fe (%, w/w) | 0.16 | 0.53 | 0.77 |
| Al (%, w/w) | 0.78 | 0.44 | 0.49 |
| Mg (%, w/w) | 0.18 | 0.49 | 1.13 |
| Ca (%, w/w) | 1.32 | 2.59 | 6.07 |
| K (%, w/w) | 9.2 | 5.4 | 3.6 |
| Na (%, w/w) | 0.39 | 0.15 | 0.16 |
| Cu (mg/l) | 100 | 216 | 202 |
| Ni (mg/l) | 27 | 71 | 92 |
| Zn (mg/l) | 185 | 353 | 256 |
| Cr (mg/l) | 11 | 30 | 19 |
| Pb (mg/l) | 44 | 75 | 85 |
| Hg (mg/l) | 0.2 | 0.4 | 0.2 |

# Composition of SBOs

| | A (FORSUD) | B (CVDFT110) | C (CVT230) |
|---|---|---|---|
| Aliphatic carbon | 43 | 31 | 37 |
| Amine | 10 | 8 | 7 |
| Methoxy | 4 | - | - |
| Alkoxy | 10 | 20 | 14 |
| Anomeric carbon | 3 | 7 | 4 |
| Aromatic | 10 | 16 | 13 |
| Phenolic carbon | 2 | 6 | 5 |
| Phenoxy | 1 | 2 | 2 |
| Carboxylic | 7 | 9 | 12 |
| Amide | 9 | 1 | 1 |
| Carbonilic | 1 | - | 5 |
| Lipophilic/hydrophilic ratio | 9.3 | 5.3 | 3.6 |
| Aliphatic/aromatic ratio | 3.3 | 1.3 | 1.8 |
| $E_2/E_3$ ratio | 3.83 | 2.31 | 2.38 |

# What should we study?

# What should we study?

- Performance of the SBO
  - With iron
  - Without iron
- Optimization of operational parameters
- Biocompatibility of the SBO
  - Biodegradability
  - Toxicity
- Stability and reuse
- Scale up and economic assessment?

