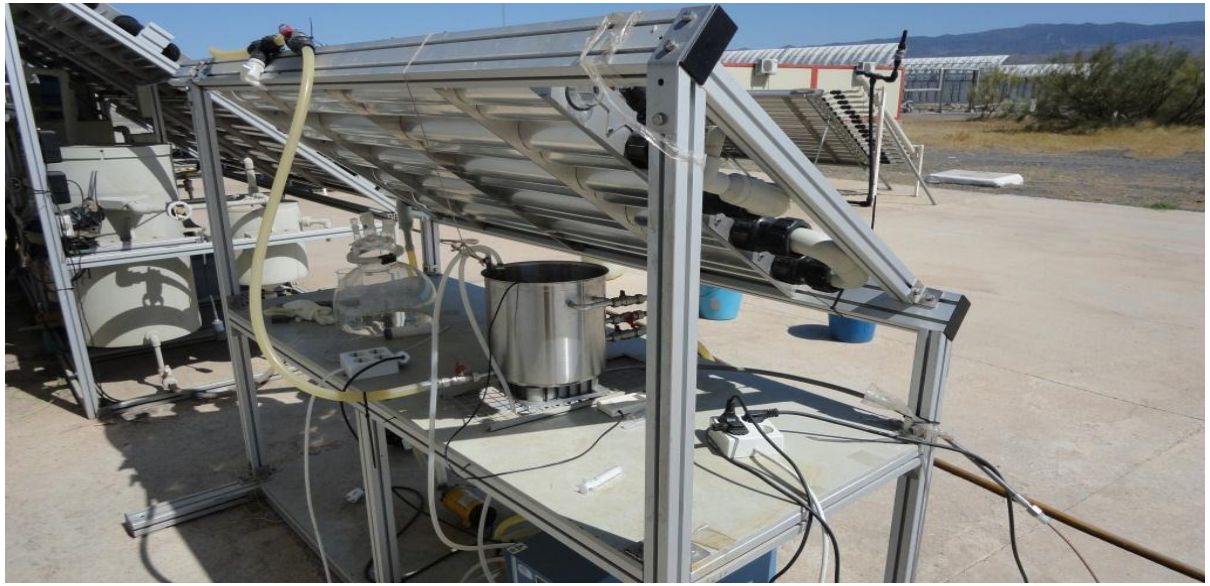
Evaluation of a coupled Ultrasound/solar photo-Fenton system for the treatment of selected contaminants



Stefanos Papoutsakis

Group of Advanced Oxidation Processes

Team Leader: Prof. Cesar Pulgarin

ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

- First worldwide attempt to couple high power Ultrasound with solar photo-Fenton
- Collaboration between EPFL, Plataforma Solar de Almeria, and the Joseph Fourier University of Grenoble

The Fenton reaction

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet \qquad k = 53 – 76\ M^{-1}\ s^{-1}$$

$$Fe^{2+} + OH^\bullet \rightarrow Fe^{3+} + OH^- \qquad k = 2.6 – 5.8 \cdot 10^8\ M^{-1}\ s^{-1}$$

$$Fe^{2+} + HO_2^\bullet \rightarrow Fe^{3+} + HO_2^- \qquad k = 0.75 – 1.5 \cdot 10^6\ M^{-1}\ s^{-1}$$

Fe^{3+} lacks the $\cdot$OH generating properties of Fe^{2+}

Reduction of Fe^{3+} is 3 orders of magnitude slower

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^\bullet + H^+ \qquad k = 1 – 2 \cdot 10^{-2}\ M^{-1}\ s^{-1}$$

$$Fe^{3+} + HO_2^\bullet \rightarrow Fe^{2+} + O_2 + H^+ \qquad k = 0.33 – 2.1 \cdot 10^6\ M^{-1}\ s^{-1}$$

$$Fe^{3+} + O_2^{\bullet -} \rightarrow Fe^{2+} + O_2 \qquad k = 0.05 – 1.9 \cdot 10^9\ M^{-1}\ s^{-1}$$

- Application of light alleviates this problem

Pignatello et al, 2006

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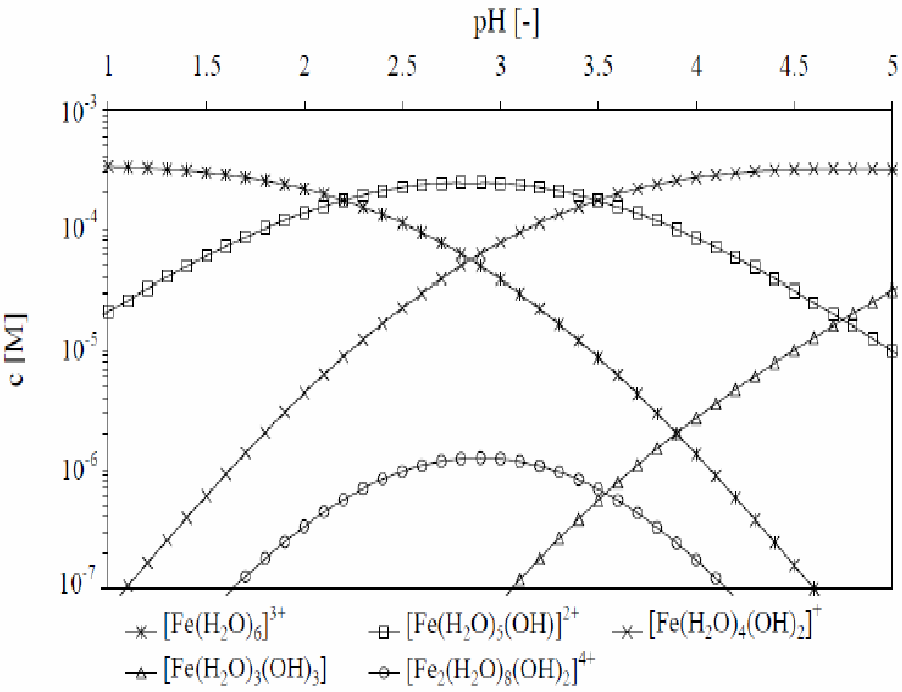
The Photo-Fenton reaction

- Ferric iron forms photoactive complexes with water and hydroxyl ligands
- Through a Ligand to Metal Charge Transfer....

$$[Fe^{3+}L] + h\nu \text{ --> } [Fe^{3+}L]^{*} \text{ --> } Fe^{2+} + L^{\cdot}$$

- Different light absorption properties depending on L



Malato et al, 2009

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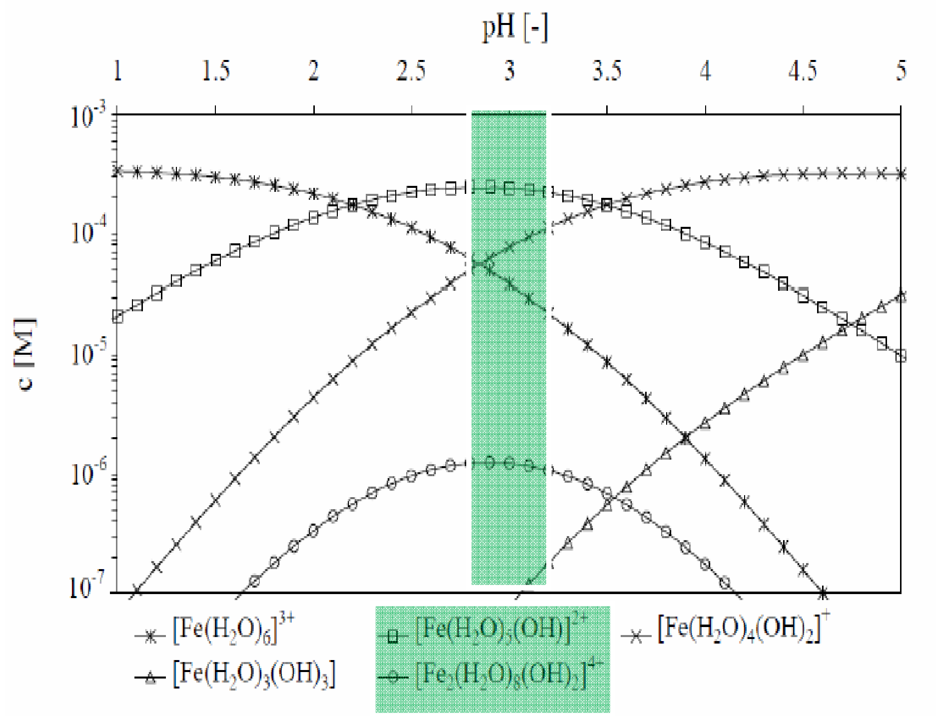


