GRUPO DE INVESTIGACIÓN
en Remediación Ambiental y Biocatálisis

UNIVERSIDAD
DE ANTIOQUIA
1803

Application of Ultrasound for the Degradation of Organic Pollutants in Waters

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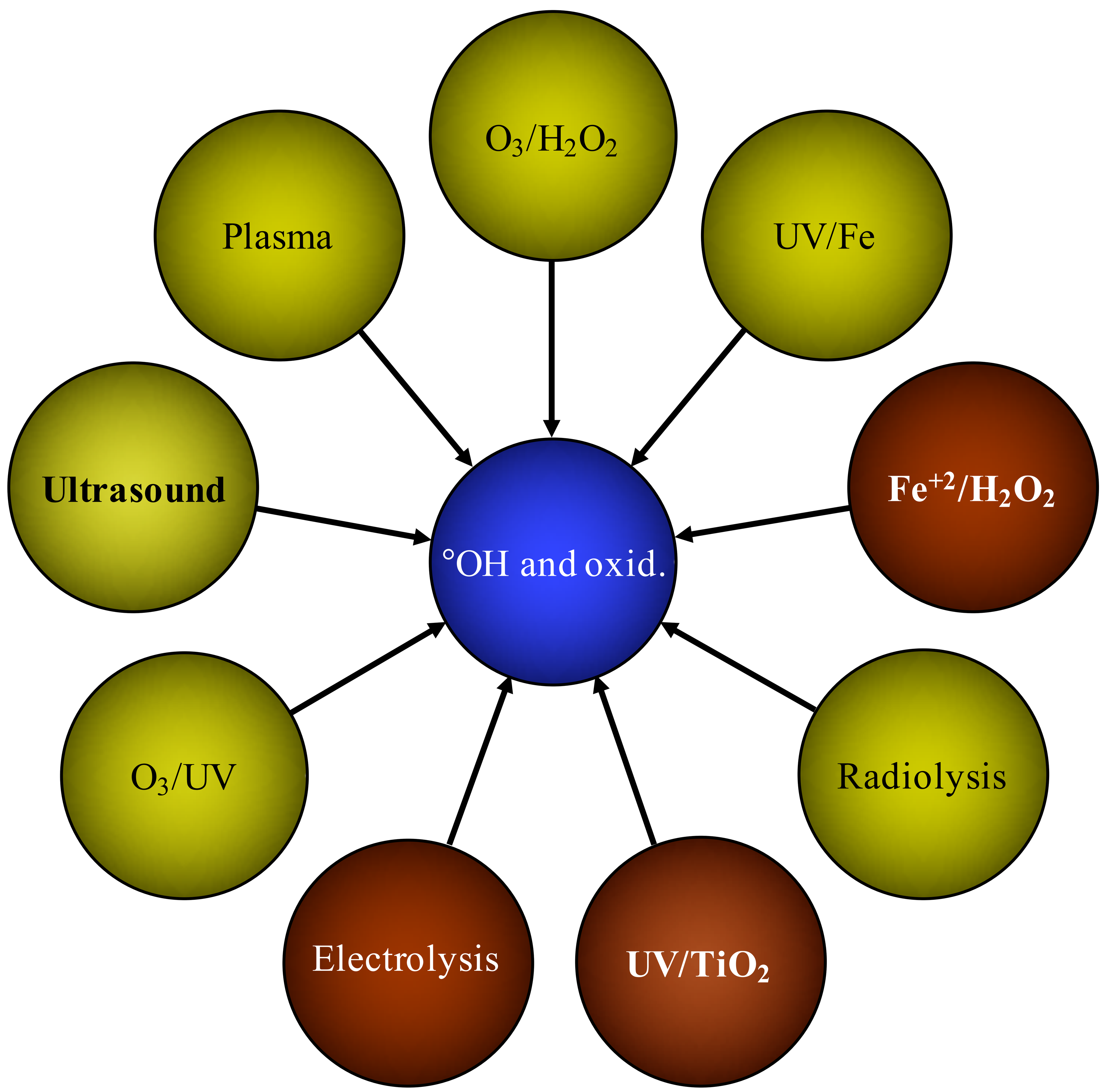
Universidad de Antioquia, Medellin, Colombia

A simplified part of the water cycle

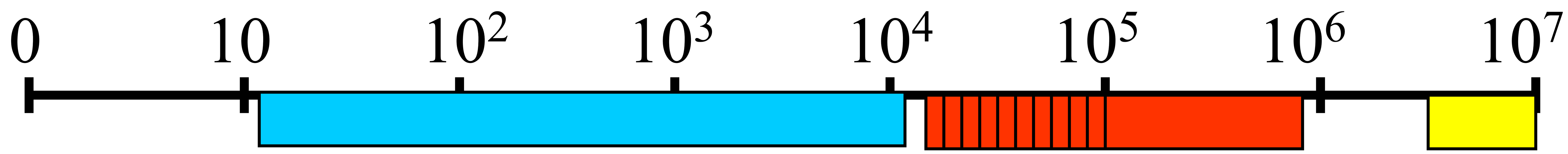
Antibiotics: Recalcitrants to the conventional primary and secondary processes in MWWTP

Advanced Oxidation Processes



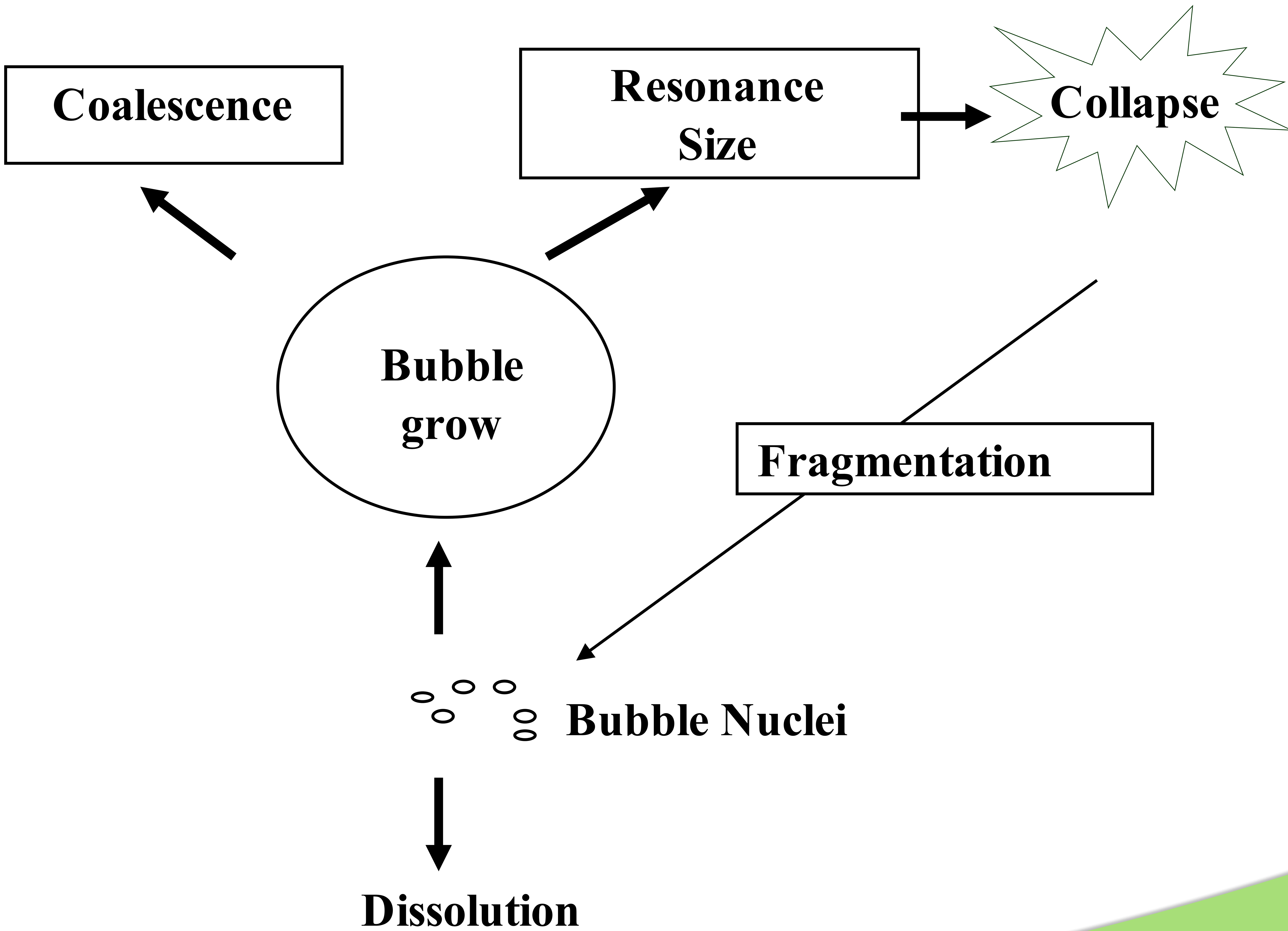
Ultrasound

Ultrasonic Frequency (Hz)

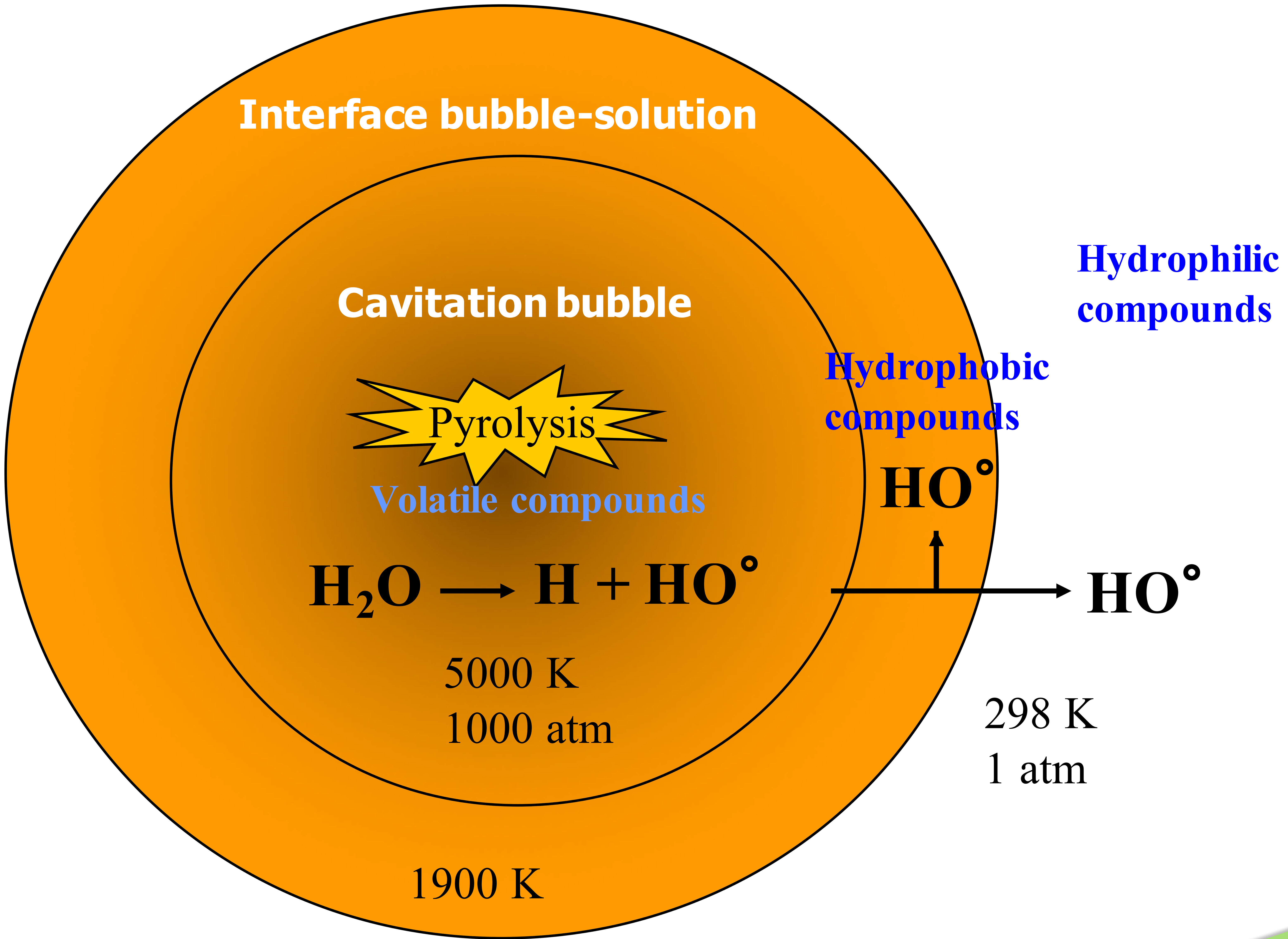


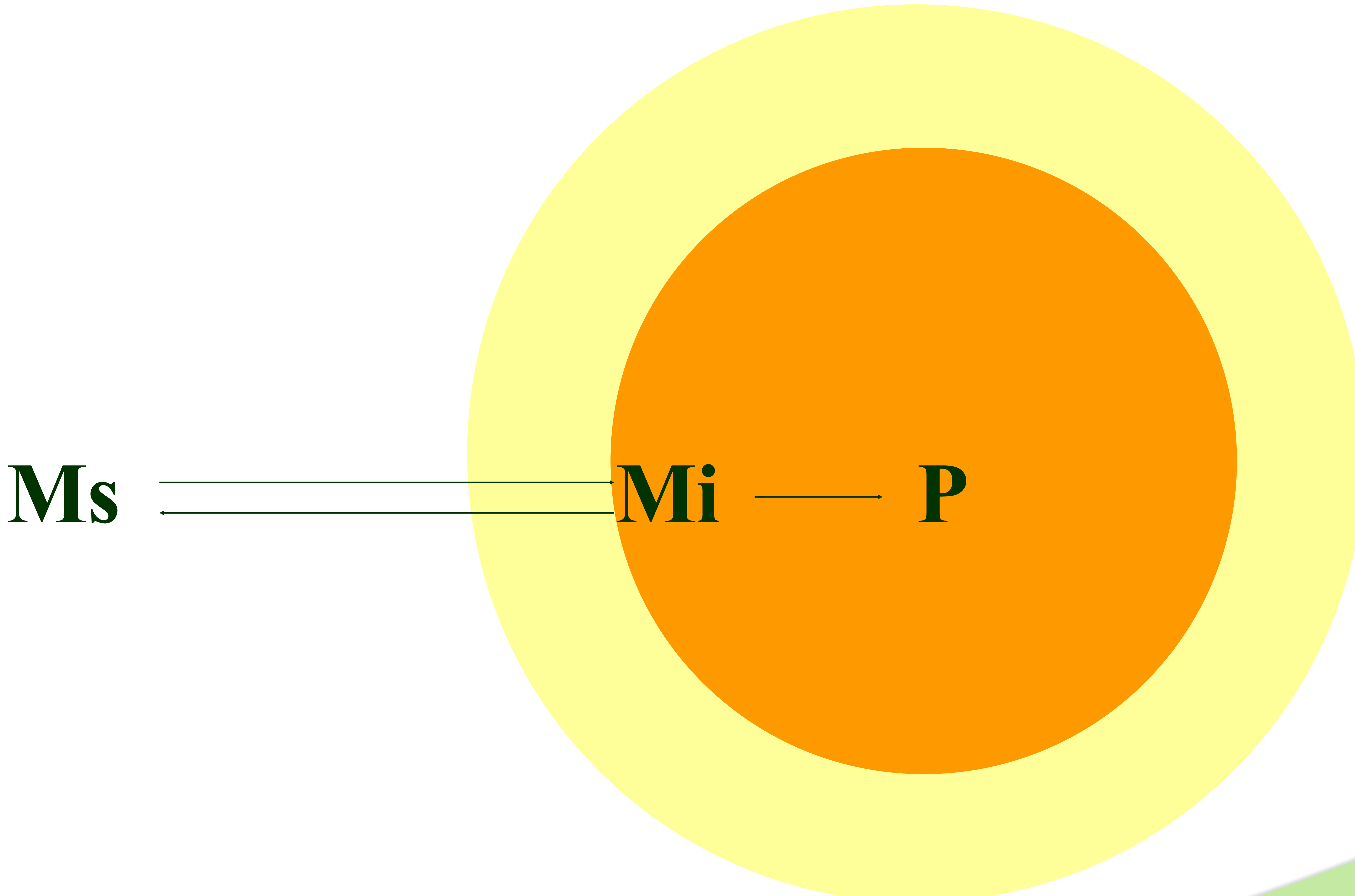
Audible sound	16 Hz - 18 kHz
Conventional ultrasound	20 kHz - 100 kHz
Sonochemical reactions	20 kHz - 1 MHz
Medical applications	5 MHz - 10 MHz