# Effect of SBO on photolysis

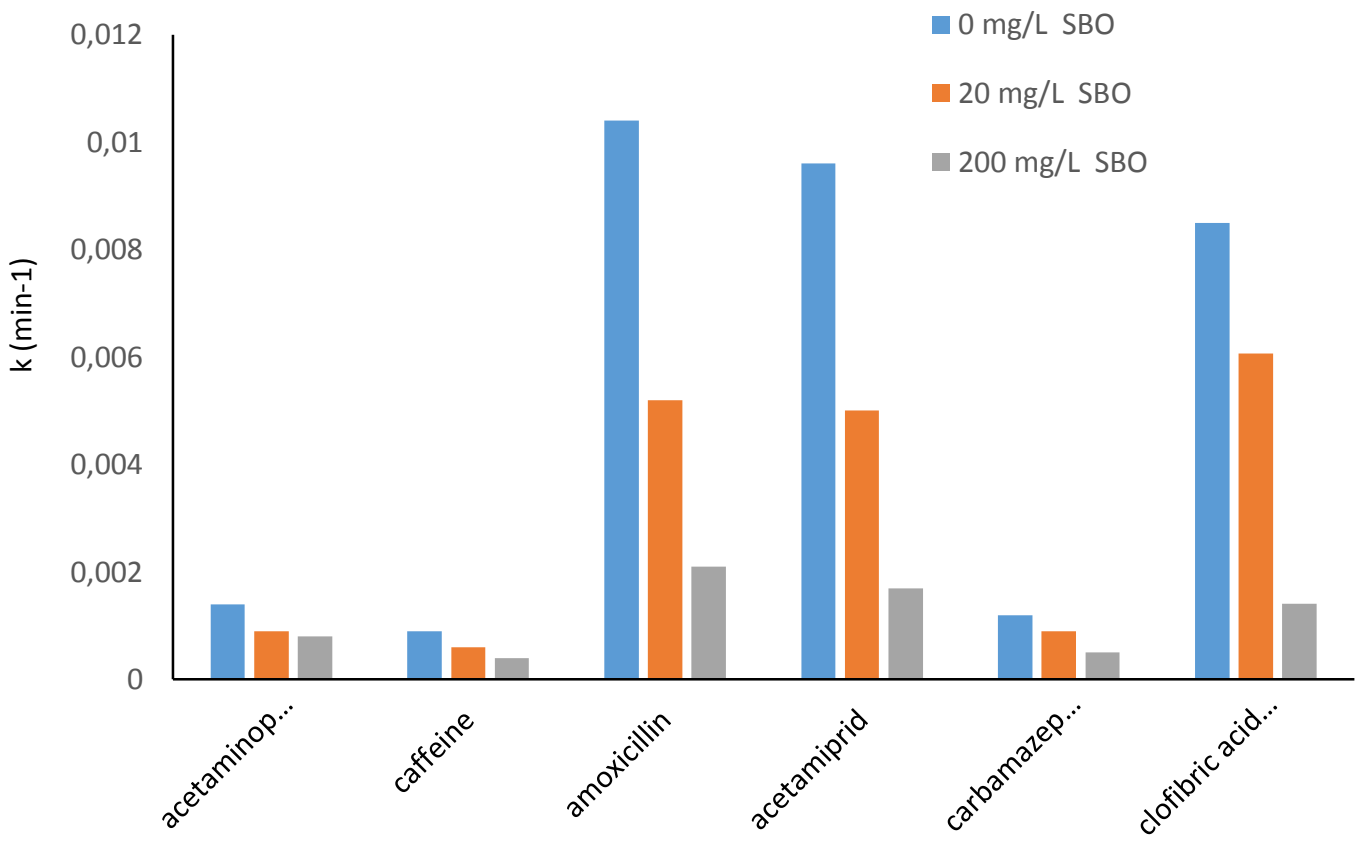
**Opposite effects:**

Improved generation of reactive species

Pre-association pollutant-catalyst

The screen effect due to the brown color of SBOs

Competition SBO-pollutant for the reactive species



# Effect of SBOs on the photolysis of 6 pollutants

**Conditions**

Rate constants with SBO were estimated if the screen effect was supressed

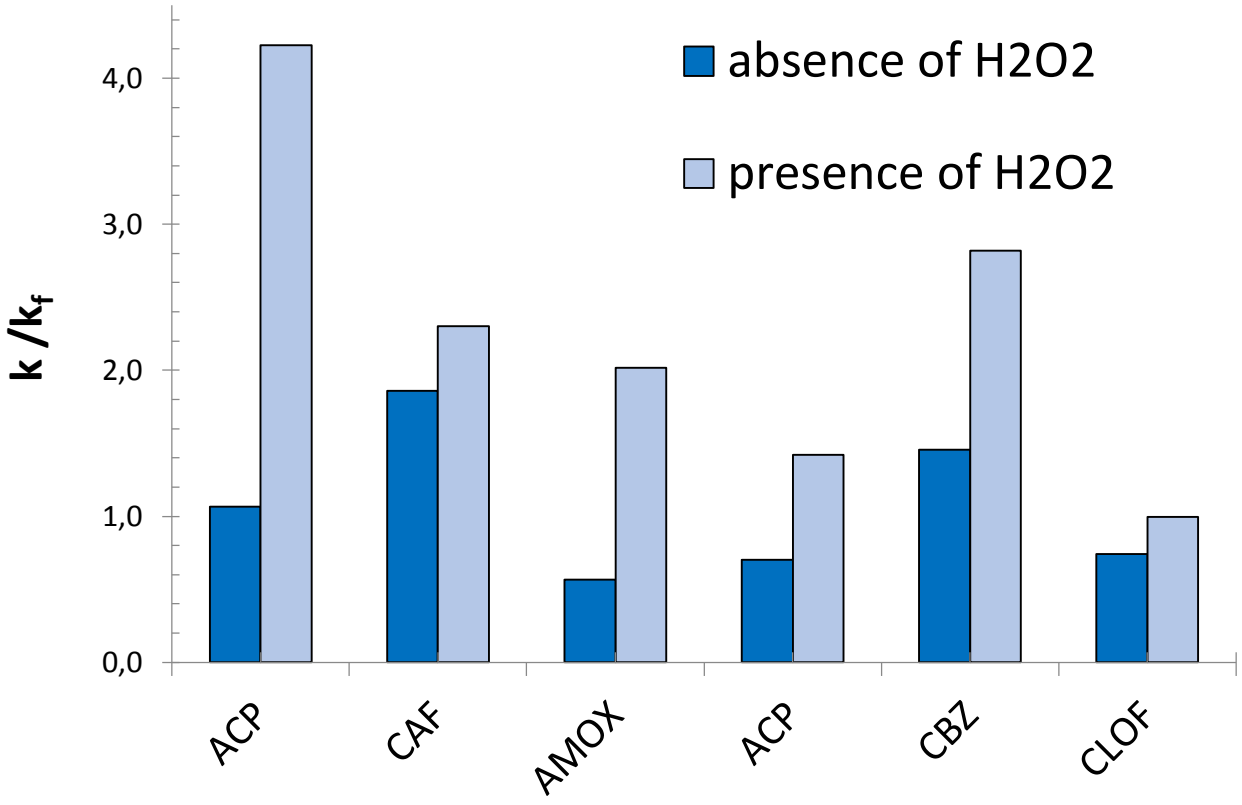
The ratio of k with and without SBO was calculated

**Results**

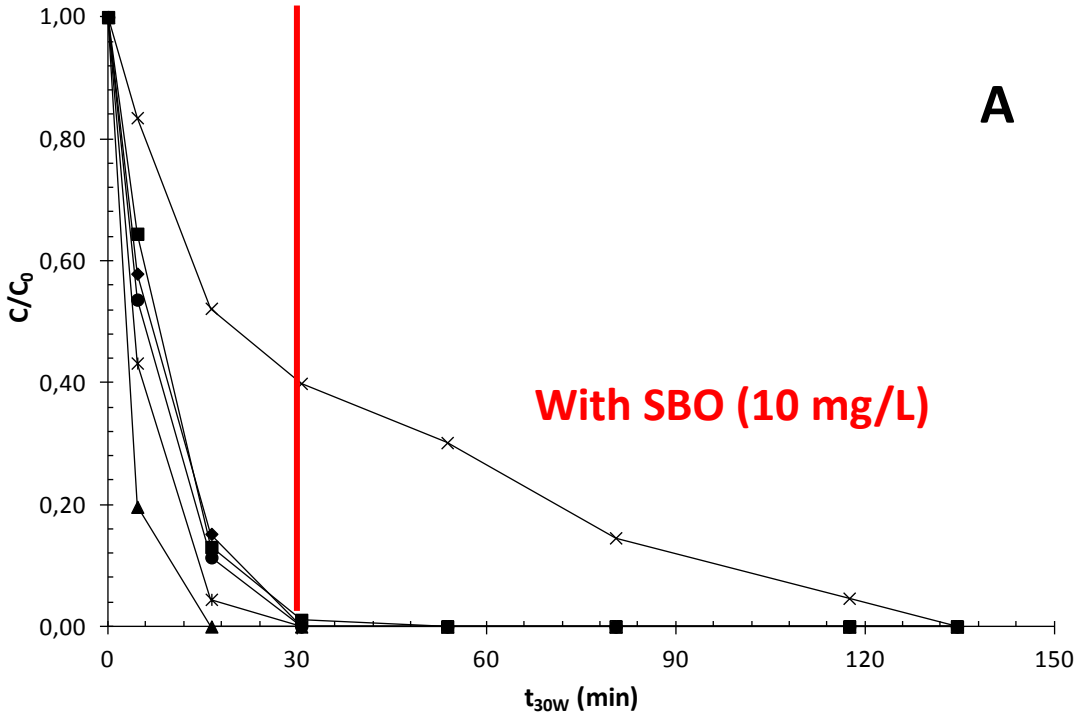
Ratios above 1 with $H_2O_2$ indicate extra generation of reactive species