Optimal pH range and quantum efficiency can be modified in the presence of other organic ligands

Malato et al, 2009

Effect of organo-*Fe* complexes and solid Fe species

1. **Solubilisation of Fe^{3+}** by organic matter at near neutral pH and

2. **Regeneration of Fe^{2+} by LMCT** with production of oxidative organic radicals ($R^{\bullet}$) that can also attack the bacteria or generate other ROS

$$[Fe(OOC-R)]^{2+} + hv \longrightarrow Fe^{2+} + CO_2 + R^{\bullet}$$

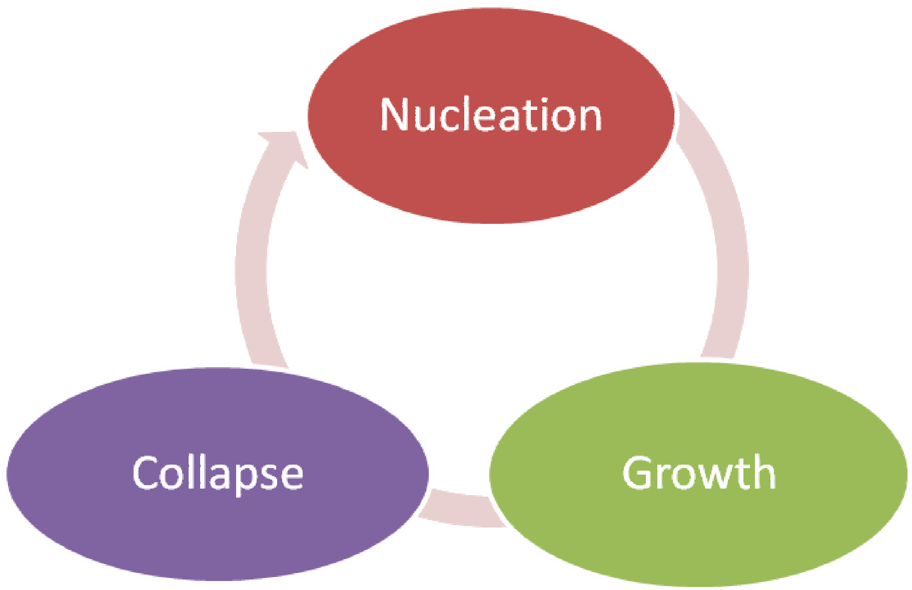
Soluble complex at neutral pH

3. Heterogeneous-homogeneous photo-Fenton equilibrium from solid Fe species influenced by chemical nature, ionic strength and buffer capability of water?

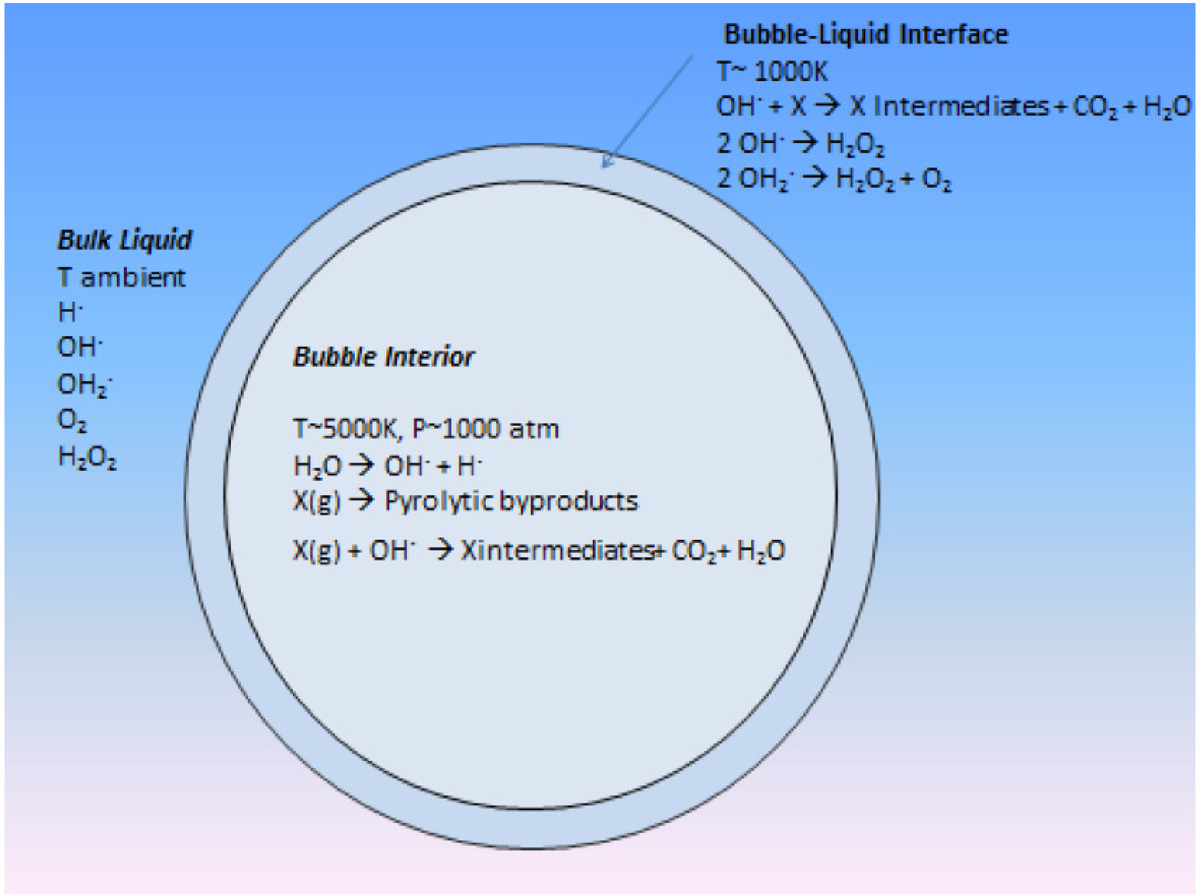
*Canonica, S., (**2007**). Chimia 61, 641–644.*
*Angela-Guiovana Rincon, Cesar Pulgarin. Catalysis Today 122 (**2007**) 128–136.*
*Alejandro Moncayo-Lasso, Janeth Sanabria, César Pulgarin, Norberto Benítez. Chemosphere 77 (**2009**) 296–300.*
*Frederic Sciacca, Julian A. Rengifo-Herrera, Joseph Wethe, Cesar Pulgarin. Chemosphere 78 (**2010**) 1186–1191.*
*Dorothee Spuhler, Cesar Pulgarin. Applied Catalysis B: Environmental 96 (**2010**) 126–141.*

Ultrasound and cavitation

- Regions of positive and negative pressure formed as ultrasound propagates.
- Cavitation occurs when negative pressure exceeds medium tensile strength.



The cavitational bubble



Combining photo-Fenton and Ultrasound

Photo-Fenton

- High reactions rates
- Non-selective
- Destruction via oxidation
- Reliance on Fe^{2+}
- Regeneration can be catalyzed either by lamps or solar light

Ultrasound

- Moderate reaction rates
- Selective
- Destruction via oxidation and pyrolysis
- May aid dissolution of iron at non-optimal pH
- Homogenization of solutions
- Moderate energy consumption

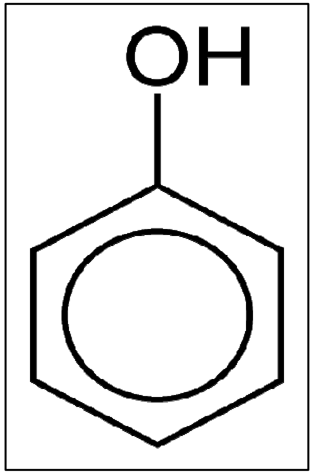
Possible synergy between the two processes