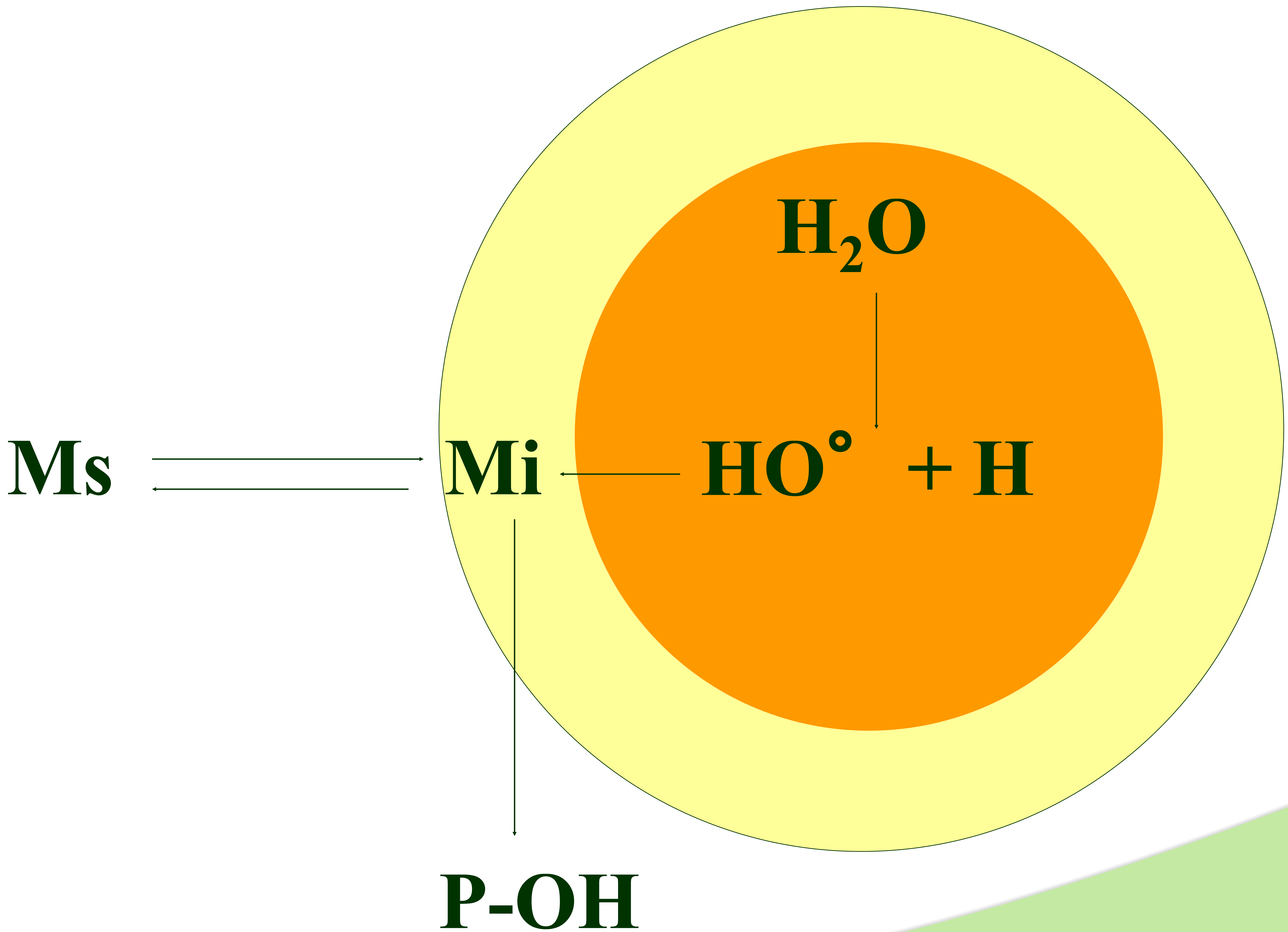
Fate of bubbles in liquids under ultrasound



Fate of bubbles in liquids under ultrasound




Ms
Mi
P

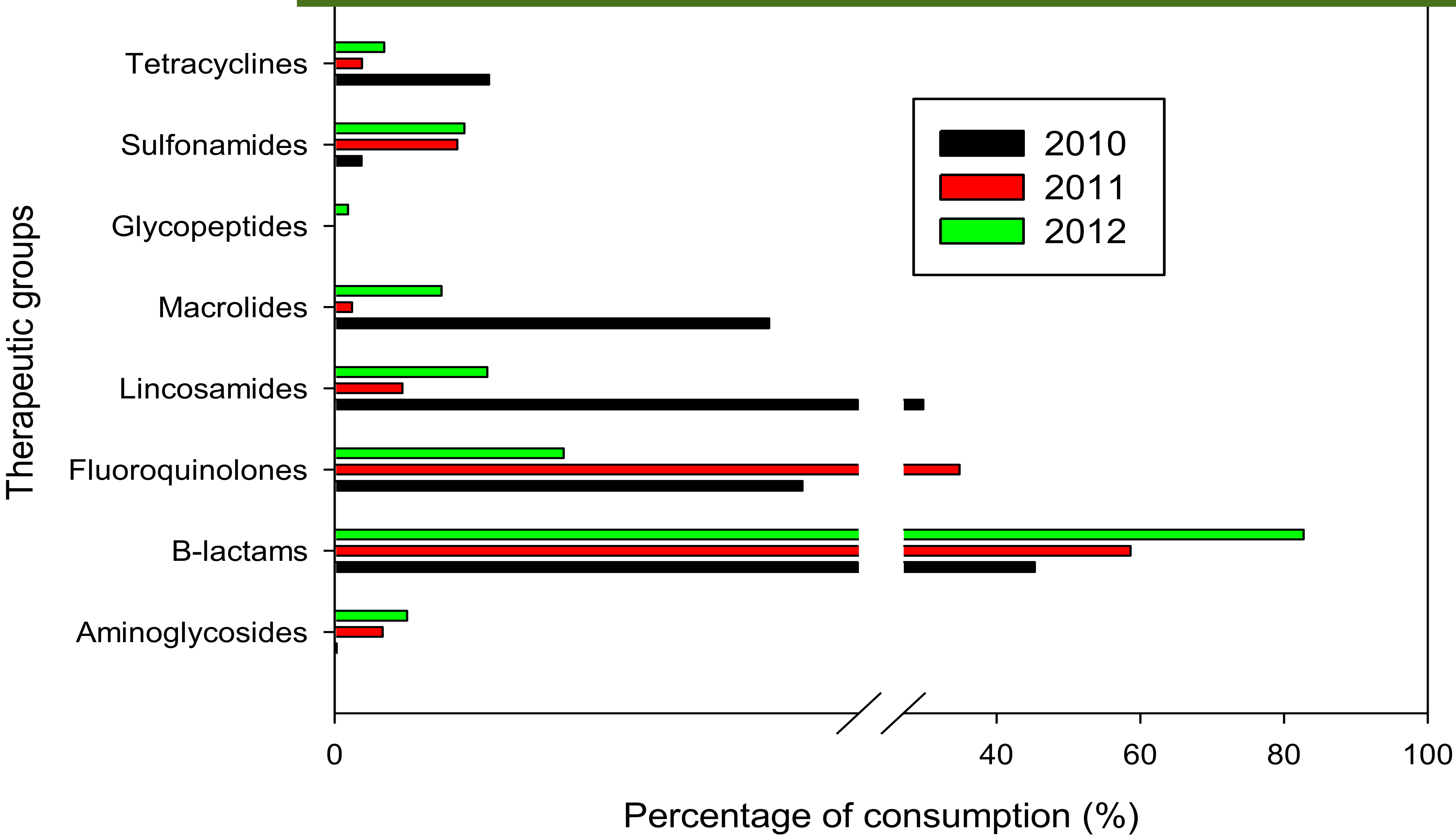

H_2O
Ms
Mi
HO°
+ H
P-OH

Emergent pollutants: Antibiotics

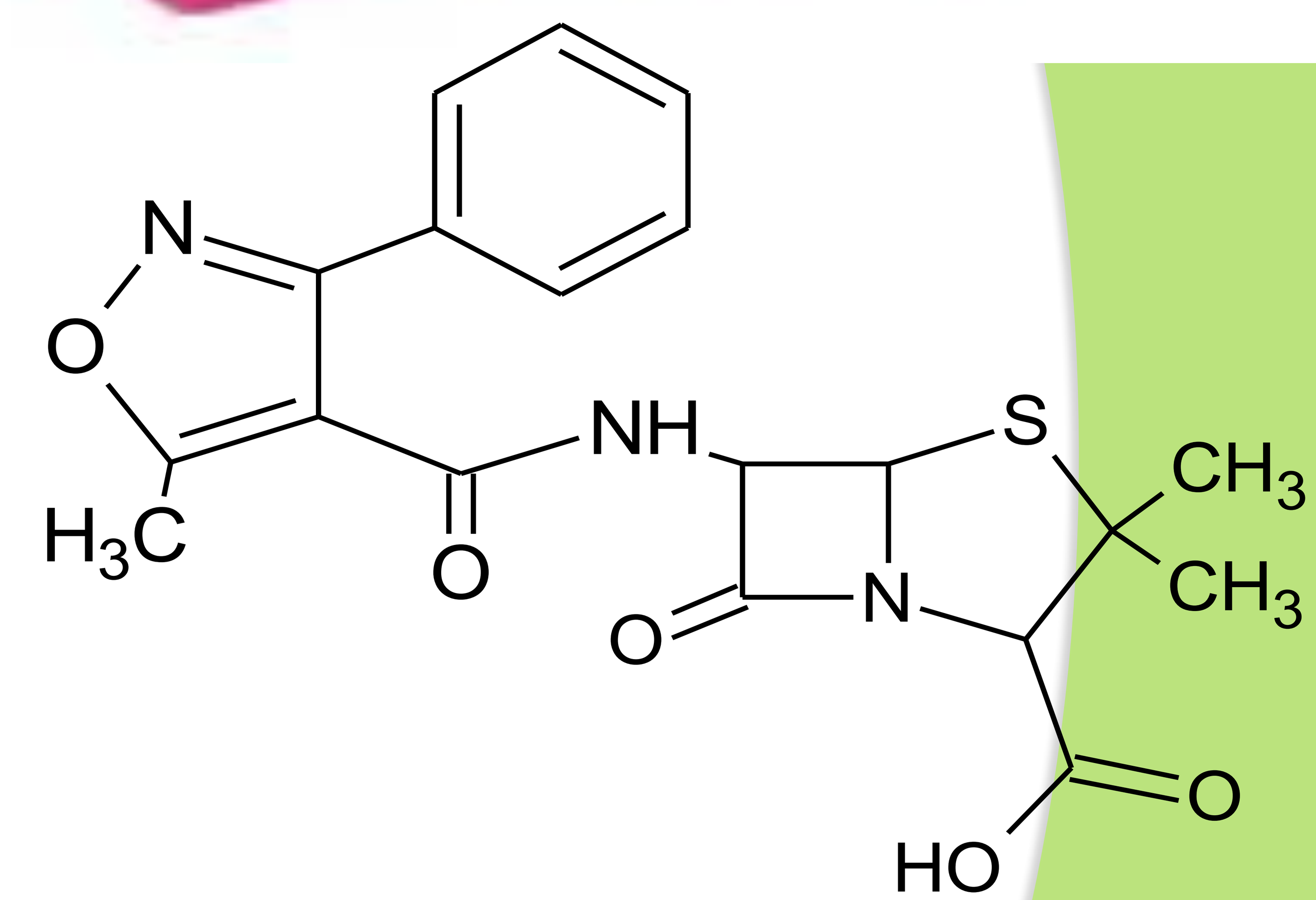
Superbugs

Antibiotics consumption

β-lactams also are in the first place of antibiotics consumption in the world



SISMED, Colombia (2010-2012)



OXA resistant bacteria have been reported in Latin-American and in USA

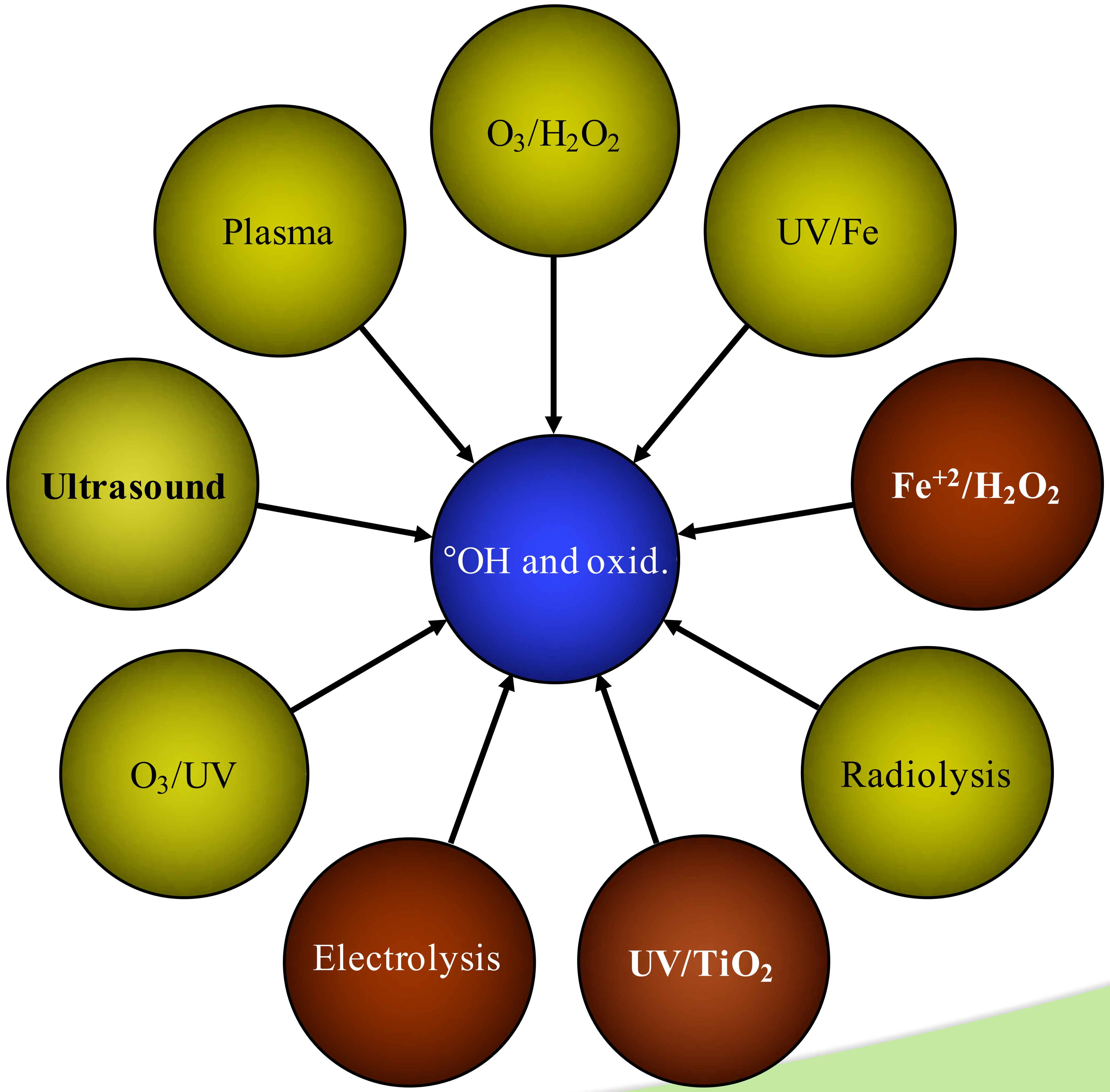
J. Chromatogr. A, vol. 1115, no. 1–2, pp. 46–57, May 2006