This was not always true for irradiation

The iron present in the SBO might drive a photo-Fenton process

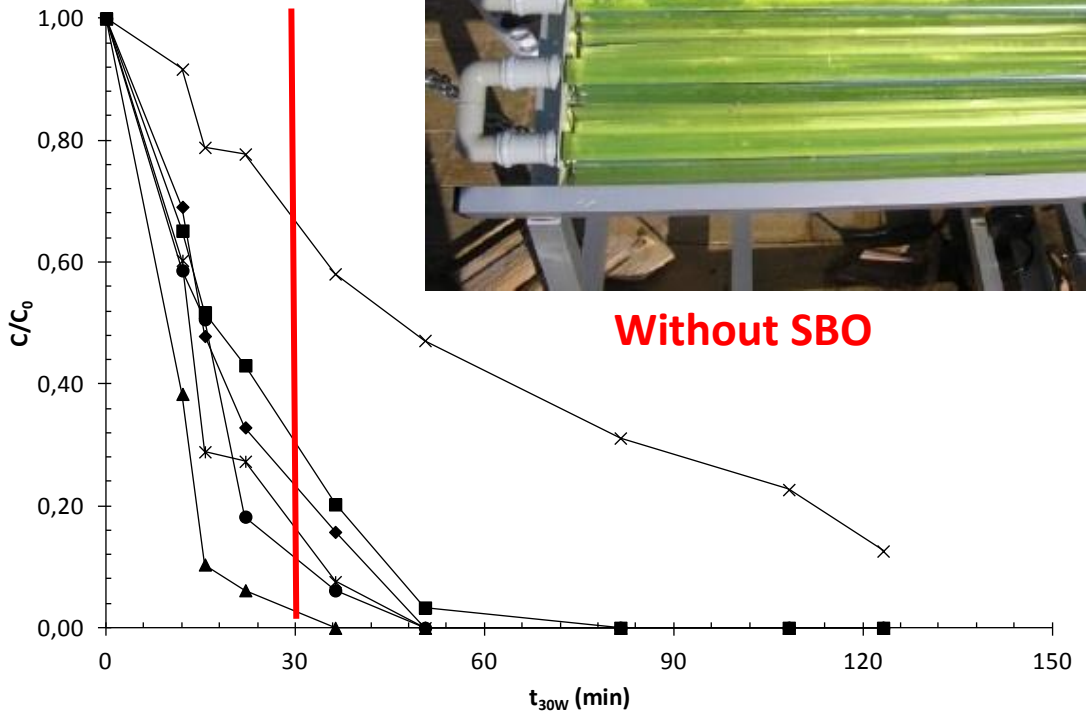


# Use of SBOs in solar photo-Fenton (pH = 5.2)




A

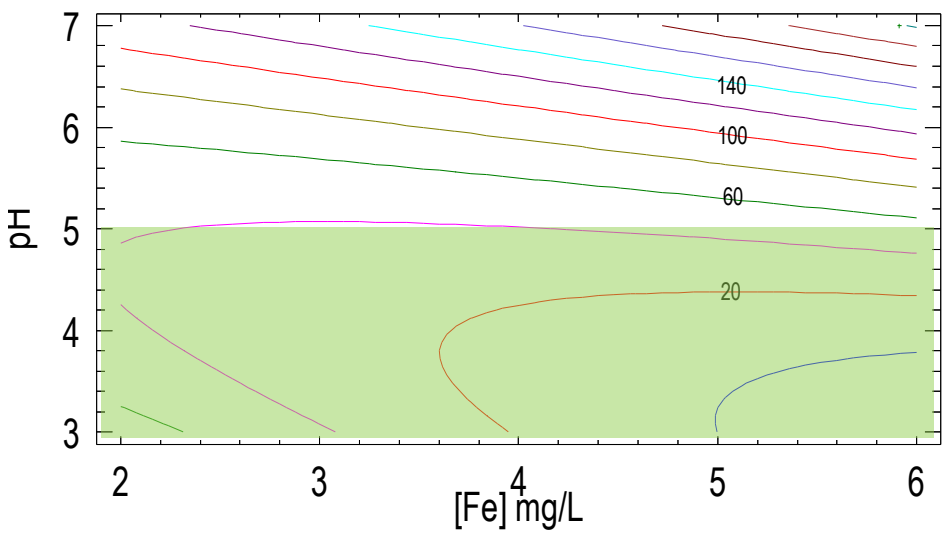
With SBO (10 mg/L)