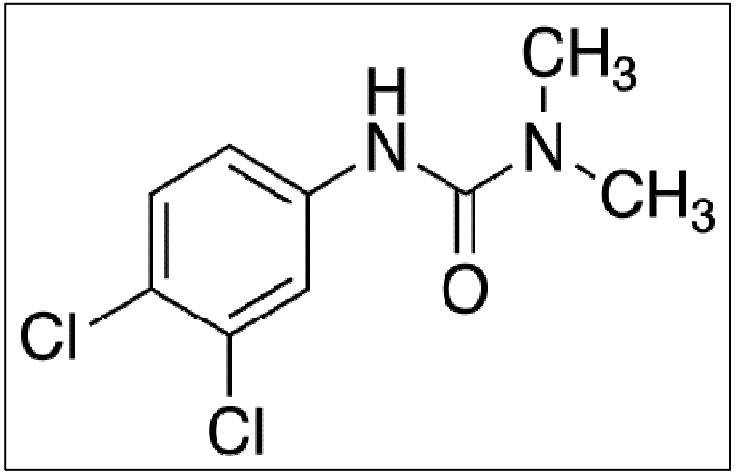
System components

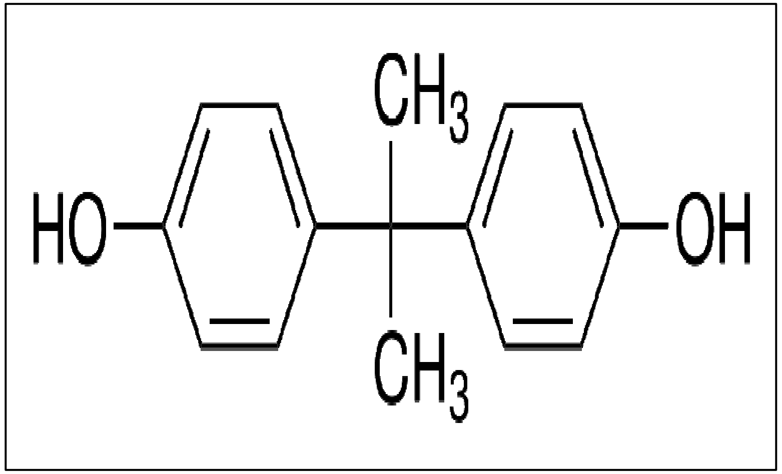
Compound Parabolic Collector Reactor

Treated volume: 7 L

Transducer operating frequency: 400 KHz
Power output: 500 W
Treated volume: 2 L







Phenol
M.W: 94.11
S=83 g/L
Vp=0.35 mmHg

Diuron
M.W: 233.1 g/mol
S= 42 mg/L
Vp= $6.9*10^{-8}$ mmHg

Bisphenol A
M.W: 228.3
S=300 mg/L
Vp=$3.7*10^{-8}$ mmHg

Experimental conditions

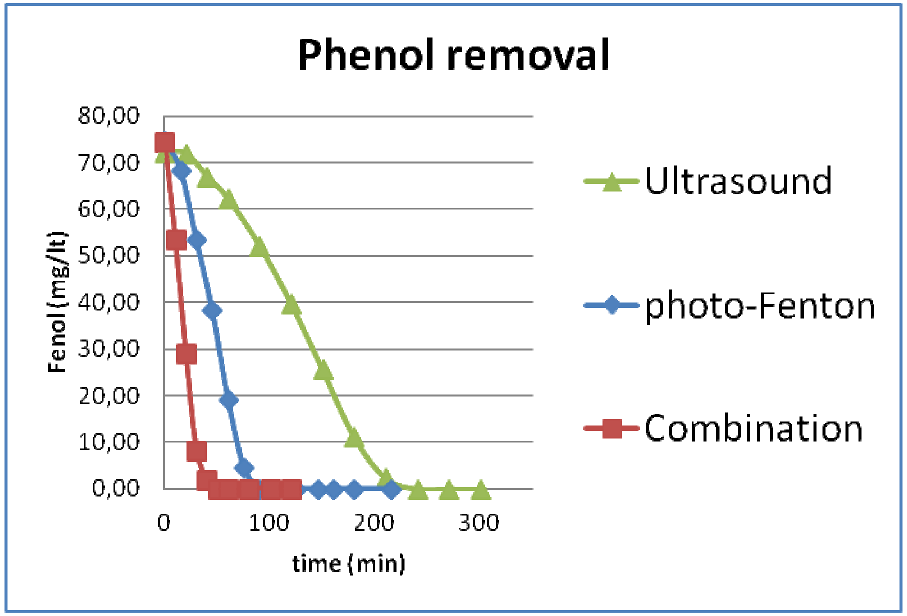
- Initial H_2O_2 concentration 200 mg/L and always maintained above 100 mg/L.
- Natural pH – Phenol: 6.18

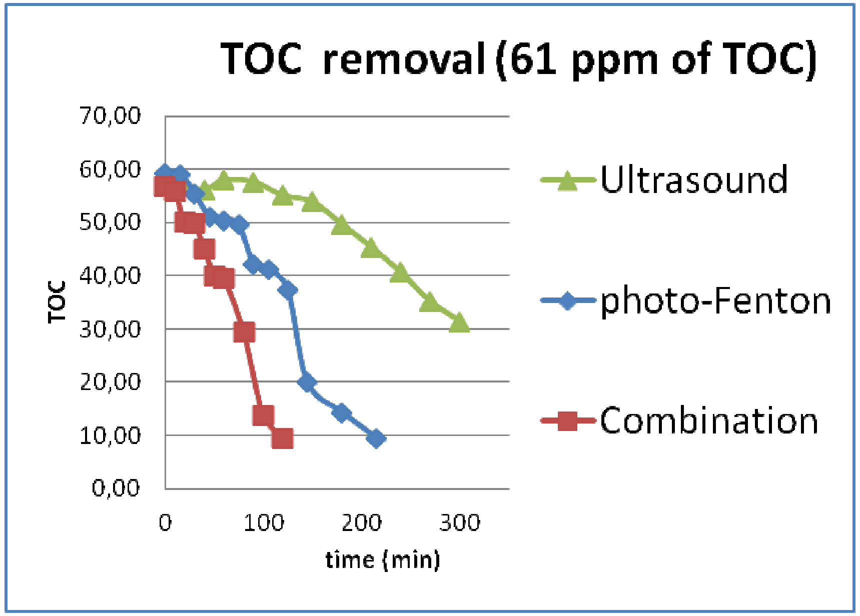
  Diuron: 5.40 (100 ppm)

  Bisphenol A: 4.83(80 ppm), 4.53(400 ppm)
- Fe^{2+} concentration: Phenol and BPA : 1 ppm

  Diuron: 1 and 5 ppm

Phenol (80 ppm)