Diabet. Foot Ankle, vol. 3, pp. 1–6, 2012

J. Environ. Manage., vol. 92, no. 10, pp. 2304–47, Oct. 2011

Advanced Oxidation Processes

- ✓ Whether or not ultrasound can be of special interest: To compare the ability of the sonochemical system with photo-Fenton, TiO_2 photocatalyssis and electrochemical oxidation to eliminate the antimicrobial activity of water solutions containing oxacillin in presence of some pharmaceutical additives



Experimental part : Photochemical systems

Oxacillin: 47.23µmol L^{-1} (20 mg L^{-1})
Initial pH = 5.6

✓ TiO_2 photocatalysis:
- 0.05 mg L^{-1} TiO_2
- **150 W (λ_{max} = 365 nm)**
- 100 mL

✓ Photo-Fenton:
- 90 µM Fe^{2+}
- 1000 µM H_2O_2
- 150 W (λ_{max} = 365 nm)
- 100 mL

Experimental part : Ultrasonic and sonochemical systems

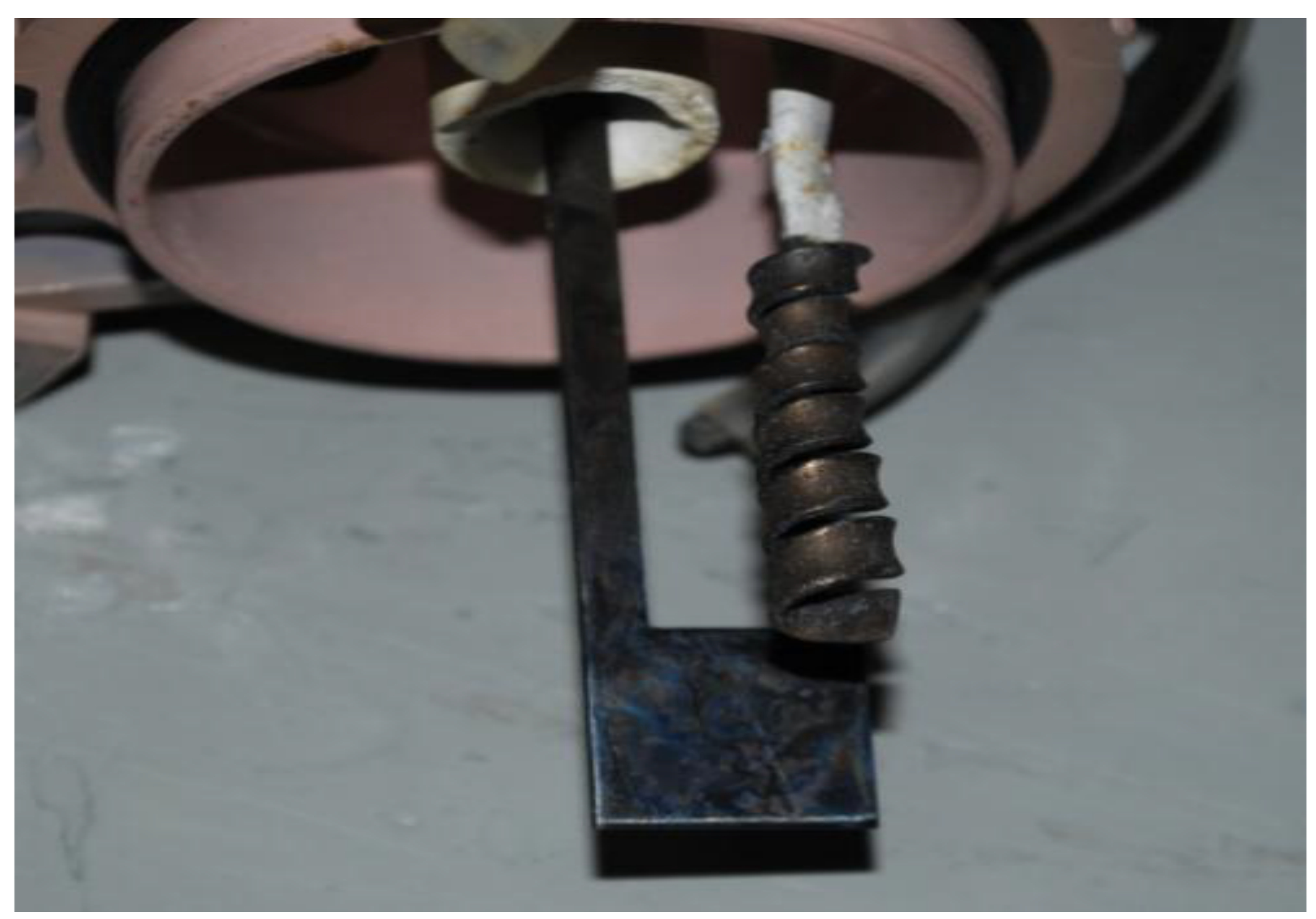
✓ Ultrasound:

- **60 W (275 kHz)**
- 250 mL

Oxacillin: 47.23µmol L^{-1} (20 mg L^{-1})
Initial pH = 5.6

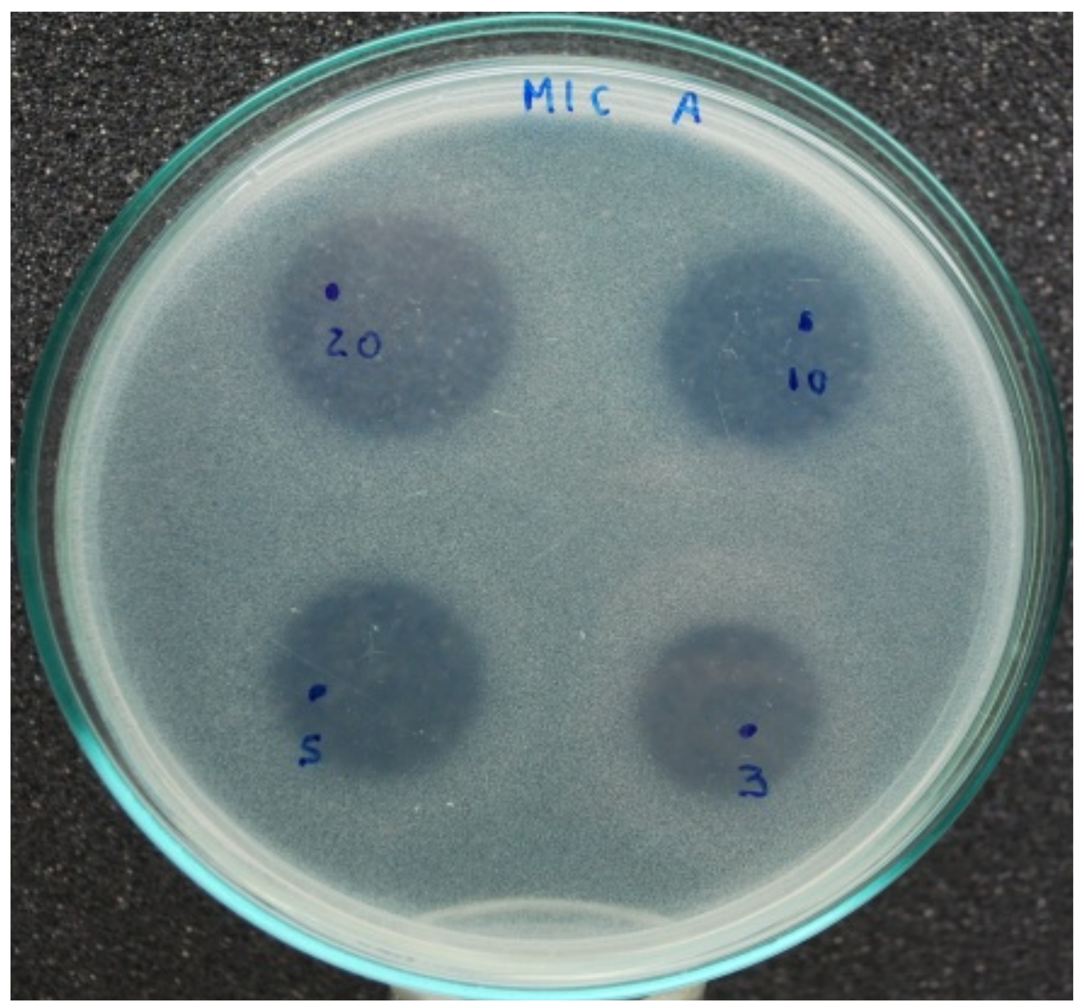
✓ Anodic oxidation:

- **Anode: Ti/IrO_2**
- Catode: Zr
- **0.0625 M NaCl**
- 5 mA cm^{-2}
- 150 mL



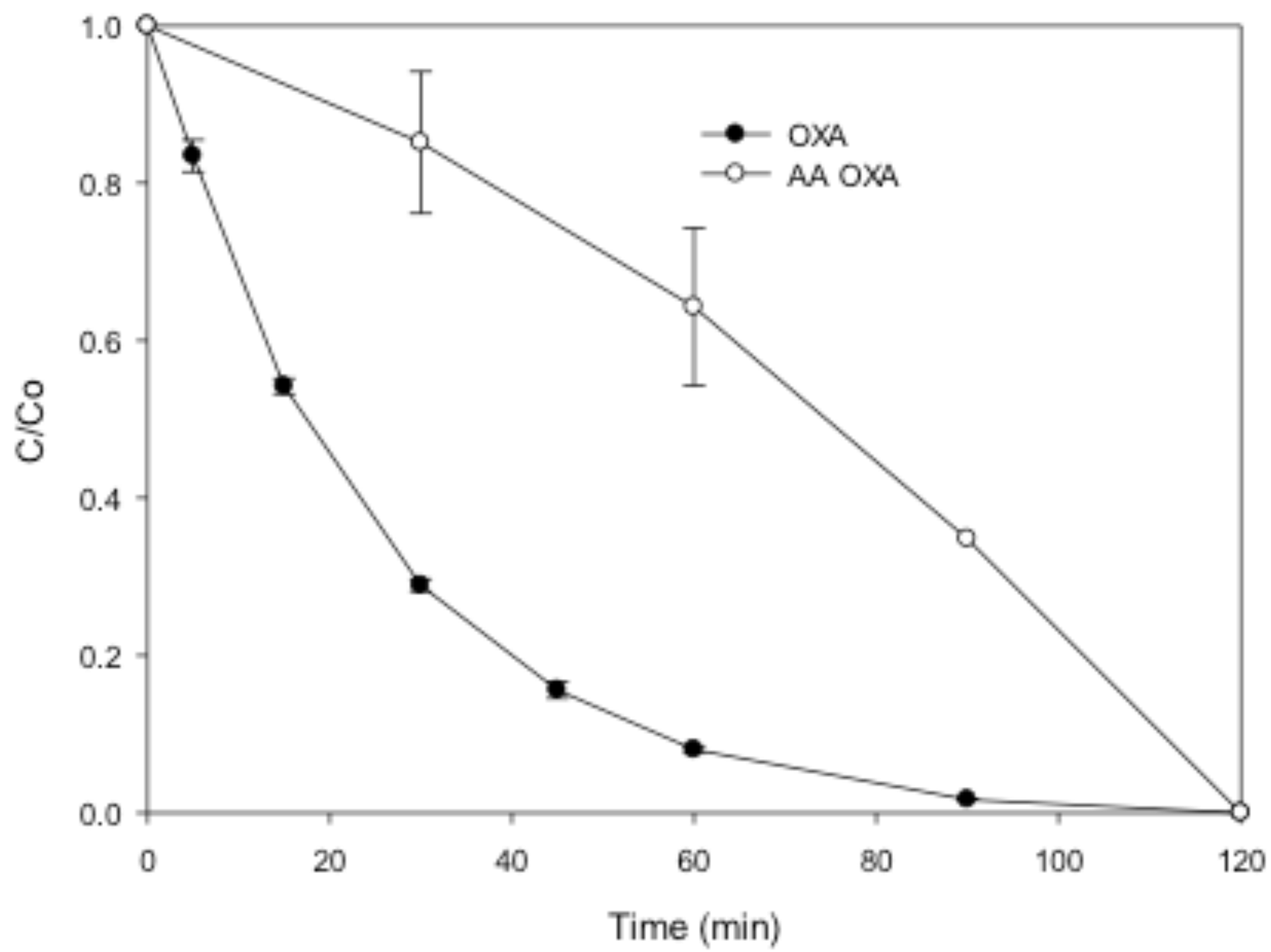
Experimental part: Analysis

- ✓ Antimicrobial activity (AA): Inhibition halo methodology (*Staphylococcus aureus*)