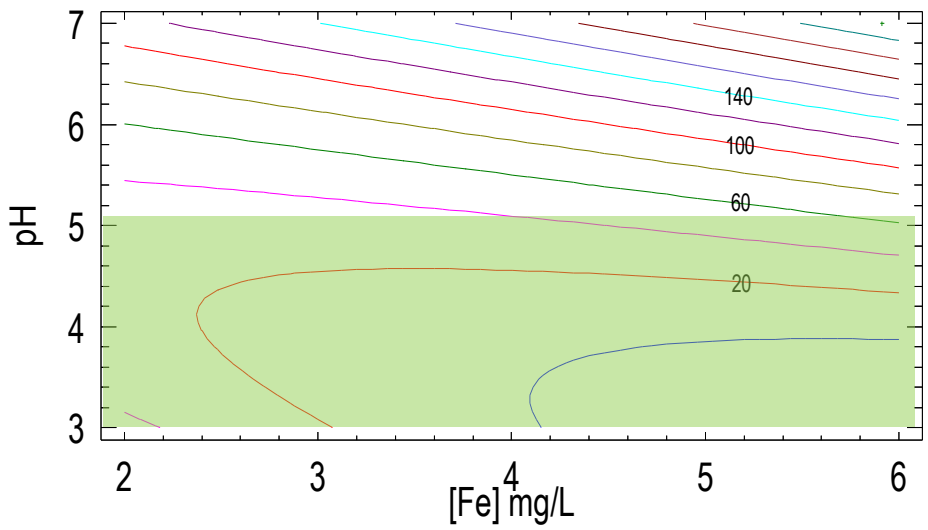

Without SBO

# Effect of the operational variables: caffeine

[SBO] = 15 mg/L



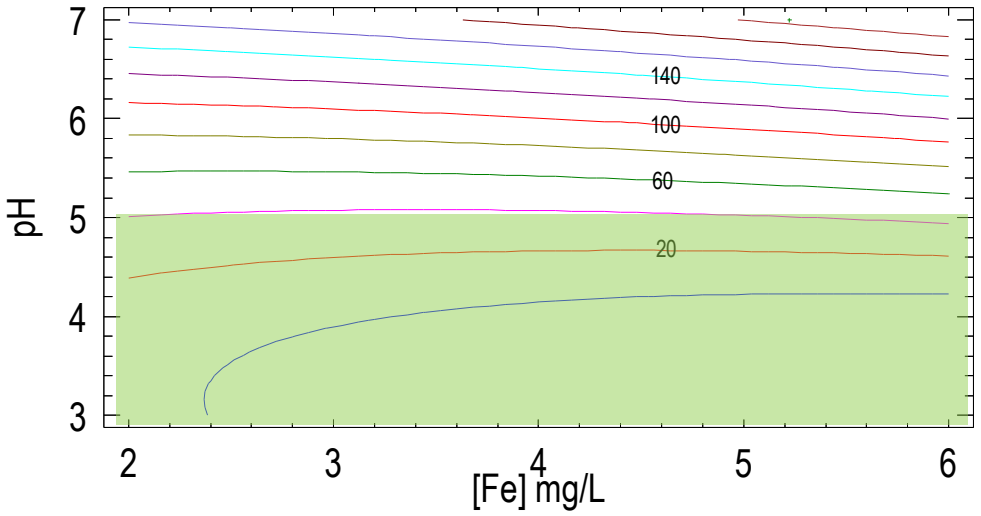

[SBO] = 25 mg/L



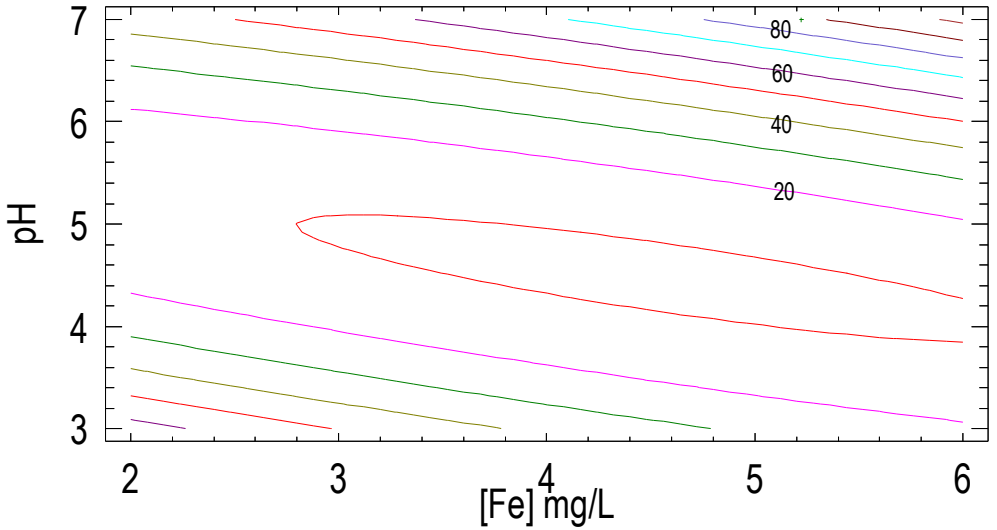

The photo-Fenton reaction can be extended to pH values close to 5, without too remarkable loss of efficiency