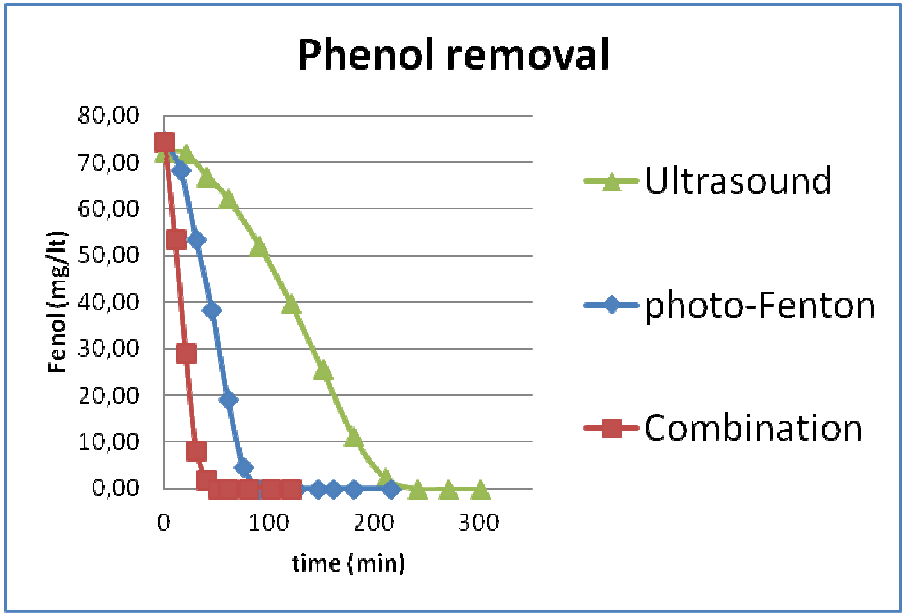


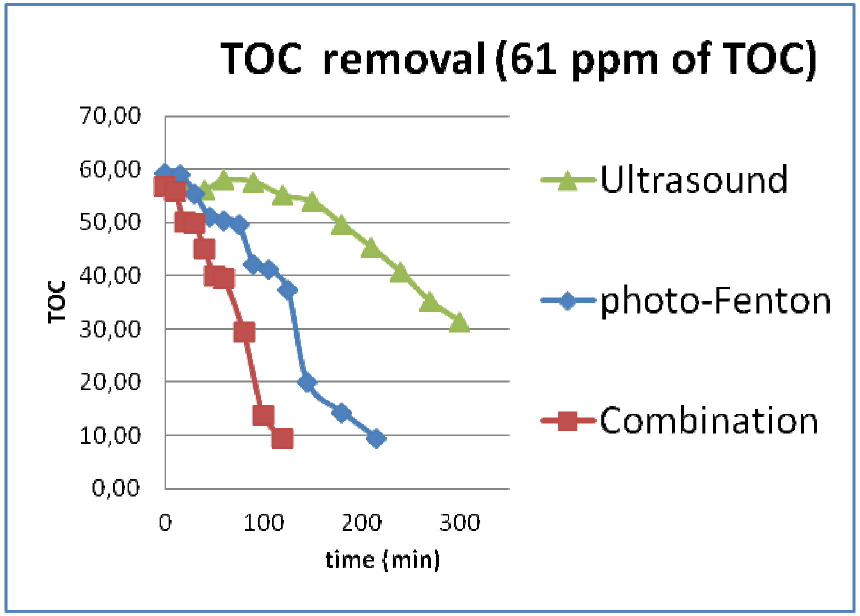
- Strong process synergy both for for degradation of phenol and TOC removal

S_{phenol}=1.42 S_{TOC}=1.58

- Synergy calculated for 40 mins of reaction for phenol degradation and 120 minutes for TOC removal.

Phenol (80 ppm)

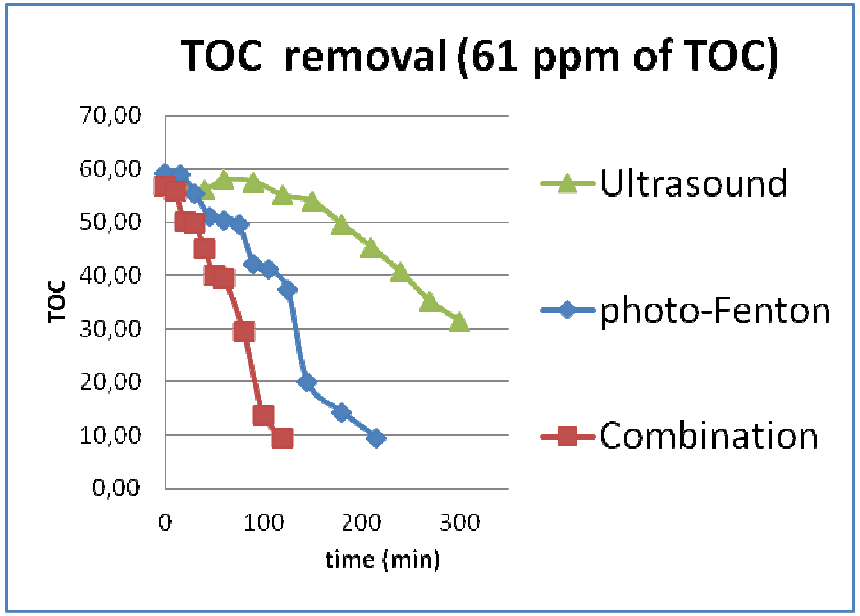


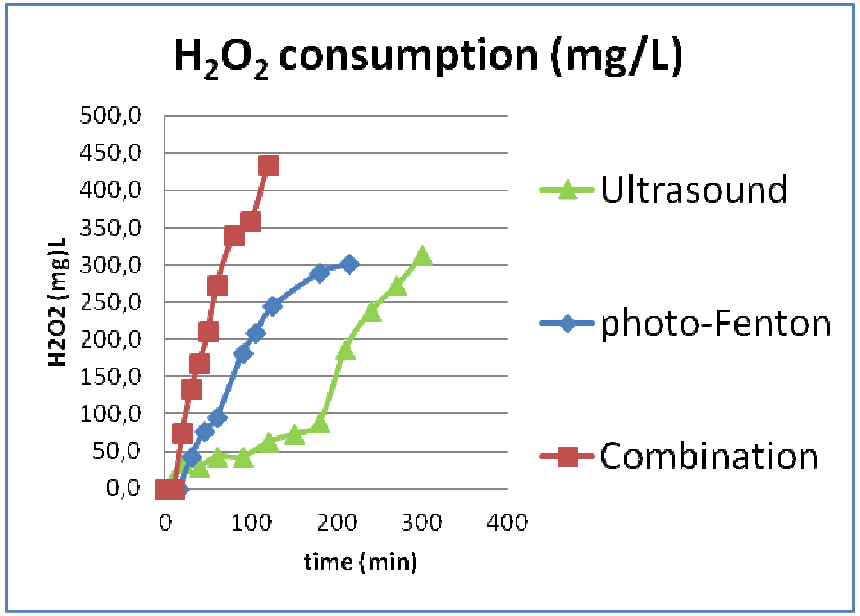


- Sensitive to US treatment despite high phenol hydrophilicity, possibly due to compensation from its relatively high volatility → Probable degradation in bubble interior

- Under US treatment alone, sharp increase in TOC removal rate from the moment phenol concentration reaches undetectable levels → Therefore, by-products preferentially mineralized by US

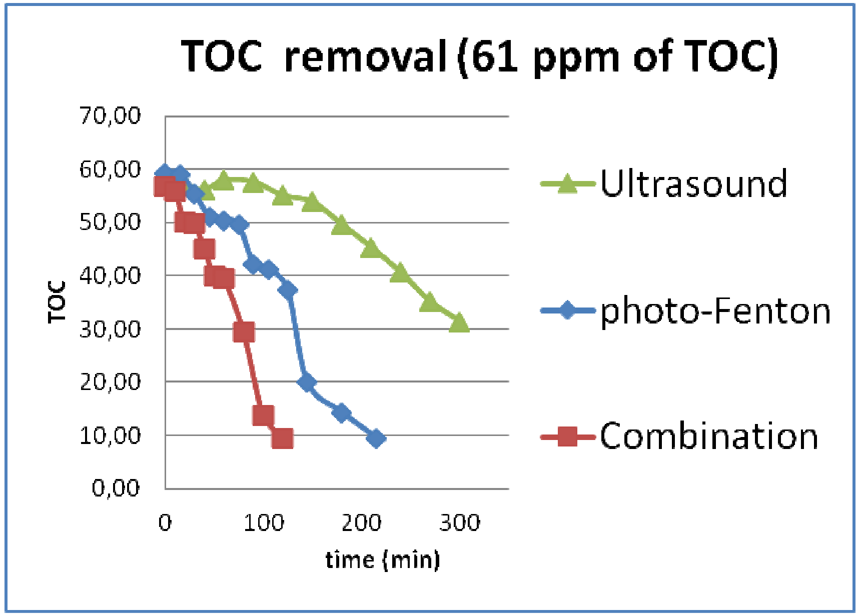
TOC and H_2O_2 consumption

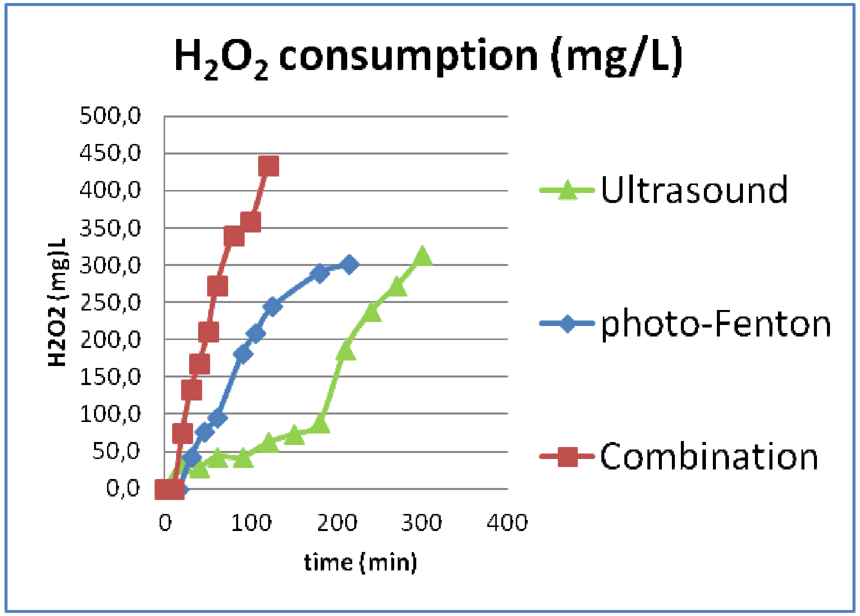




- Low H_2O_2 consumption until complete removal by US.