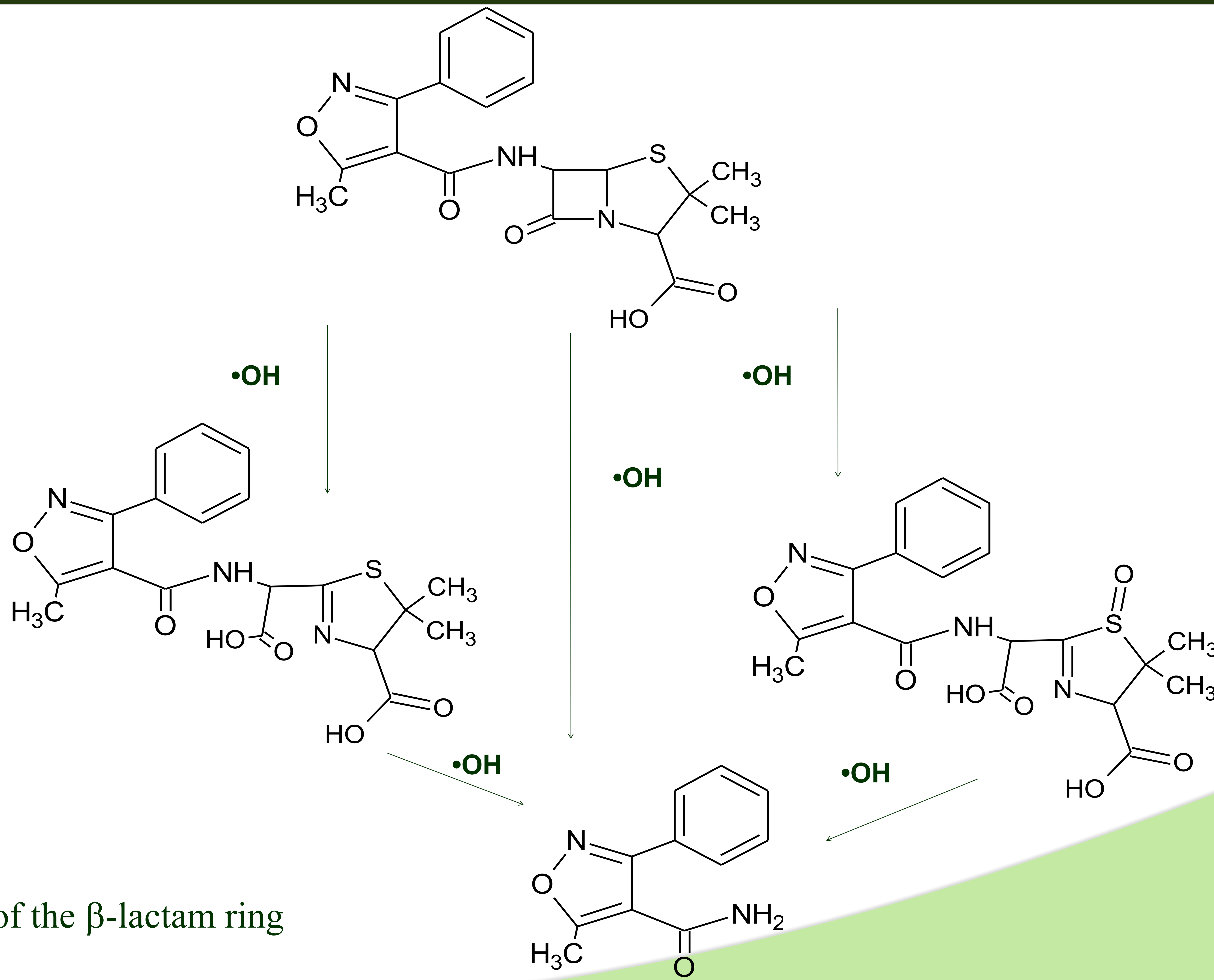


- ✓ Oxidative species: Iodometry (UV)
- ✓ Oxacillin (HPLC)
- ✓ Initial organic by-products (HPLC/MS)

Results and discussion: Ultrasound action
Antibiotic degradation vs Antimicrobial removal

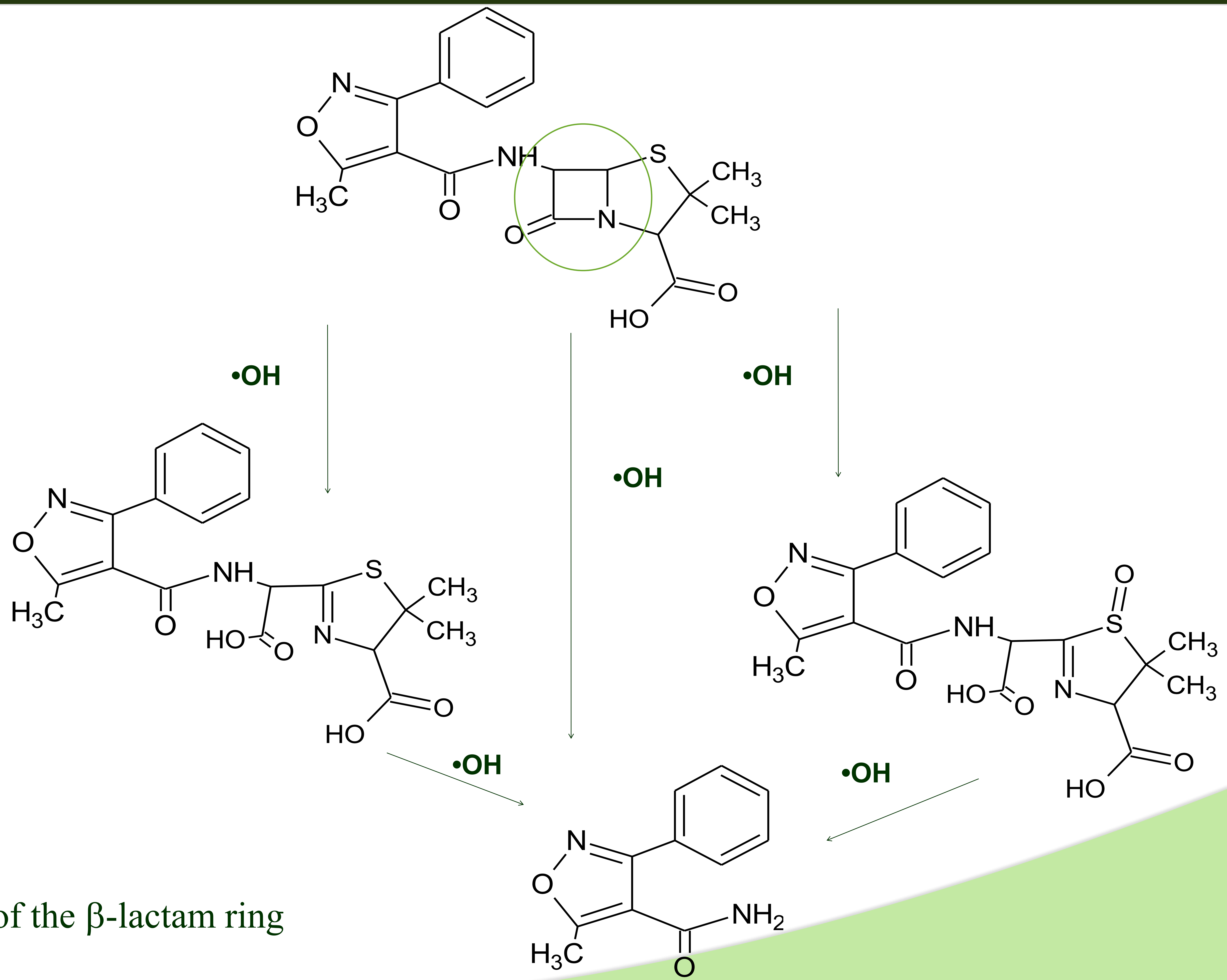


Results and discussion: By-products upon ultrasonic action



- ✓ Disruption of the β-lactam ring

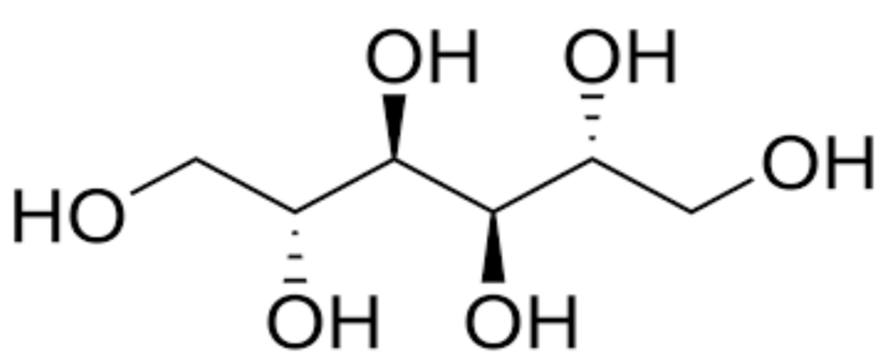
Results and discussion: By-products upon ultrasonic action



✓ Disruption of the β-lactam ring

E.A. Serna-Galvis et al. / Chemical Engineering Journal 284 (2016) 953–962

Results and discussion: Pharmaceutical additives

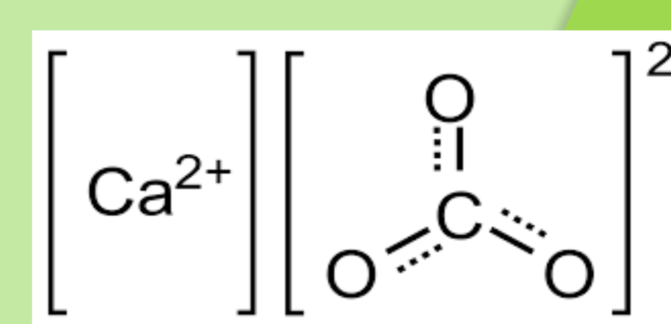


Mannitol (MAN)

Antibiotic production

10 times more concentrated than OXA

Calcium carbonate (CC)



Handbook of Pharmaceutical Excipients, Sixth. London: Pharmaceutical Press, 2009.

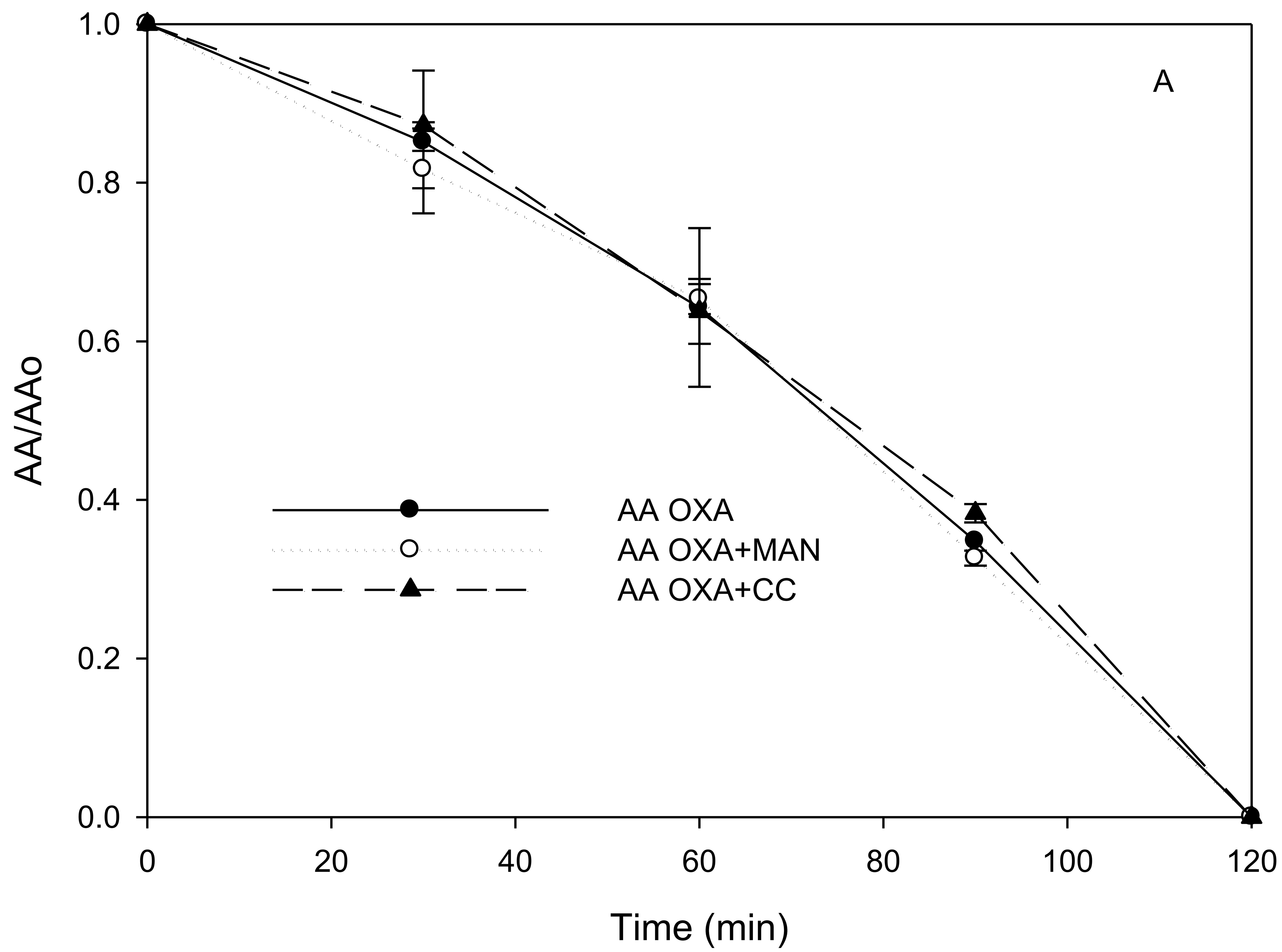
Results and discussion:
Antibiotic degradation upon ultrasonic action