# Effect of the operational variables: amoxicillin

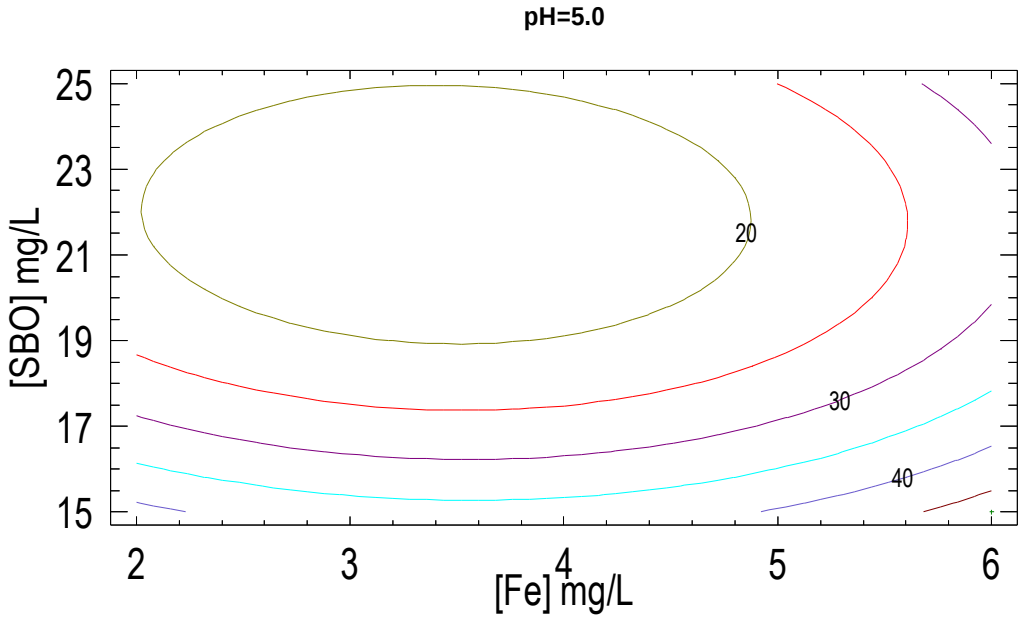
[SBO] = 15 mg/L



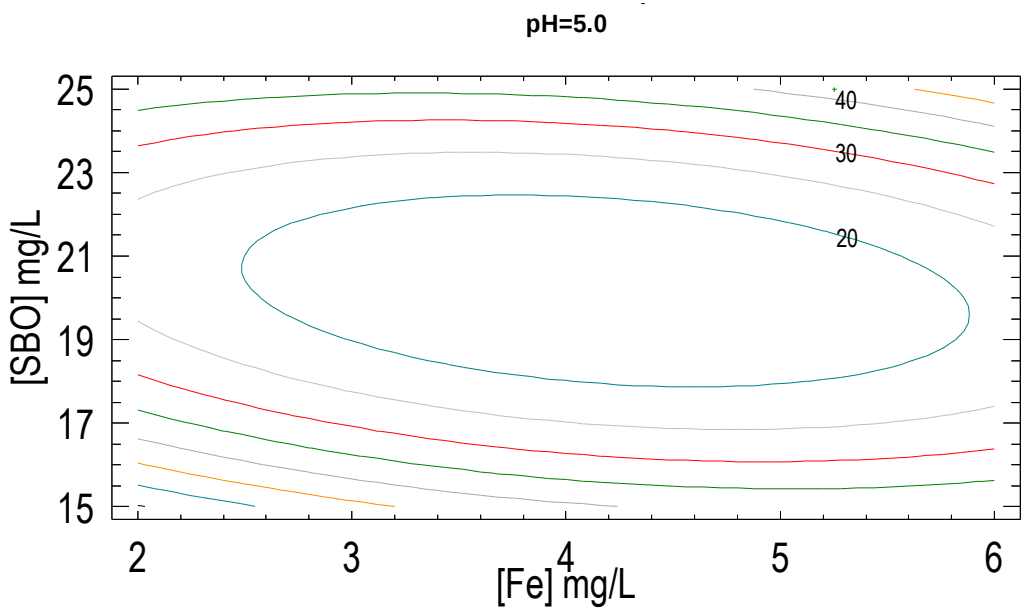

[SBO] = 25 mg/L



# Effect of the operational variables at pH = 5



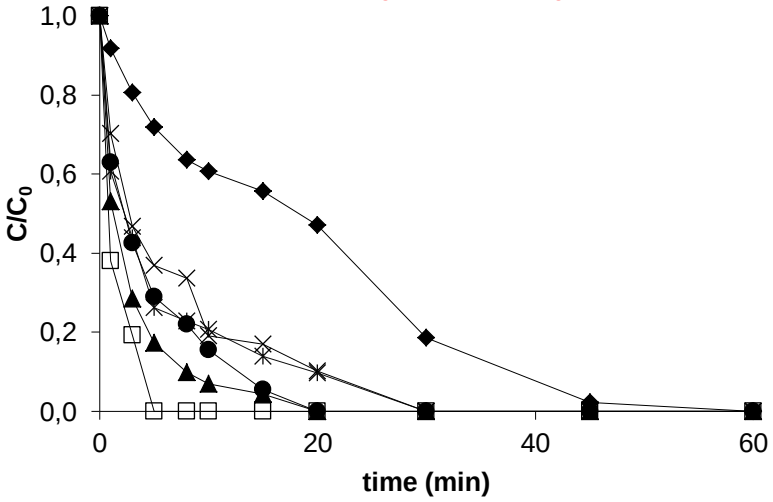

Carbamazepine



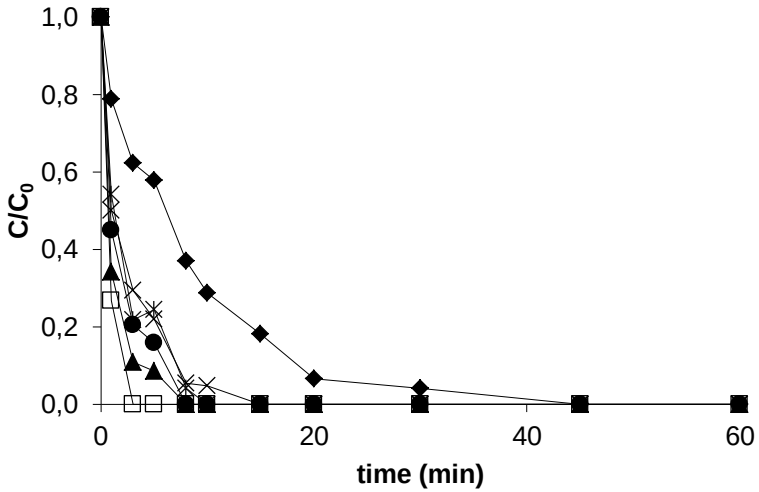

Amoxicillin

# Effect of different SBOs

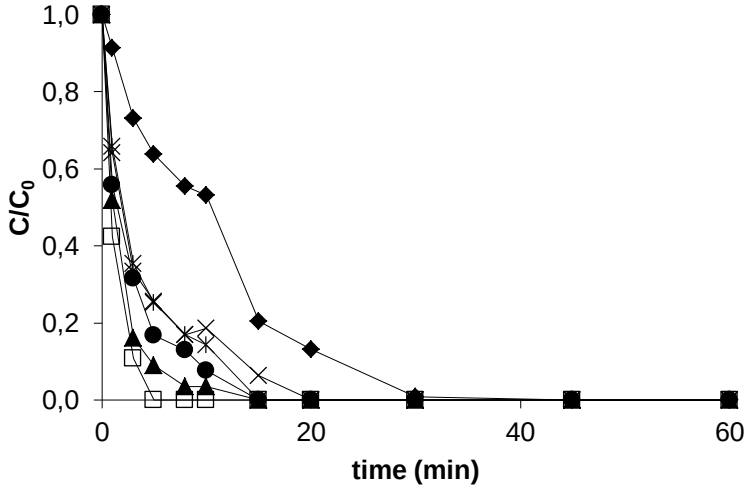