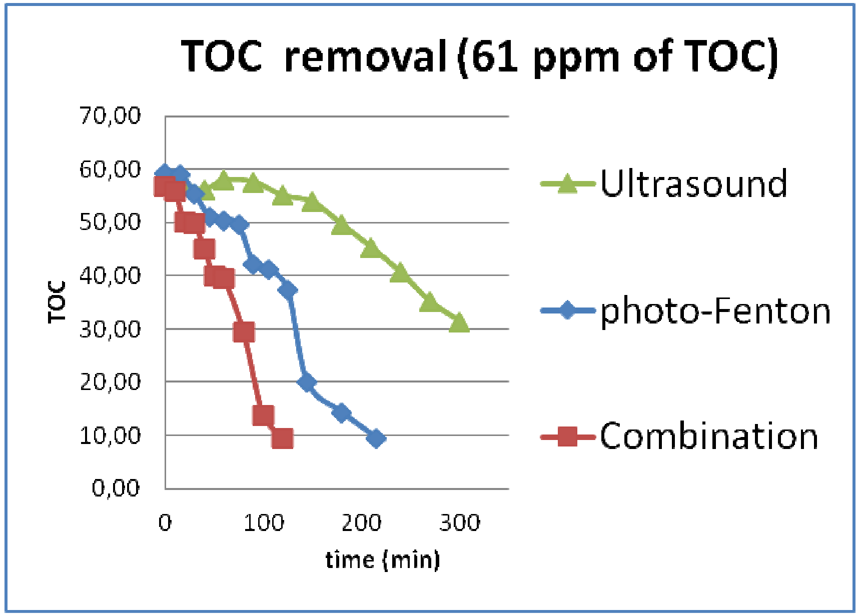
TOC and H_2O_2 consumption

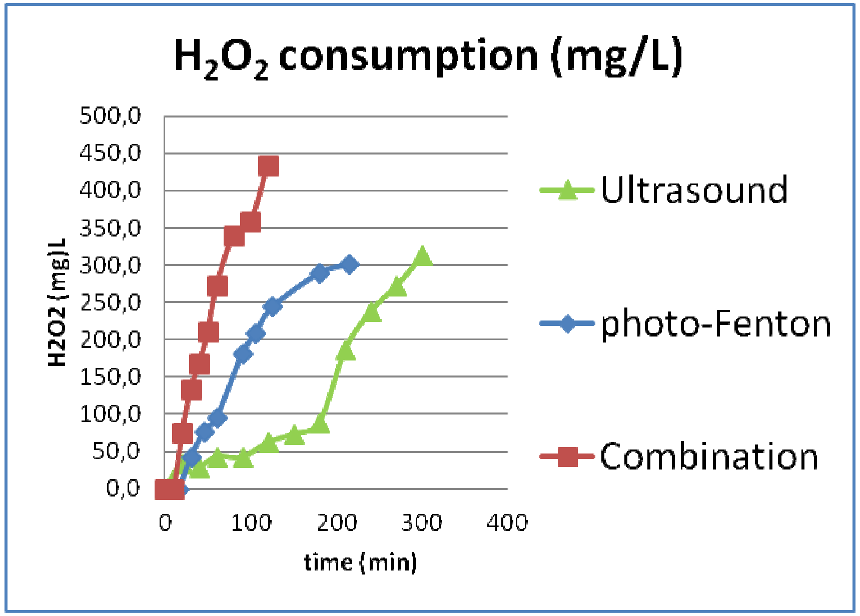




- Low H_2O_2 consumption until complete removal of phenol by US
- Sharp rise in consumption from that moment onwards
- Not effective in terms of H2O2 consumption/TOC removal → Possible dissociation of H_2O_2 But no radical reactions follow due to more hydrophilic byproducts being far from the cavitation area.

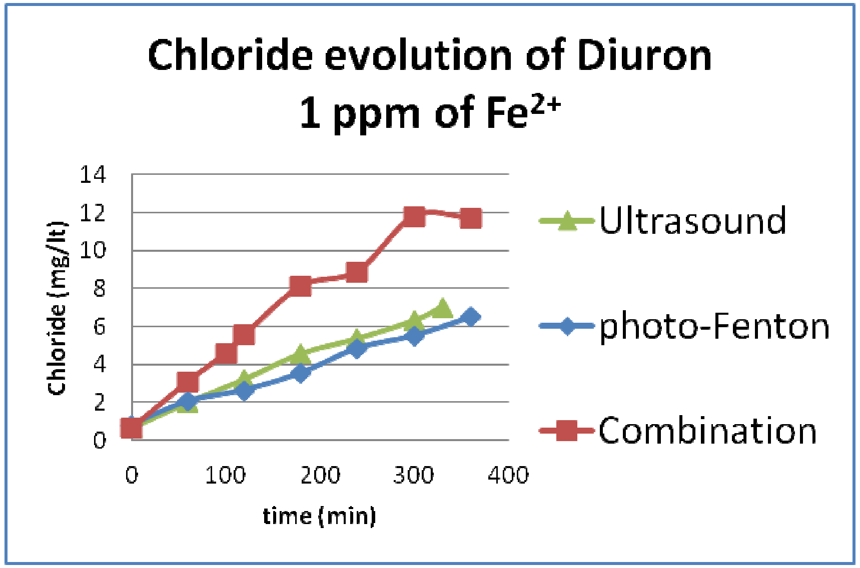
TOC and H_2O_2 consumption

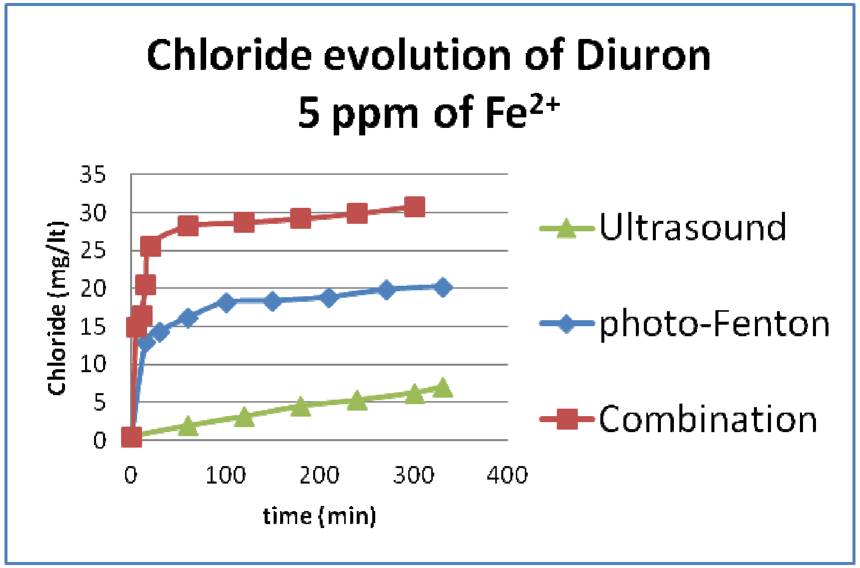




In terms of H_2O_2 consumption, combined treatment not beneficial

Diuron (100 ppm)