Table 1. Rates of pollutant degradation (rd) in different additives

	Water	OXA	OXA + MAN	OXA + CC
r_d (μM min^{-1})	1.4±0.0	1.3±0.1	1.4±0.1	

E.A. Serna-Galvis et al. / Science of the Total Environmnet, In press

Results and discussion: Antibiotic degradation vs Antimicrobial removal

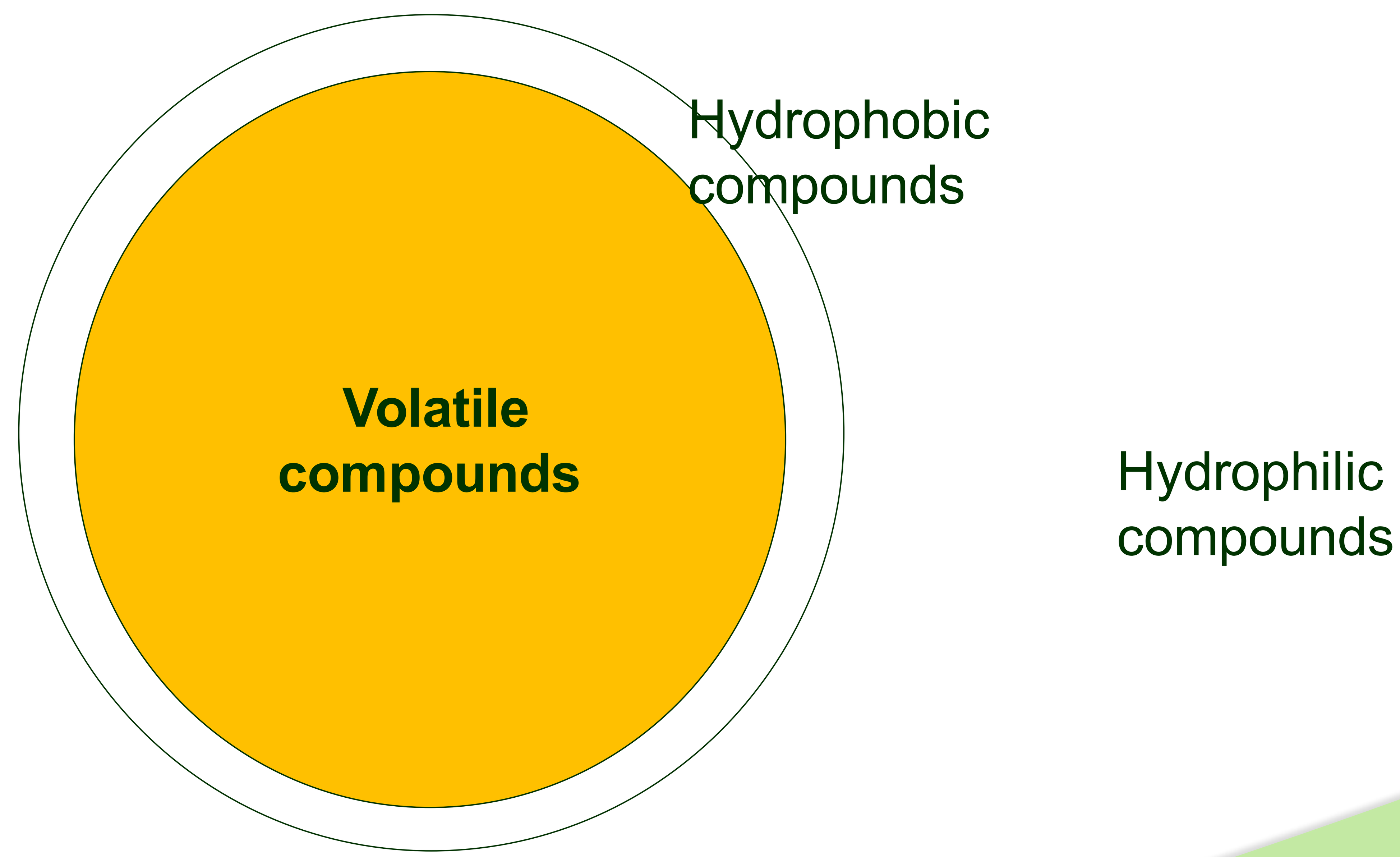


E.A. Serna-Galvis et al. / Science of the Total Environmnet, In press

Results and discussion: Antibiotic degradation vs Antimicrobial removal

Kow
Hydrophobicity indicator

Sustance	Kow
OXA	2.38
MAN	-3.10
CC (HCO_3^-)	-4.01



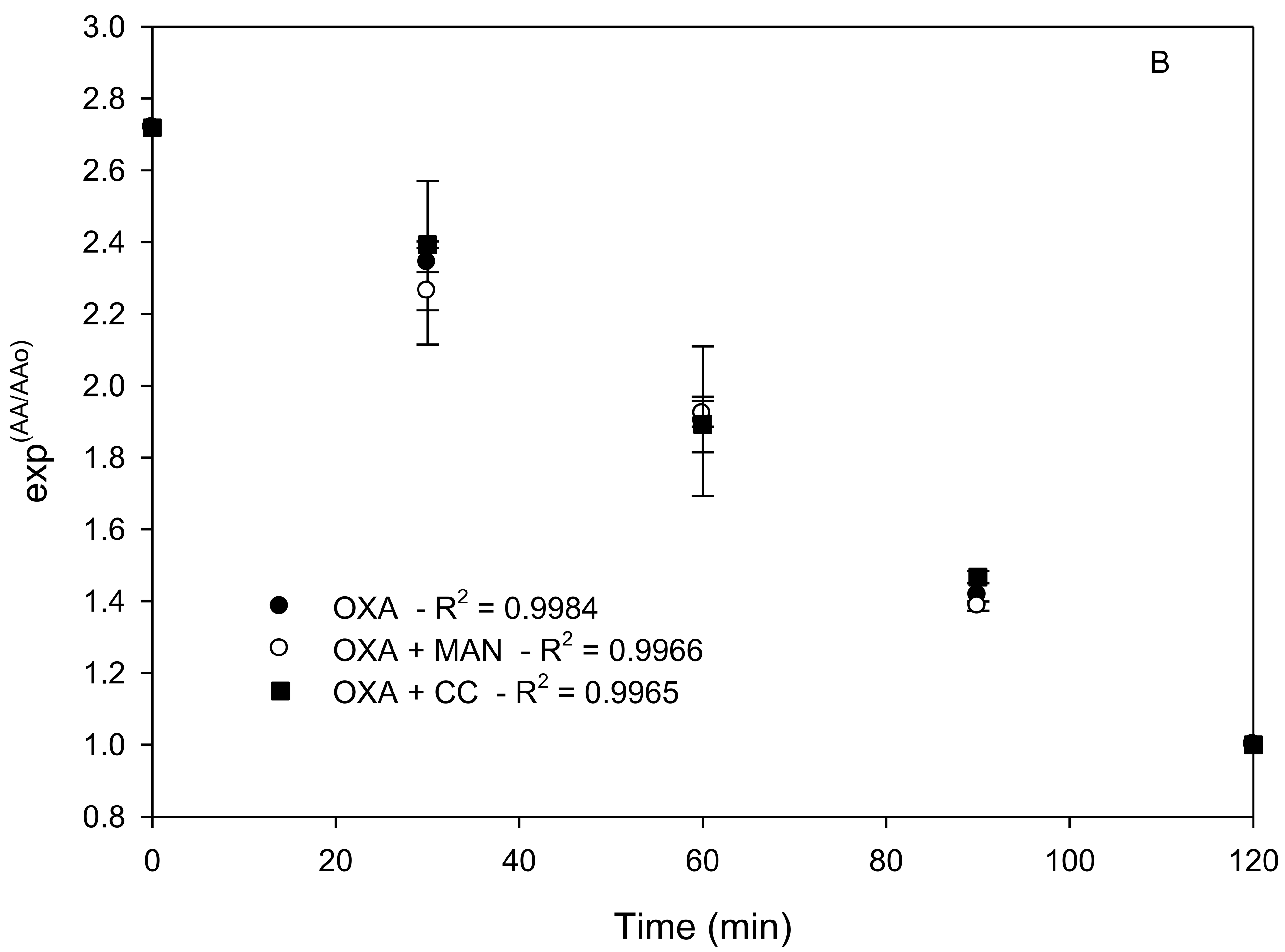
Results and discussion:
Antibiotic degradation vs Antimicrobial removal

AA evolution

$$\exp^{(AA/AAo)} = -kt + b$$

AA/AAo = Normalized evolution of AA

k = kinetic constant (min^{-1}) ; t = time (min)



E.A. Serna-Galvis et al. / Science of the Total Environmnet, In press

Results and discussion: Antibiotic degradation vs Antimicrobial removal

$$exp^{(AA/AAo)} = -kt + b$$

$$\downarrow$$

$$r_k = k_{OXA+additive} / k_{OXA}$$

r_k >1, accelerator

r_k =1, no effect

r_k < 1, inhibitor

E.A. Serna-Galvis et al. / Science of the Total Environmnet, In press

Results and discussion: Antibiotic degradation vs Antimicrobial removal

$exp^{(AA/AAo)} = -kt + b$

$r_k = k_{OXA+additive} / k_{OXA}$

$r_k > 1$, accelerator

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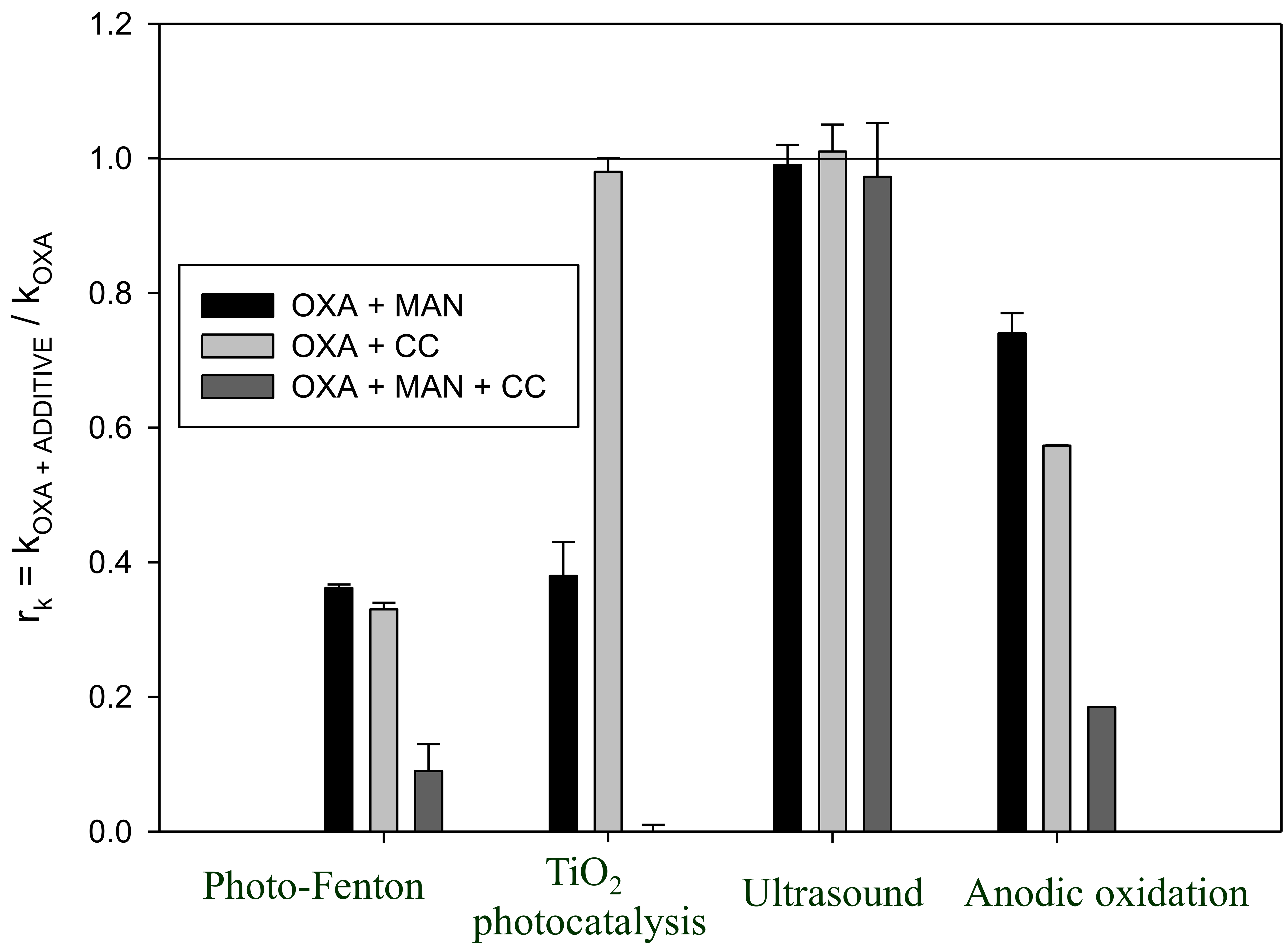
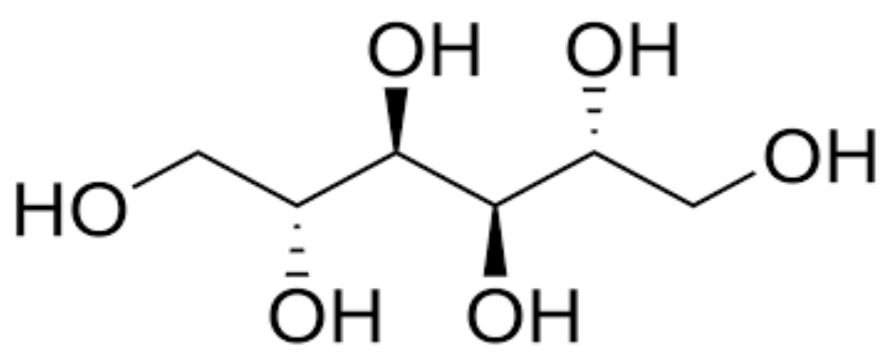


E.A. Serna-Galvis et al. / Science of the Total Environmnet, In press

Results and discussion: Pharmaceutical additives



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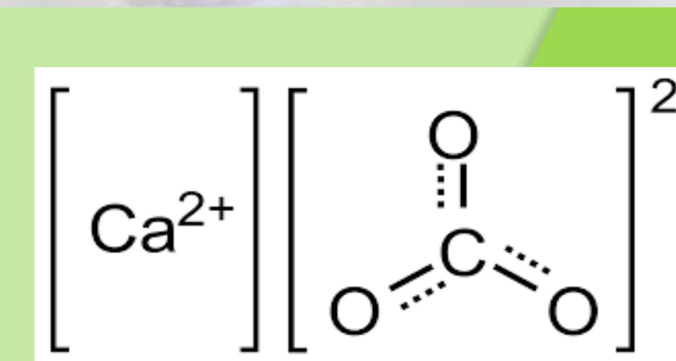
Calcium carbonate (CC)



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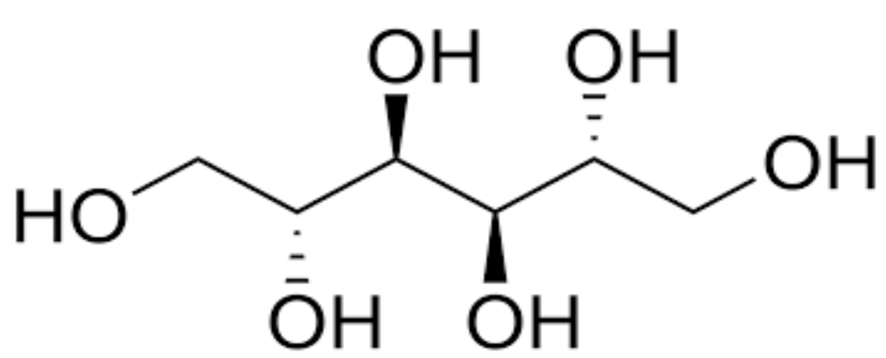
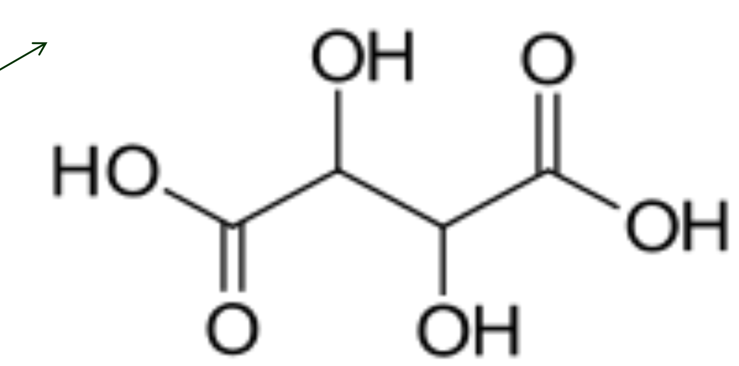
Results and discussion: Pharmaceutical additives

Antibiotic production

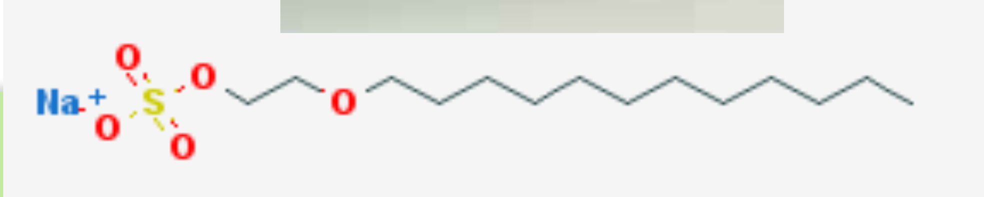


Mannitol (MAN)

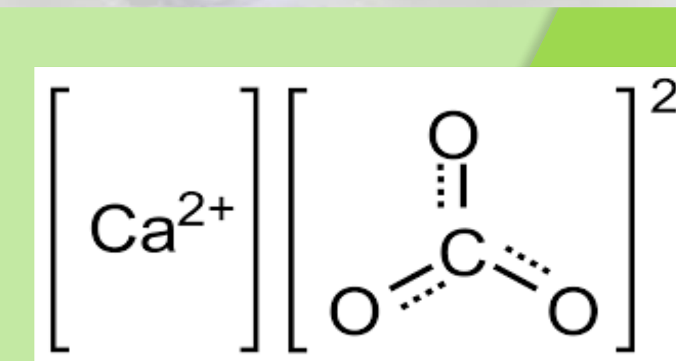


Tartaric acid (TA)

Sodium lauryl ether sulfate (LES)



Calcium carbonate (CC)