**A (FORSUD)**



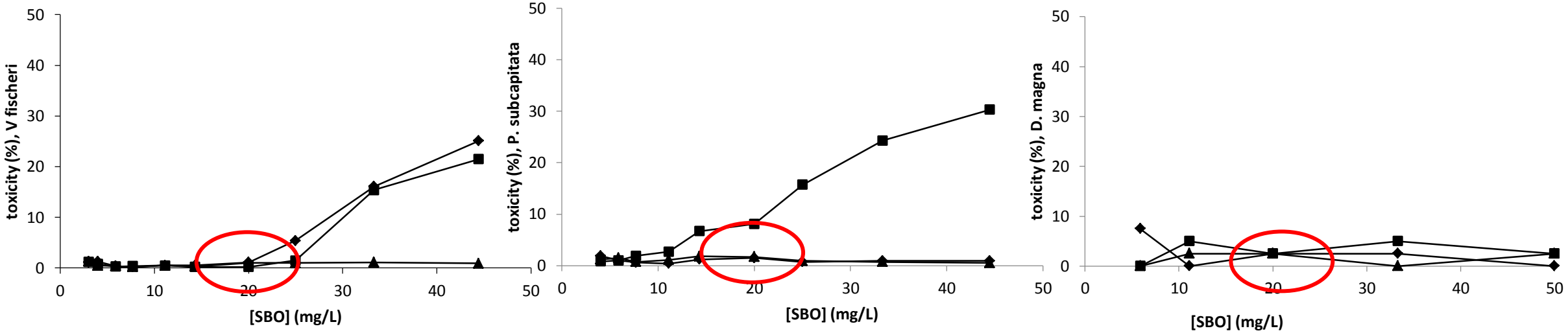

**B (CVDFT 110)**




**C (CVT230)**



# Biocompatibility of the SBOs



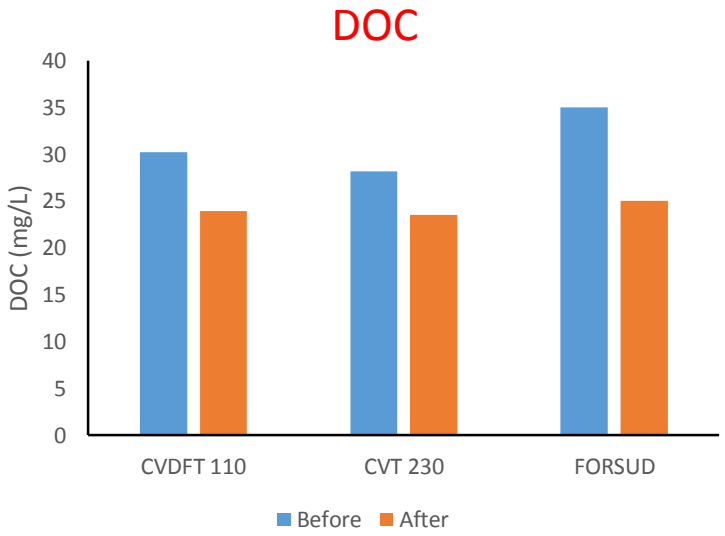

(CVDFT 110 (♦) CVT 230 (■), FORSUD (▲)

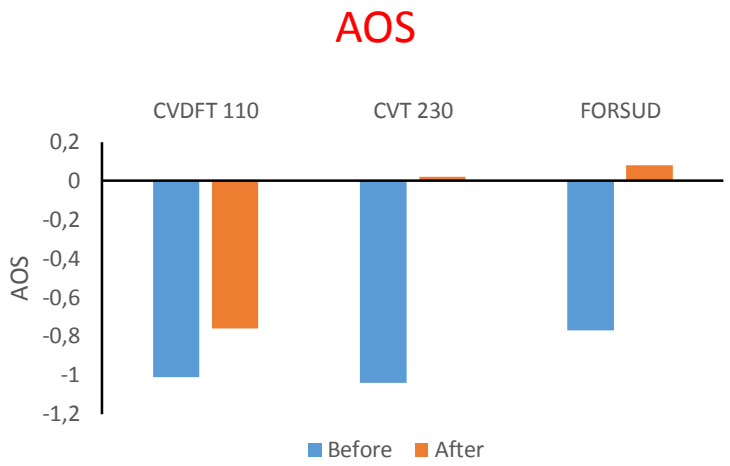
| | 100 mg/l | | 1 g/l | |
|---|---|---|---|---|
| | BOD (mg/l) | BOD/COD | BOD (mg/l) | BOD/COD |
| CVDFT 110 | 6 | 0.06 | 20 | 0.02 |
| CVT 230 | 4 | 0.04 | 30 | 0.03 |
| FORSUD | 10 | 0.09 | 80 | 0.08 |