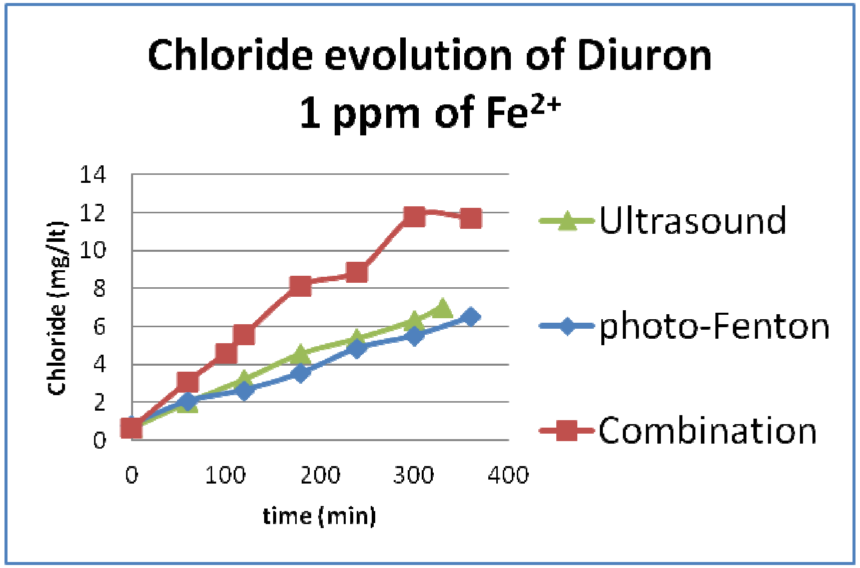


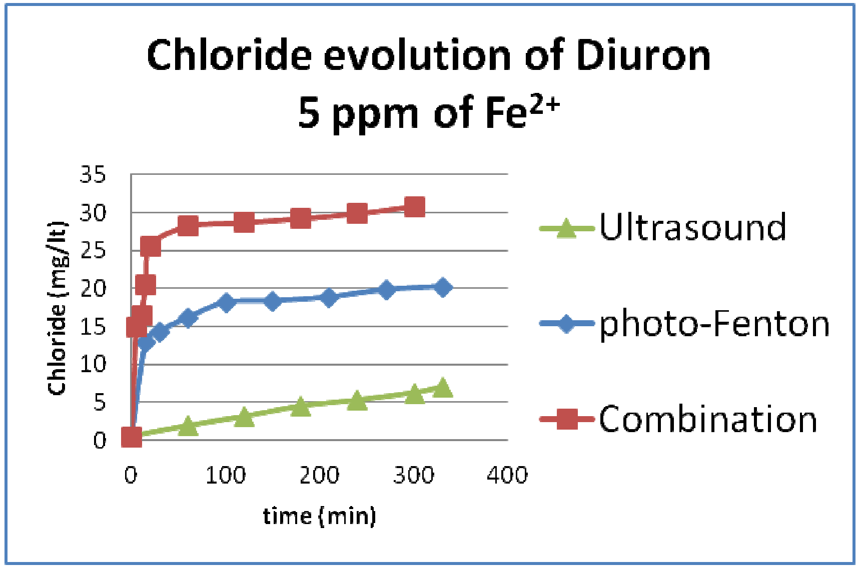
- Diuron supersaturated (2.4 times the solubility) in order to study homogenization properties of US

Experiments made with 1 and 5 ppm of iro

- Diuron degradation monitored via the release of chloride ions in solution
(30 ppm of Cl- corresponding to 100% degradation)

Diuron (100 ppm)





1 ppm of iron:

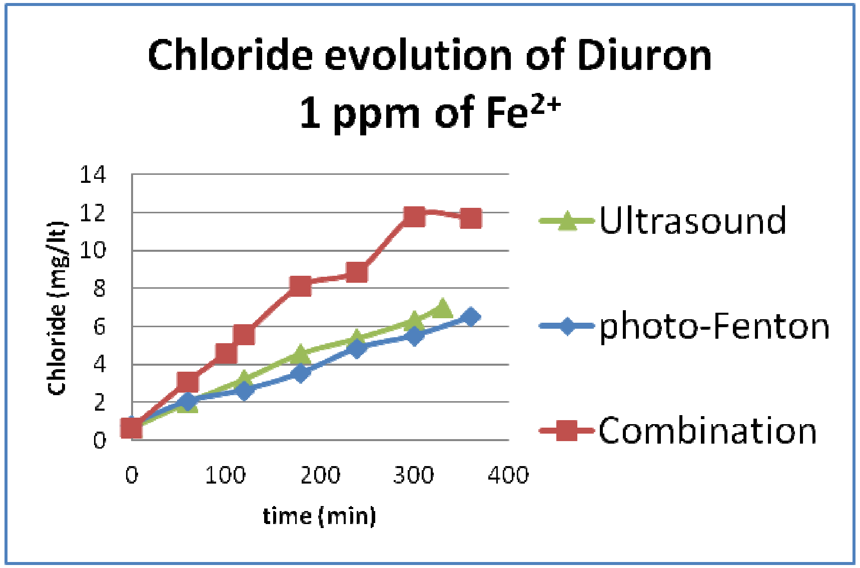
- US and p-Fenton behavior similar
- Additive effect of 2 processes when combined, with slight synergy (S=1.13)

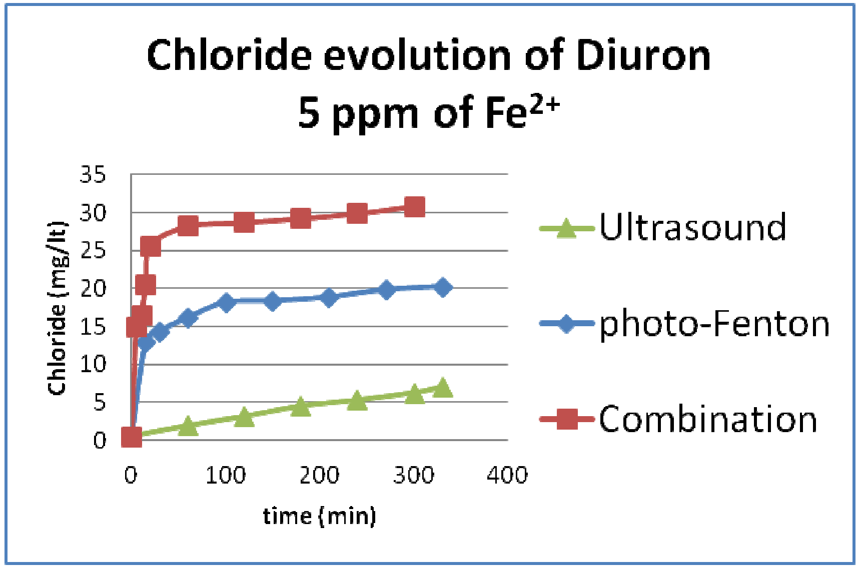
5 ppm of iron:

- Photo-Fenton alone restrained due to slow dissolution kinetics.
- **Nearly 100% degradation with 5 ppm of iron after only 30 mins of combined treatment**

Excellent synergy: S=2.31

Diuron (100 ppm)



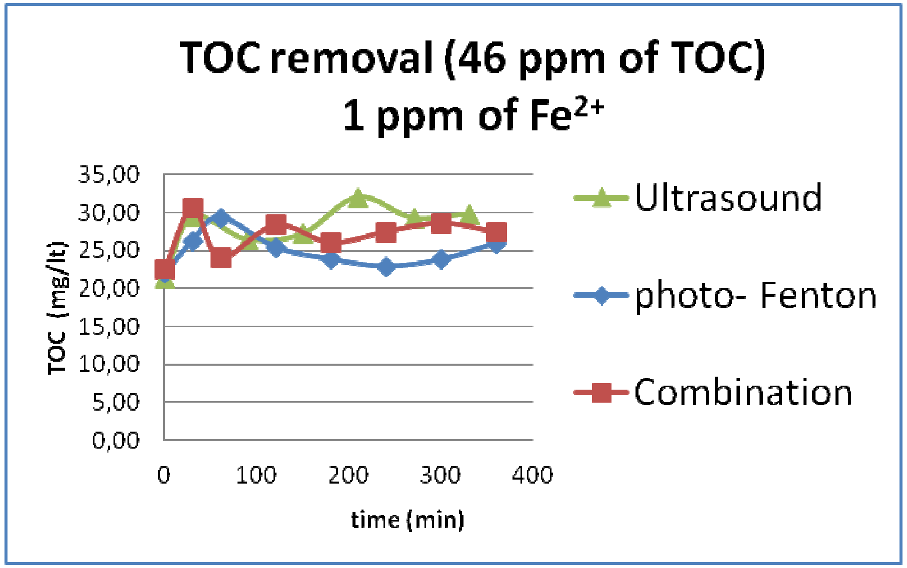


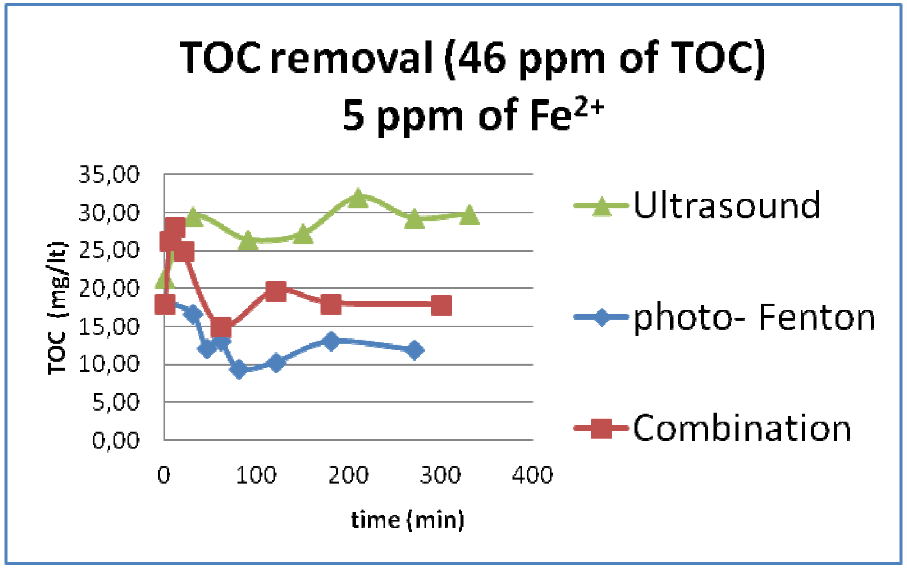
US exceptional for solubilizing diuron.