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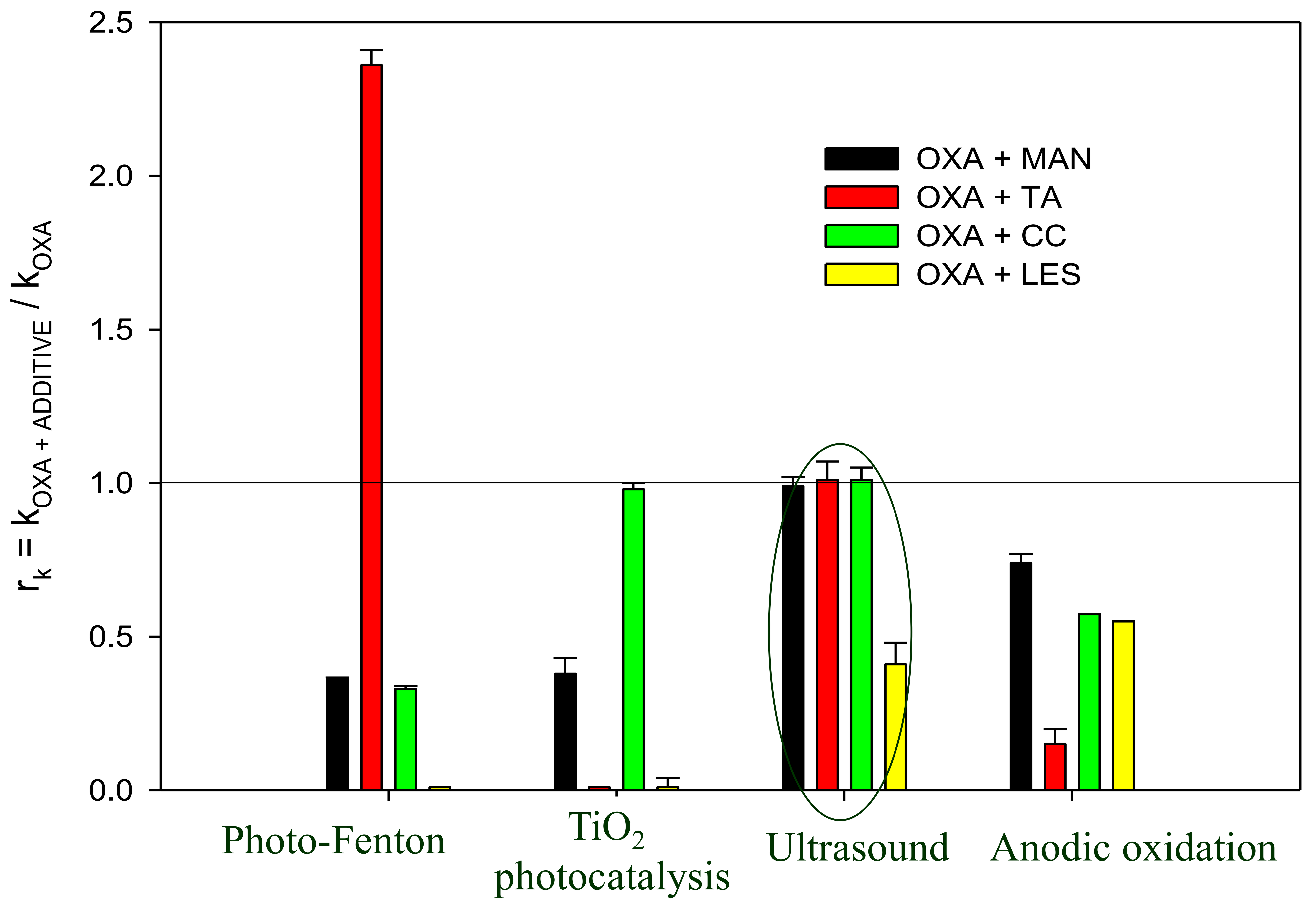
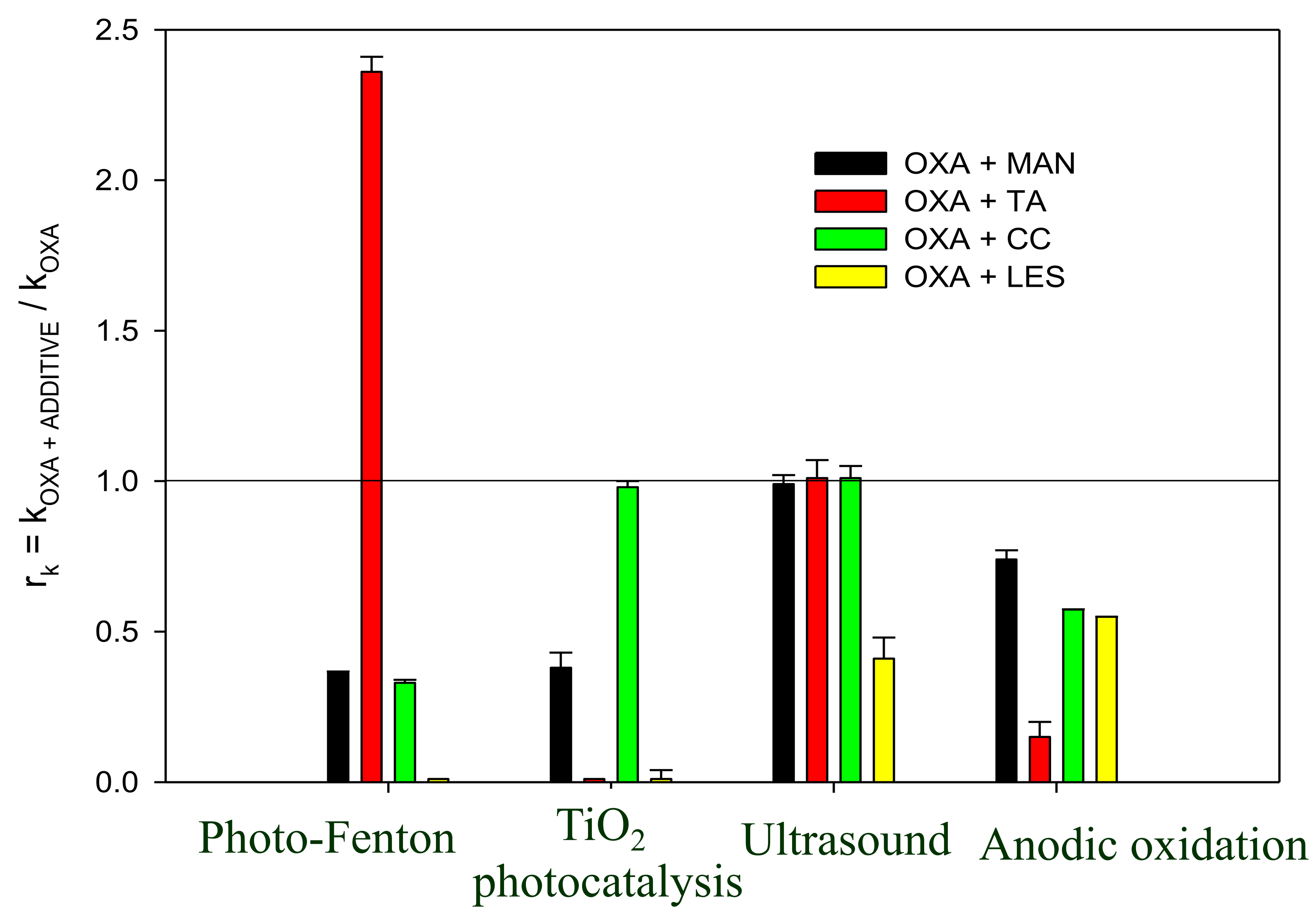
Results and discussion: Pharmaceutical additives



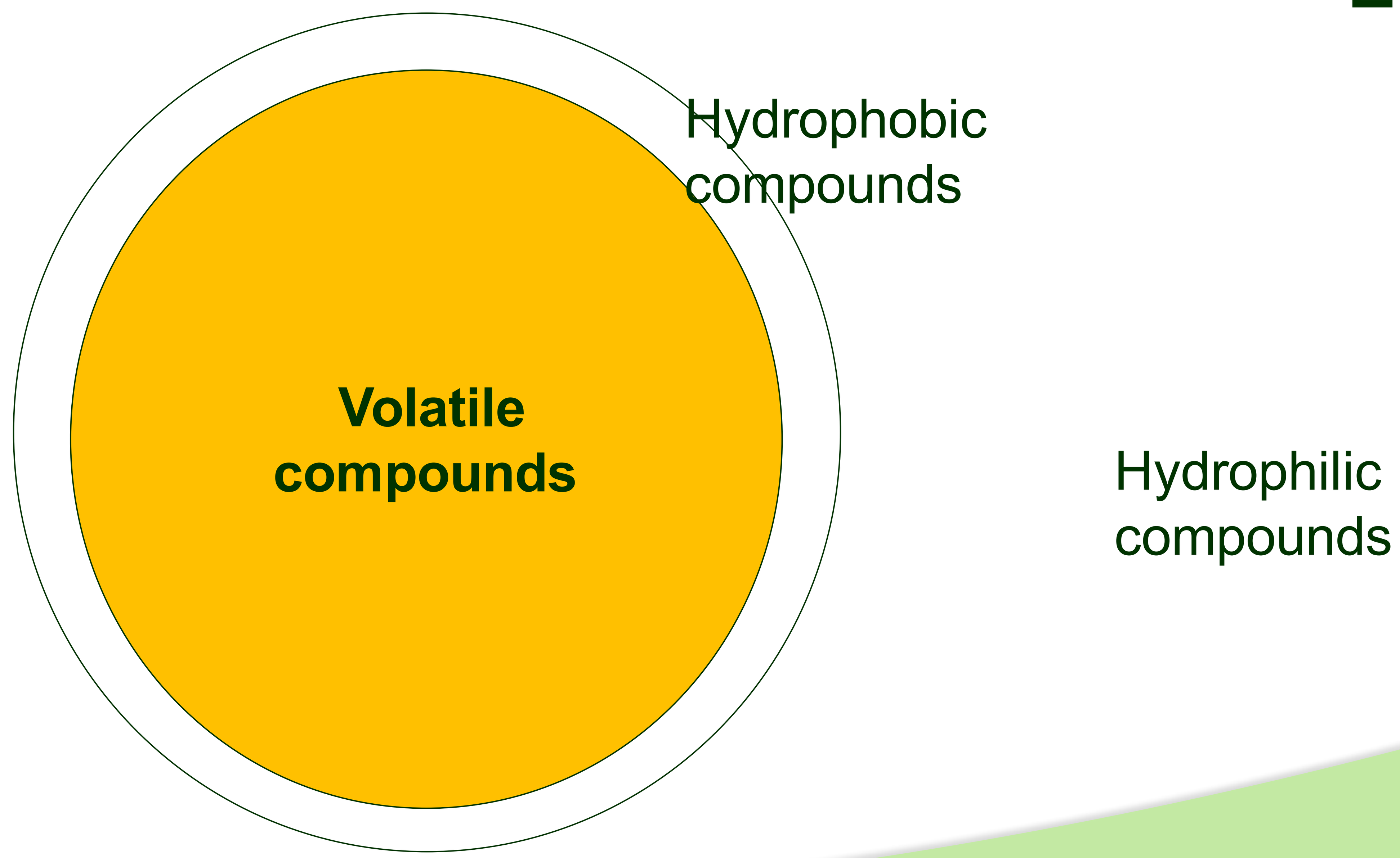
ChemIDplus Adv. URL
http://chem.sis.nlm.nih.gov/chemidplus

Results and discussion: Pharmaceutical additives



Kow
Hydrophobicity indicator

Substance	Kow
OXA	2.38
MAN	-3.10
CC (HCO_3^-)	-4.01
TA	-1.08
LES	1.87



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Results and discussion: Pharmaceutical additives

$exp^{(AA/AAo)} = -kt + b$

$r_k = k_{OXA+additive} / k_{OXA}$

$r_k > 1$, accelerator

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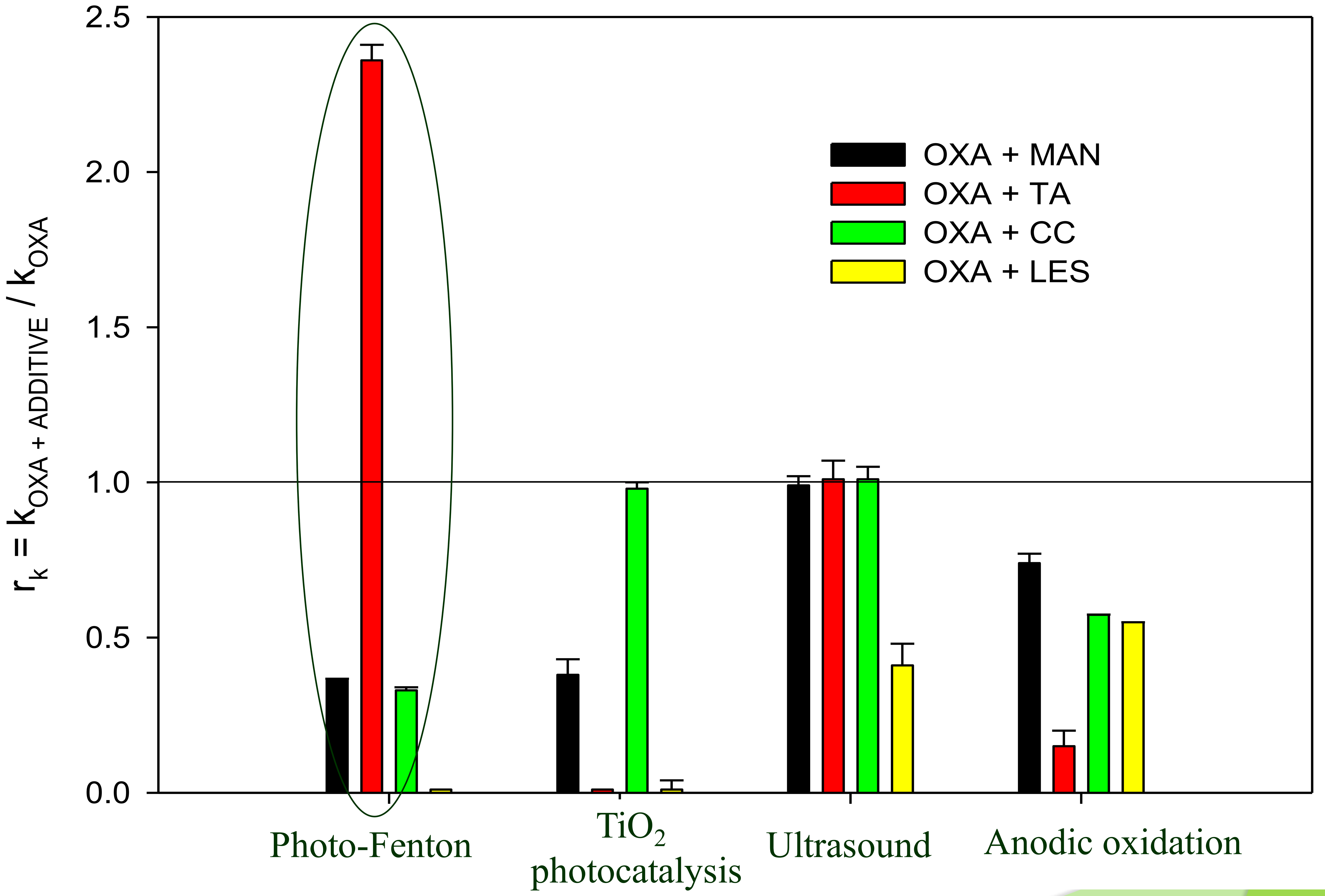


$$[Fe (RCOO)]^{2+} + hv_{(UV\text{-}Vis)} \rightarrow Fe^{2+} + R\bullet + CO_2$$