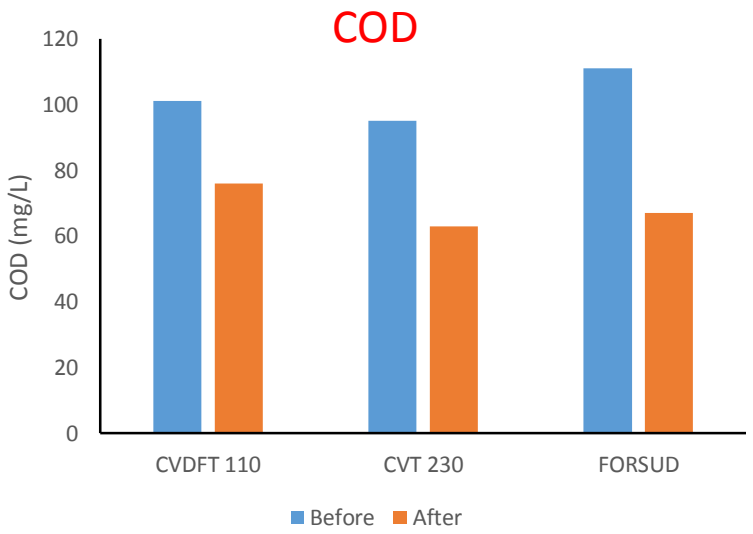
**SBOs should be considered as non-toxic and non biodegradable at the concentrations employed**

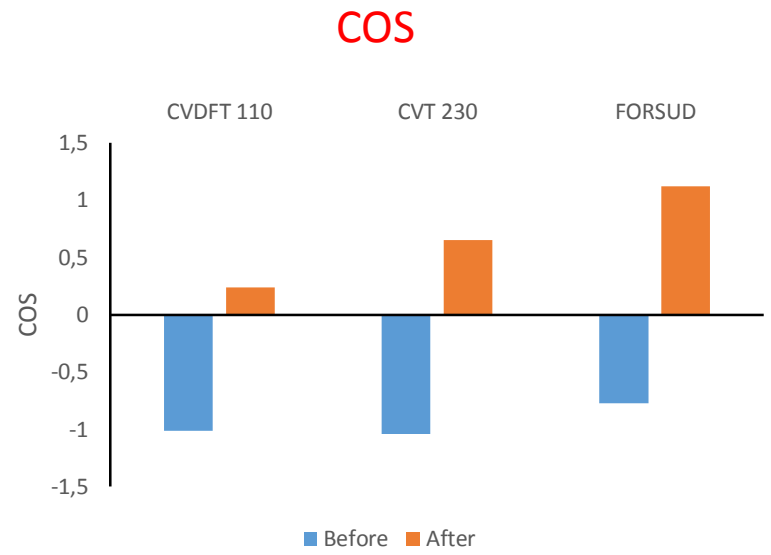
**They should not constitute an impostant concern**