Creation of additional nucleation sites on solid surfaces

Bubble collapse when surrounded by solid can be assymetrical , causing bombardment of its surface by solvent microjets

Diuron (100 ppm)



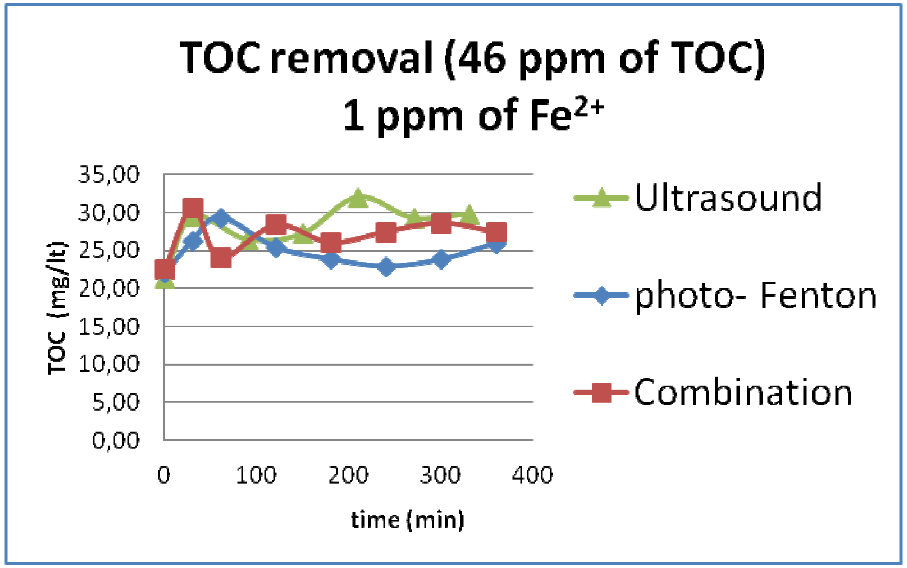


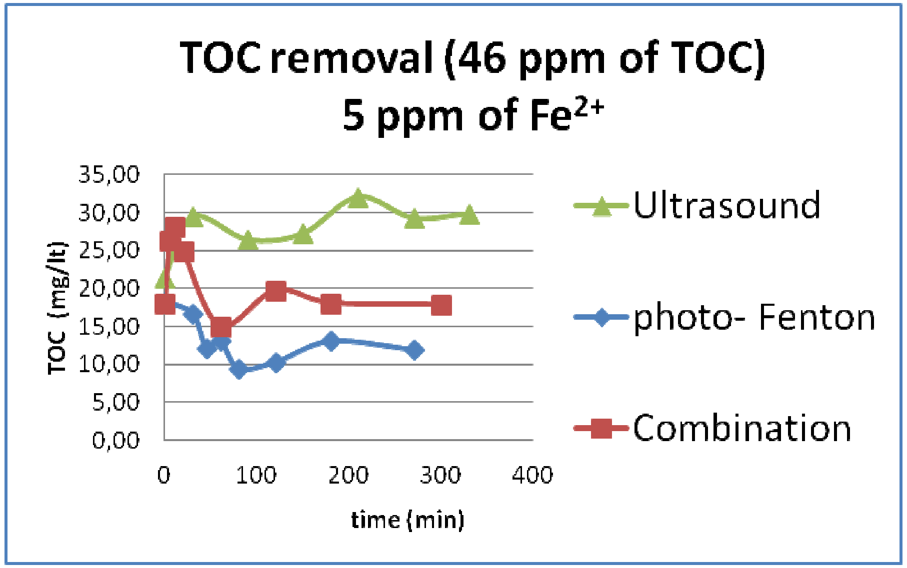
For 5 ppm of iron:

US alone – rise in TOC due to solubilization, but no significant removal
Photo-Fenton alone – lowering of TOC in solution, but no significant dissolution
Combination – Rise in TOC due to dissolution, followed by lowering.

} ***Plateau***

Diuron (100 ppm)

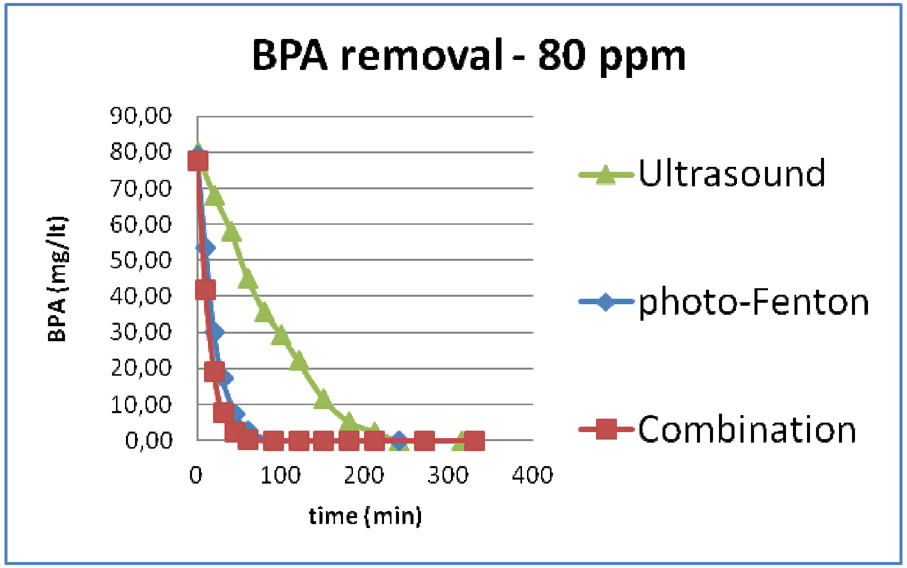


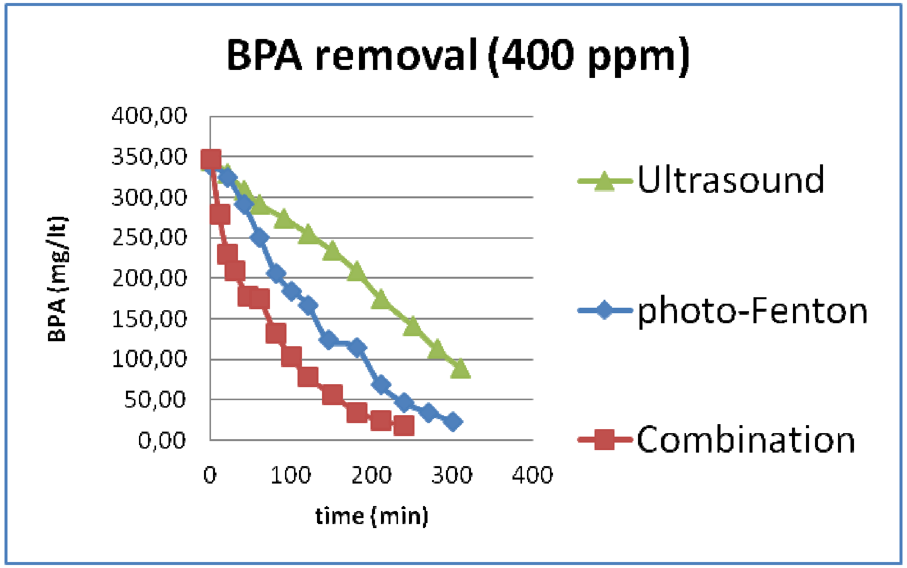


Once diuron removed from solution, combined and photo-Fenton treatment behaviour similar