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

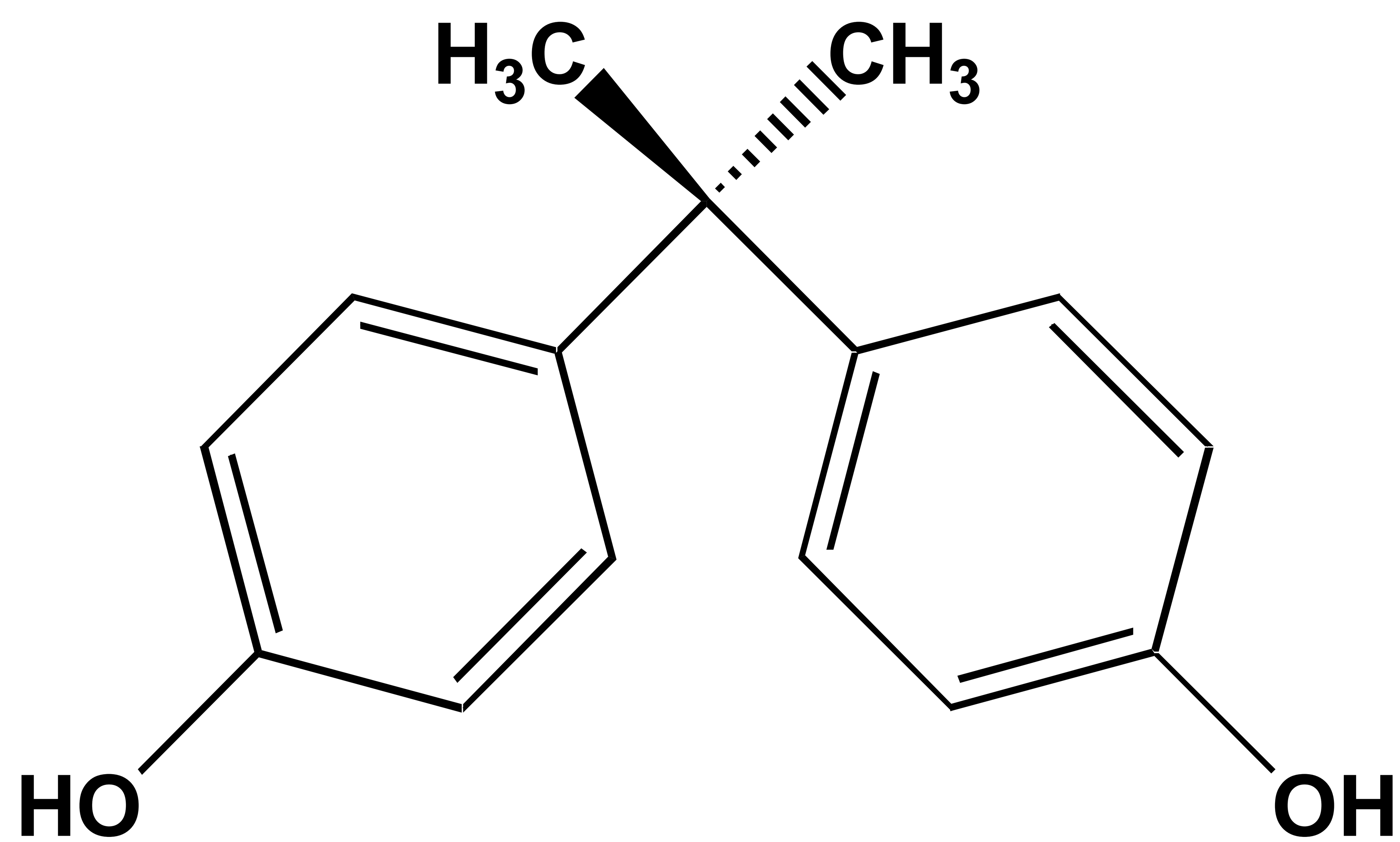
Crit. Rev. Environ. Sci. Technol. 36 (2006) 1–84

Appl. Catal. B Environ. 158-159 (2014) 30–37

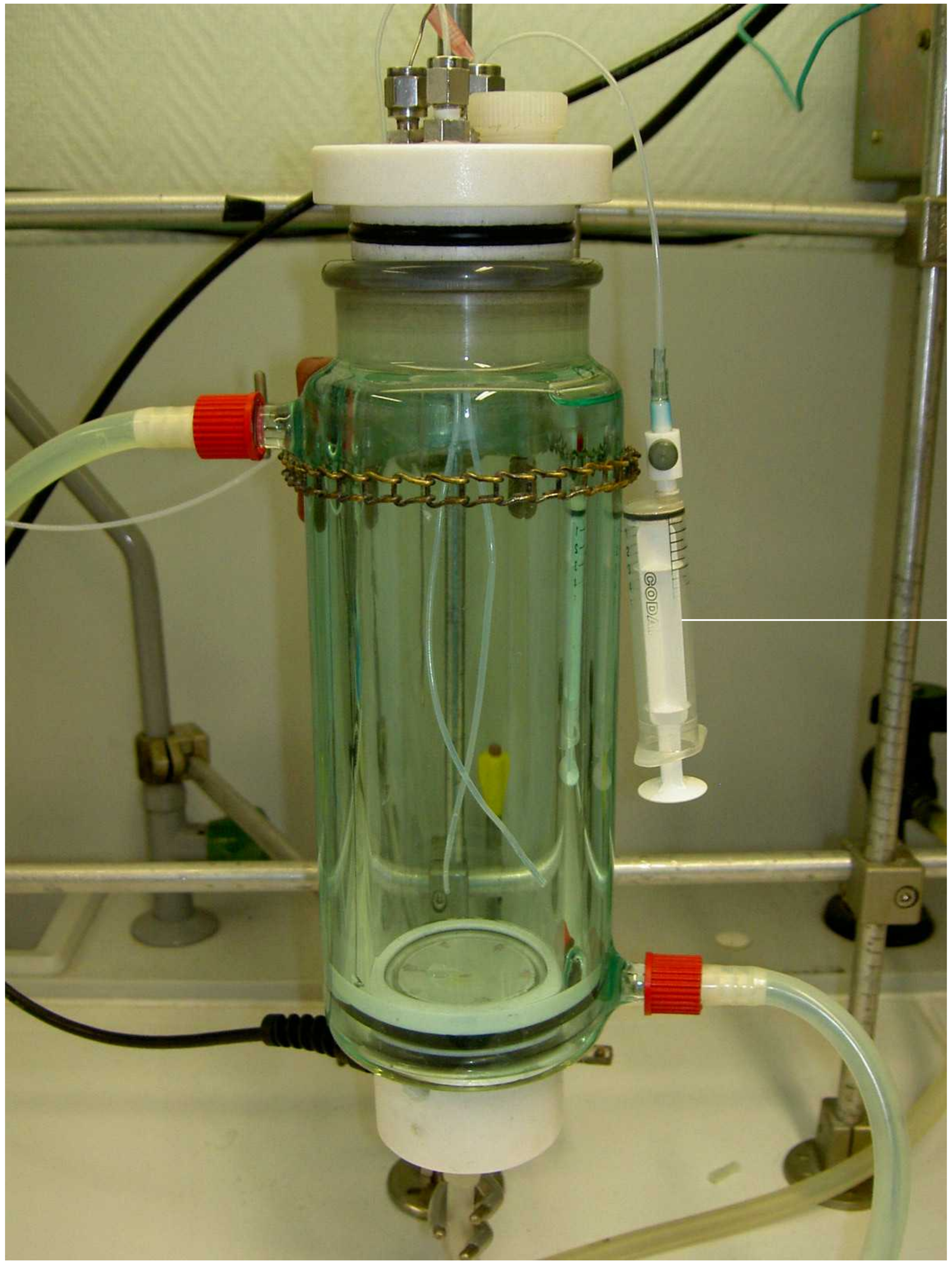
Bisphenol A: 2,2-bis(4-hydroxyphenyl)propane

- Plastic industry

- Endocrine disruptor

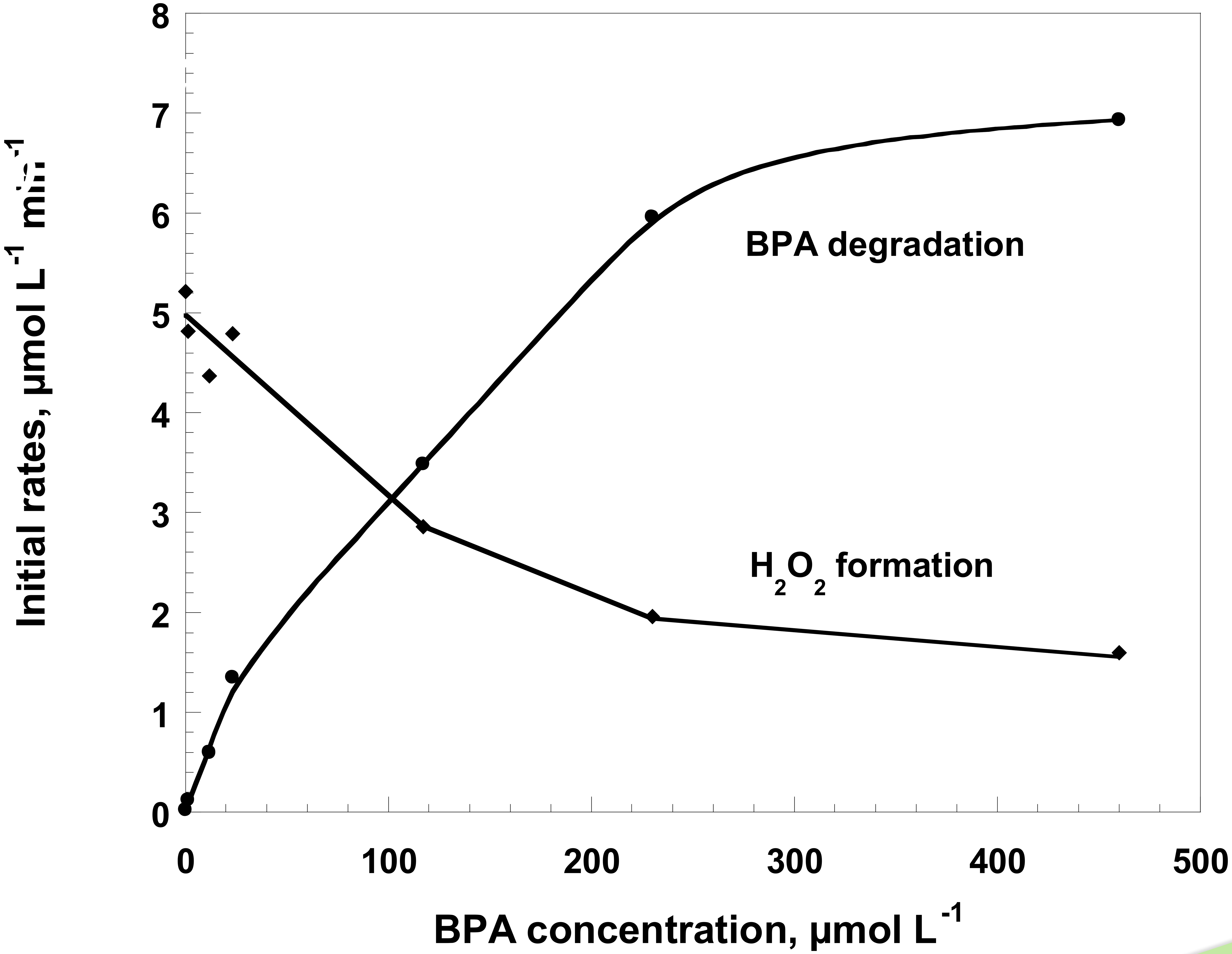


Experimental device

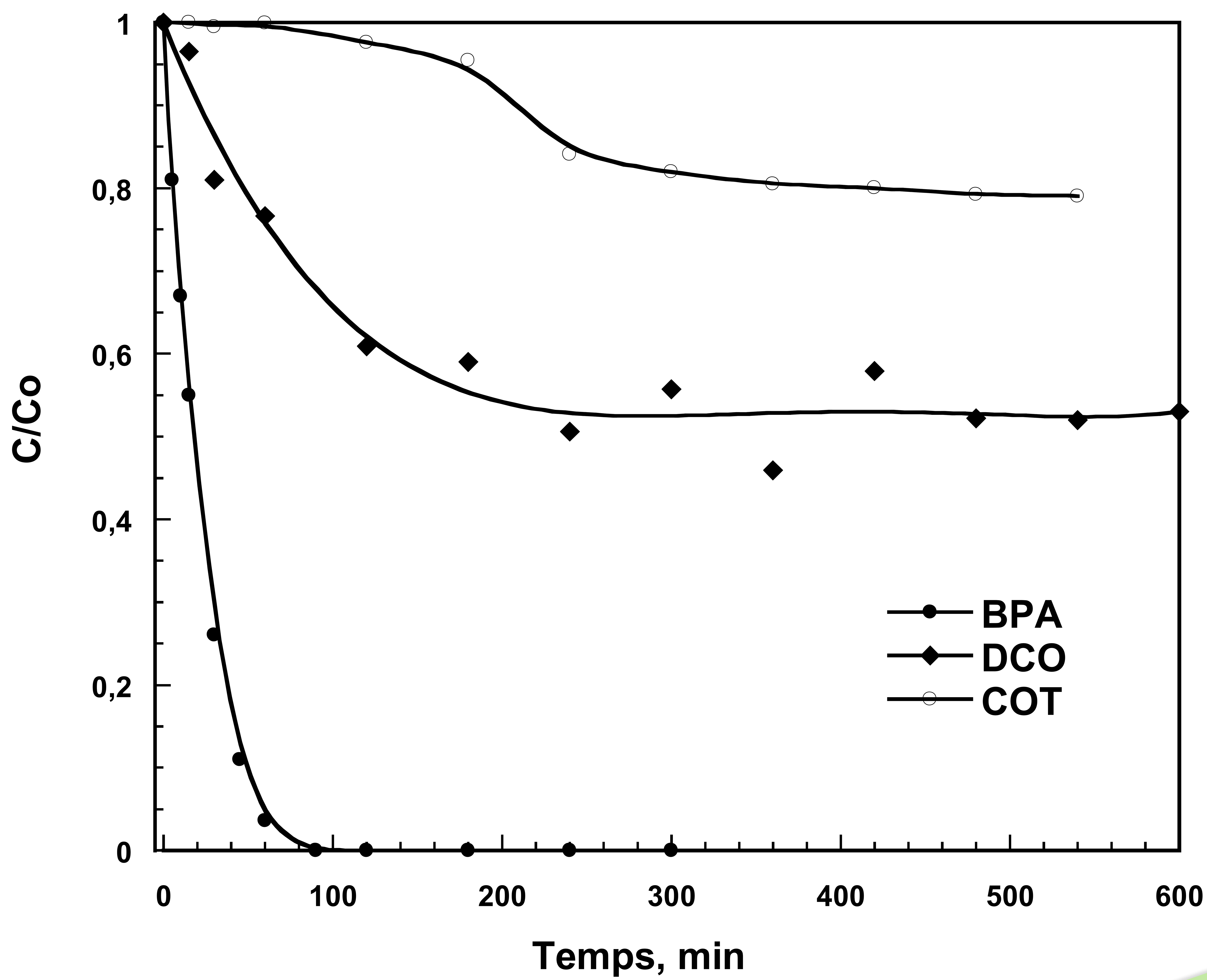


300-800 kHz, 20-80 W
300 mL, 20±1 °C
BPA 0,15-460 µmol L^{-1}
Gas: air, Ar, O_2
pH 3-9