# Photostability of the SBOs: irradiation with $H_2O_2$



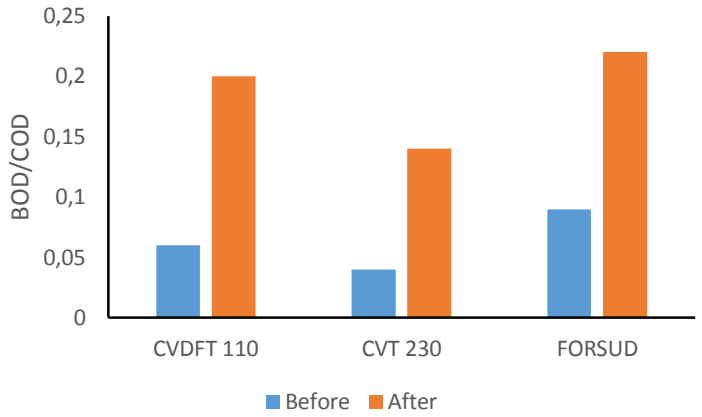



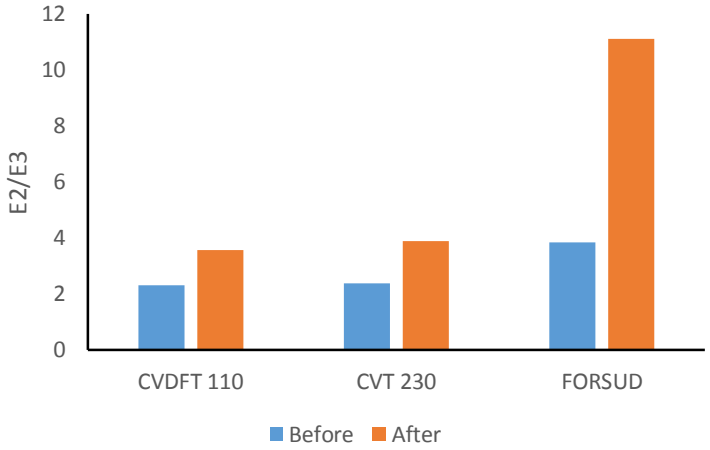



# Photostability of the SBOs: irradiation with $H_2O_2$

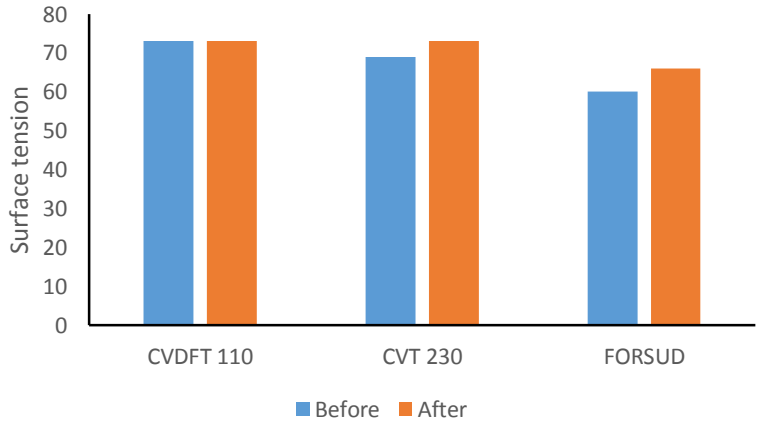
BOD/COD




E2/E3




Surface tension

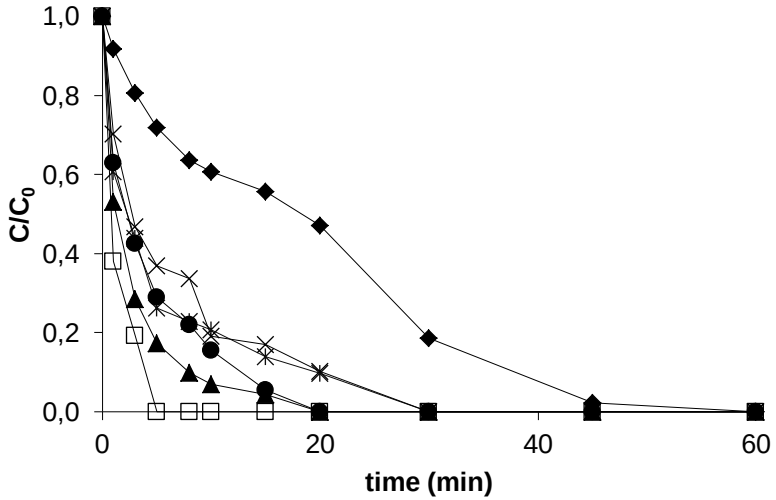


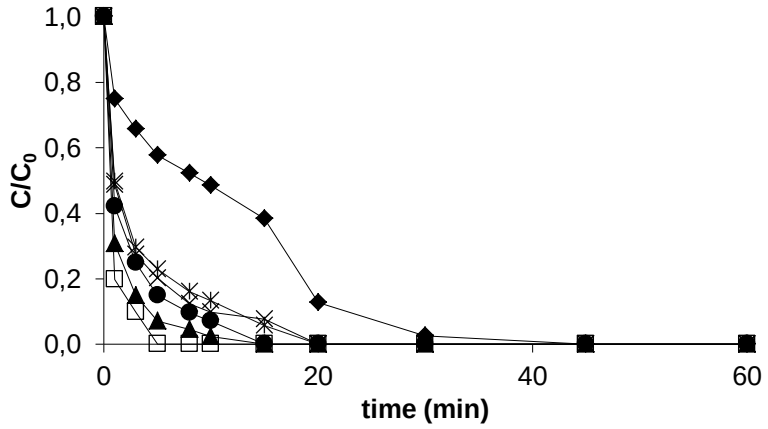

## Results:

Cleavage of the parent macromolecules to form smaller, more oxidized and more hydrophilic ones.

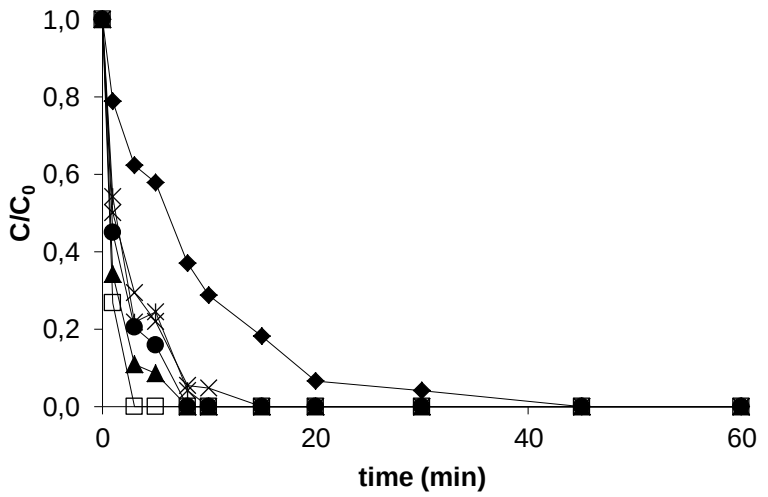
# Performance of the photo-treated SBOs

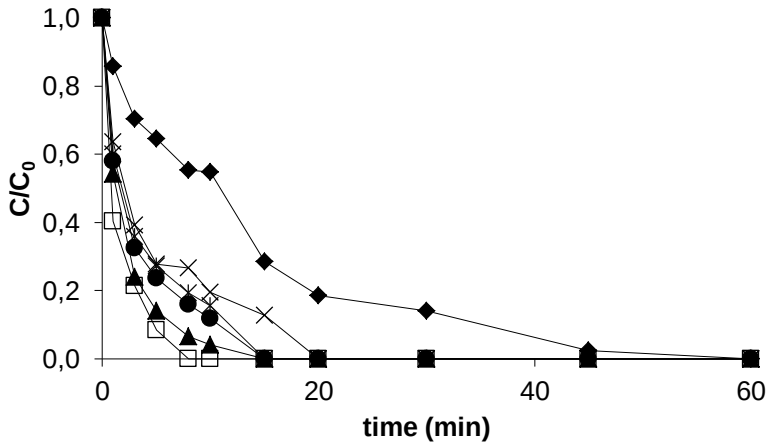
**A (FORSUD)**




**B (CVDFT 110)**




**C (CVT230)**