- More hydrophilic byproducts unaffected by US
- pH not optimal for photo-Fenton → Unavailability of iron due to precipitation
- Iron complexation with intermediates

Bisphenol A (80 and 400 ppm)

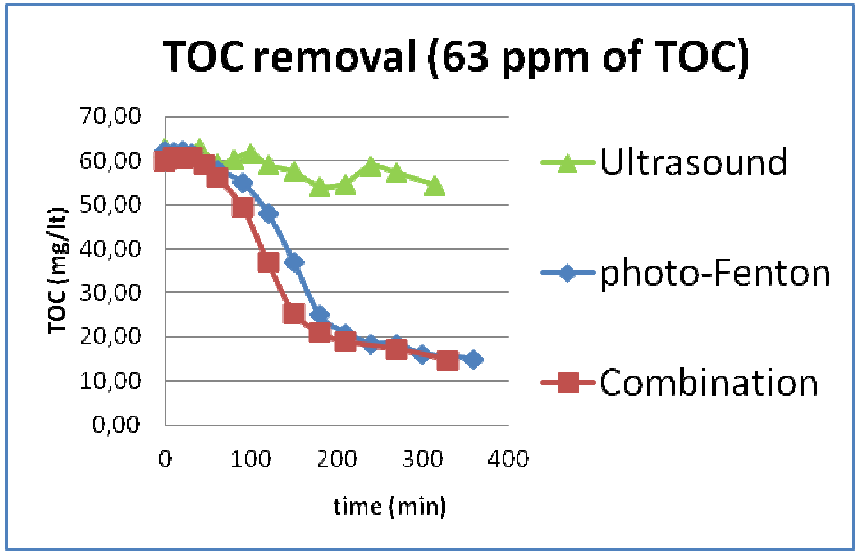


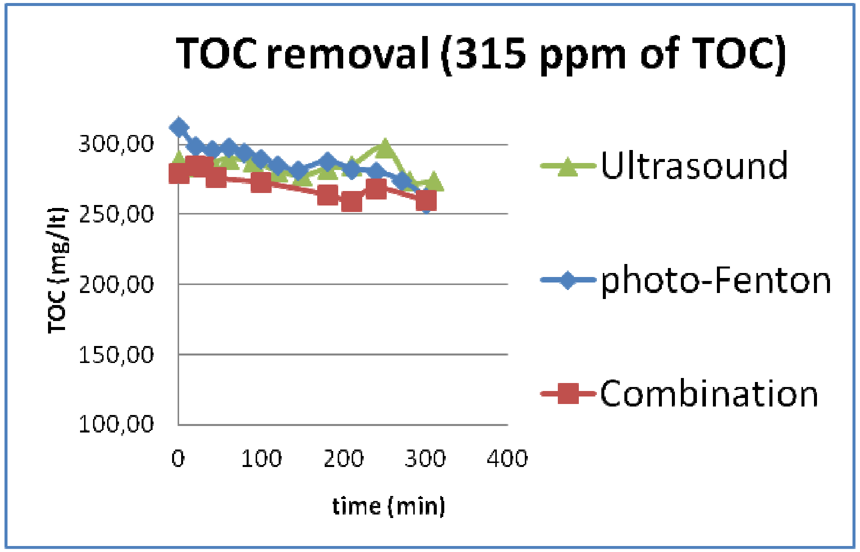


•For 80 ppm: No synergy observed, degradation kinetics dominated by photo-Fenton

•For 400 ppm: Kinetics more clearly observed- still combined process kinetics not significantly better than sum of its parts (S=1.12 for the first 60 minutes)

Bisphenol A (80 and 400 ppm)





•For 80 ppm: Slight synergy for TOC removal (S=1.21 based on 60 minutes of treatment)

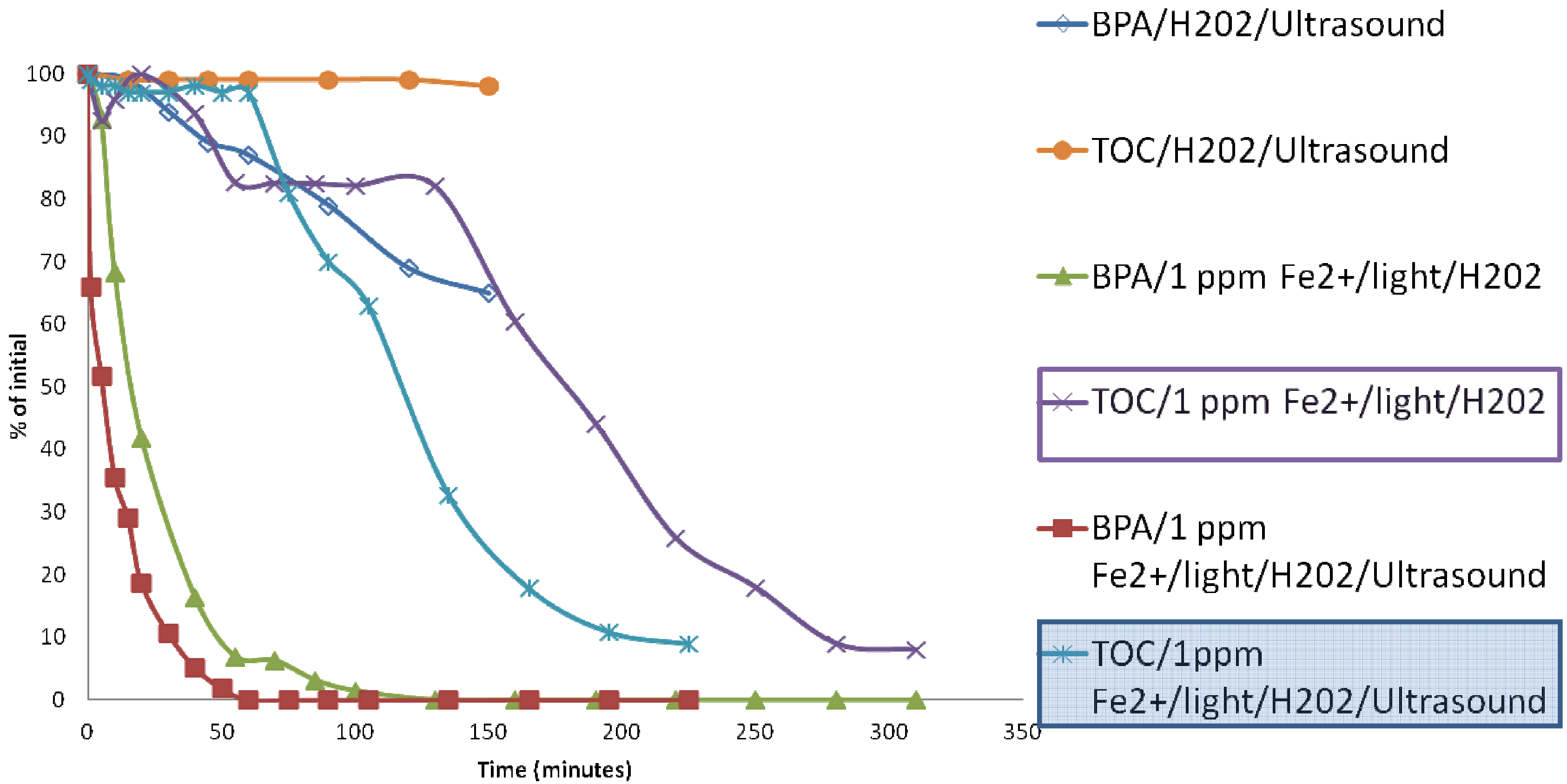
•For 400 ppm: TOC was difficult to remove.

➢ The chemical equilibria between the various Intermediate species could be significantly different and favor the predominance of more persistent compounds

➢ Light penetration limited due to dark color of concentrated intermediates

➢ pH acidid (3.4) but not optimal (2.8)→ Possible precipitation or complexation of iron

BPA degradation at 80 W, 379 KHz, different reactor geometry



Conclusions

- Synergy effects observed during the combined treatment of both phenol and diuron.
- US improves solubilization of supersaturated diuron. Possible application for homogenization of pollutants forming emulsions or suspensions?
- Necessary to find ways of limiting H_2O_2 consumption.
- Factors relating to the specific acoustic field of US reactors could account for dramatic differences.

Future research

- Continuation of research on US to clarify the most critical operational parameters
- Determination of biodegradability of the byproducts of the different treatments
- Inclusion of biological treatment step to the system.