Analyses UV
HPLC
HPLC/MS
DQO
COT

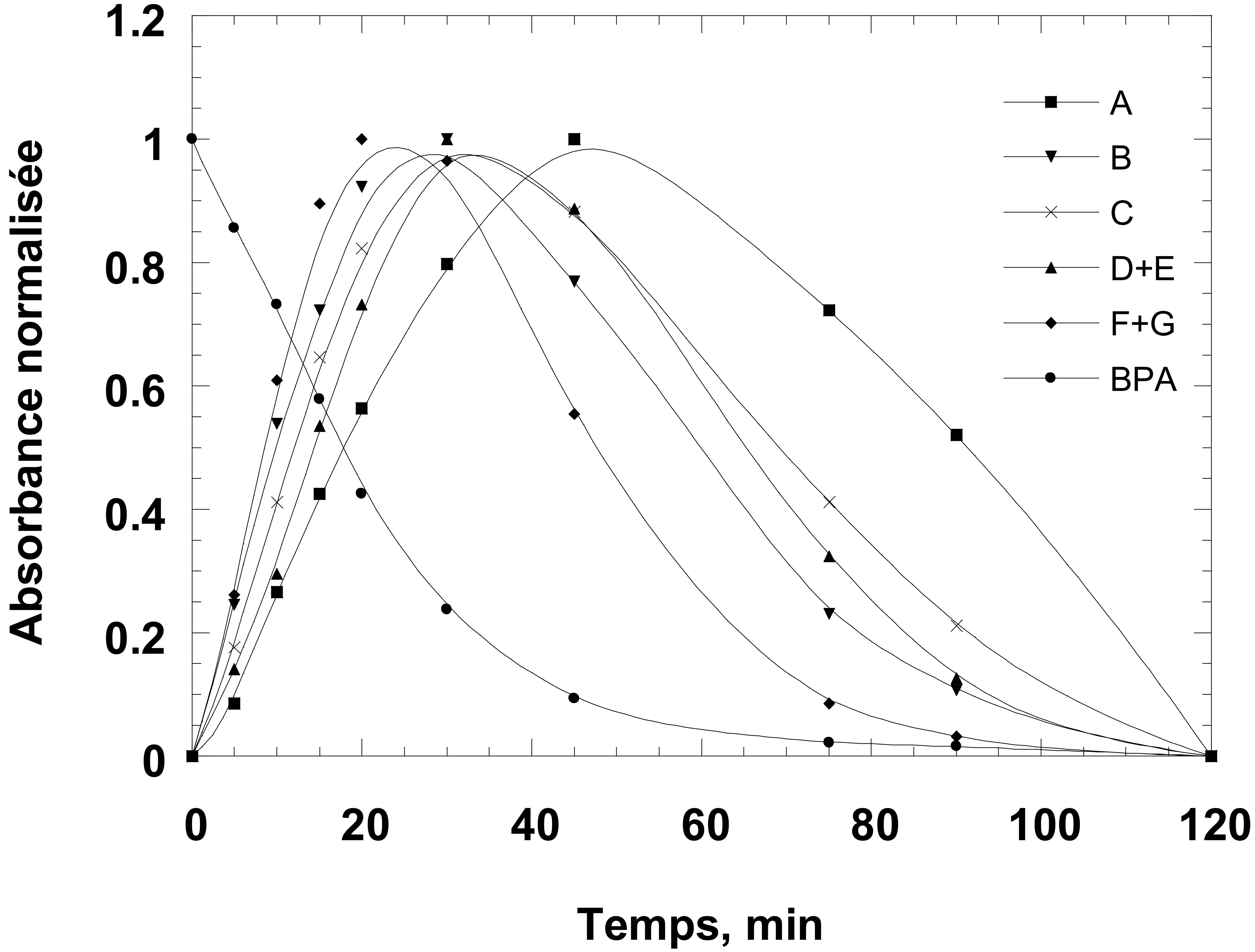

Initial rates, µmol L-1 min-1
BPA concentration, µmol L-1
BPA degradation
H2O2 formation
0
1
2
3
4
5
6
7
8
0
100
200
300
400
500

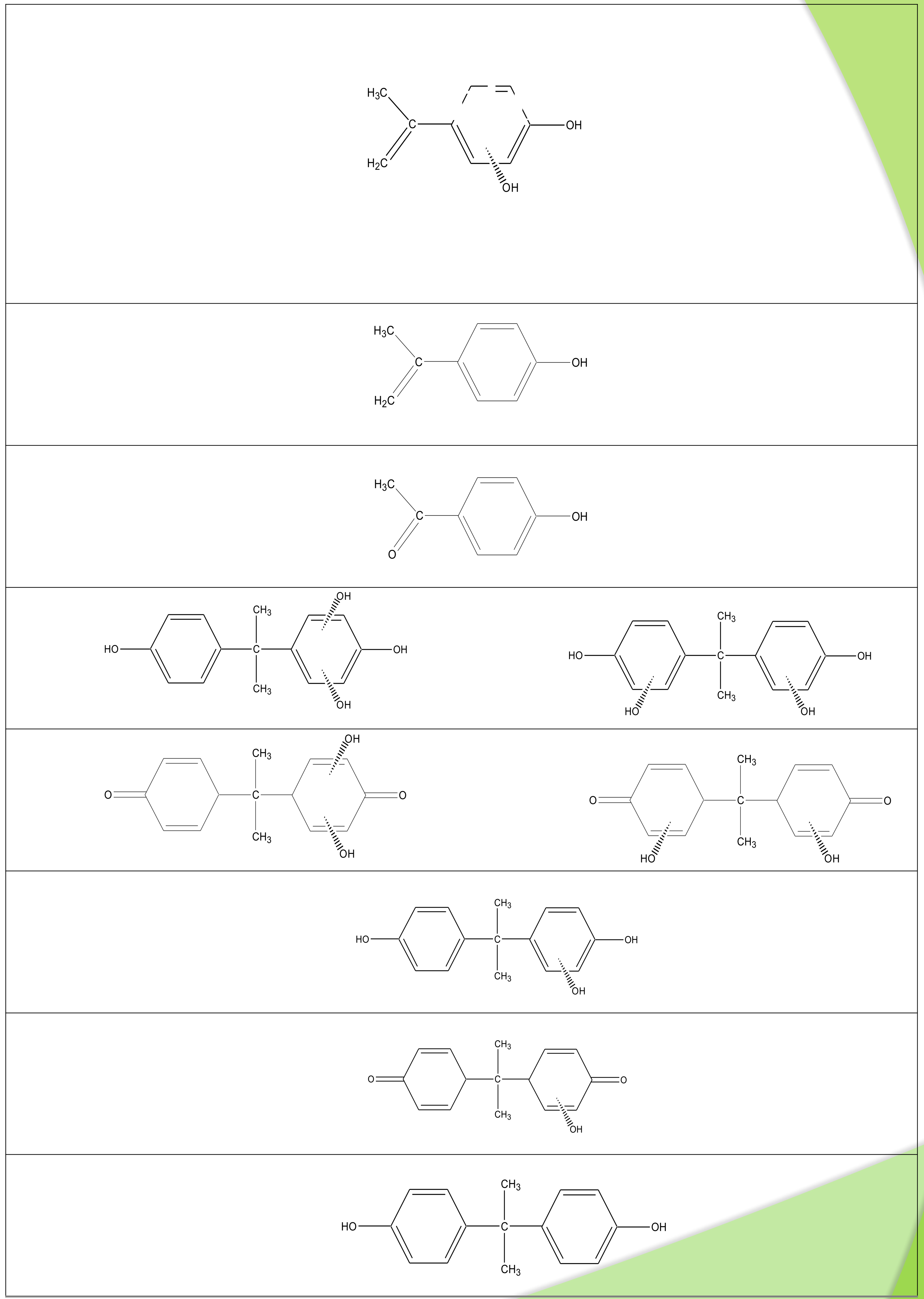
Characteristics of sonochemical BPA degradation



Frequency: 300 kHz; power: 80 W; volume: 300 mL;
gas: oxigen; BPA: 118 μmol L^{-1}

Characteristics of sonochemical BPA degradation





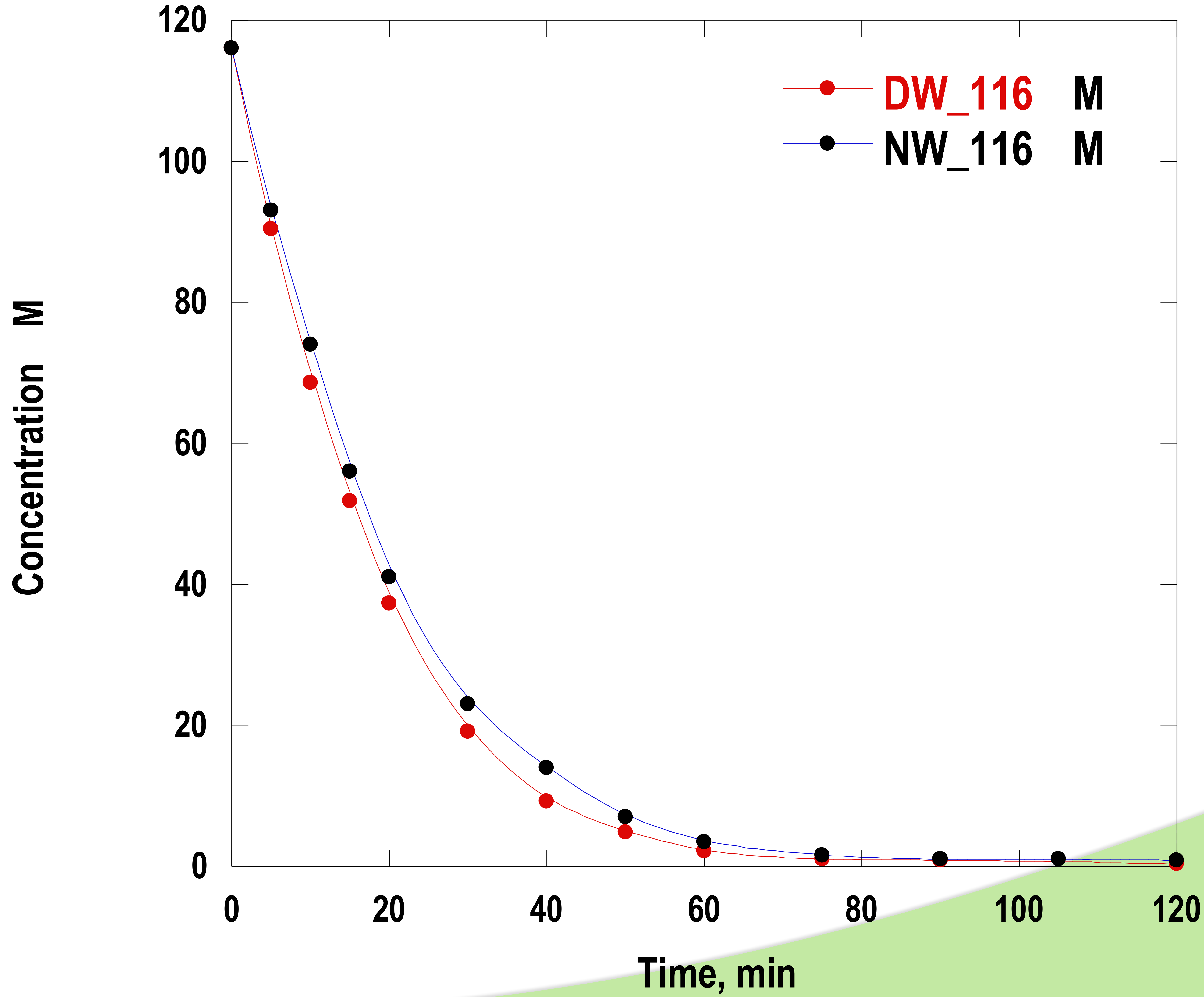
Characteristics of sonochemical BPA degradation

BPA (116 uM) in natural water

pH	Cl^- (mg L^{-1})	Ca^{2+}(mg L^{-1})	Na^+(mg L^{-1})	SO_4^{2-} (mg L^{-1})	HCO_3^- (mg L^{-1})
7.6	10	486	9.1	1187	402

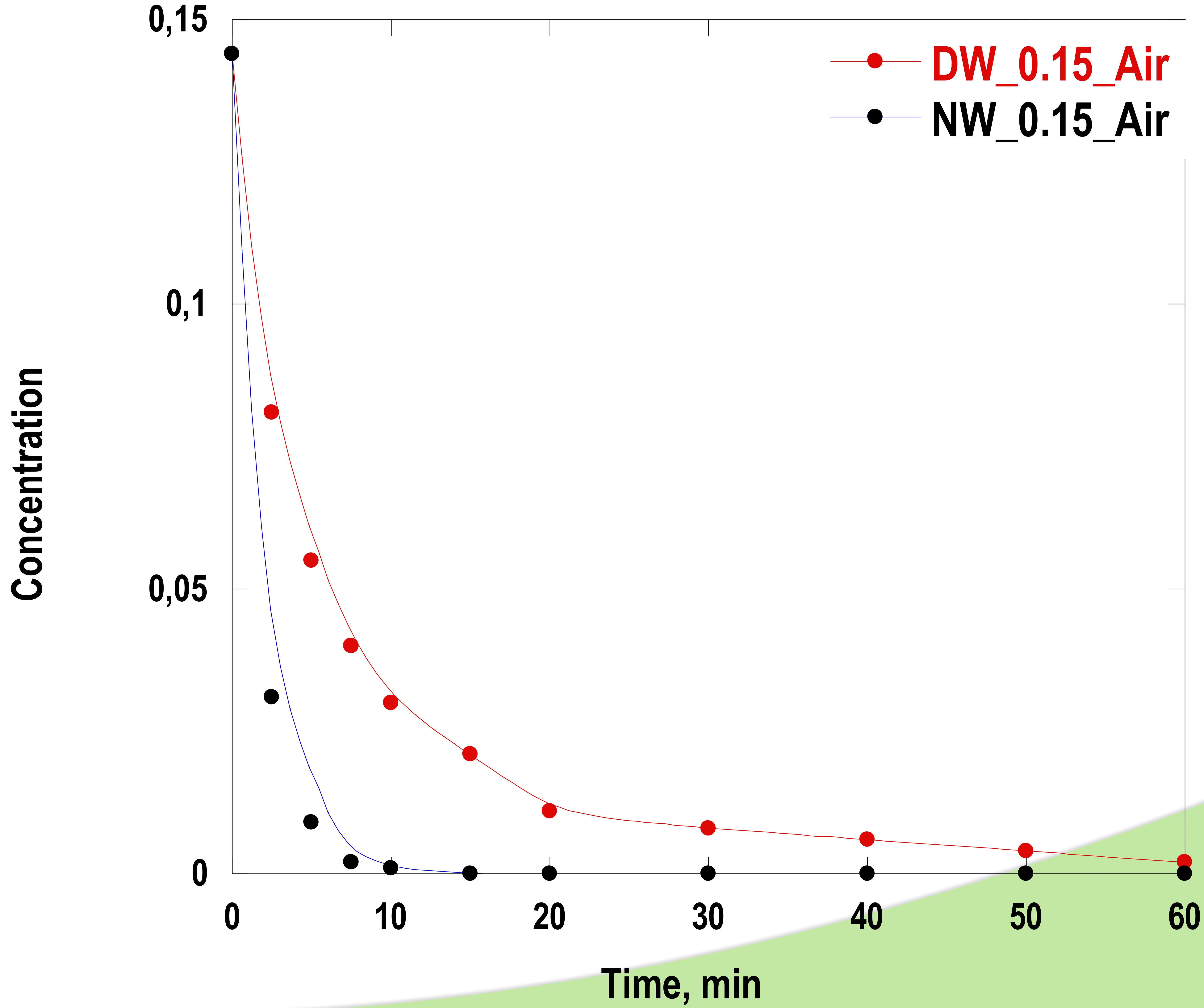
Sonochemical elimination of BPA in natural water

BPA: 116 μM ; 300 mL
Frequency: 300 kHz; Power: 80 W



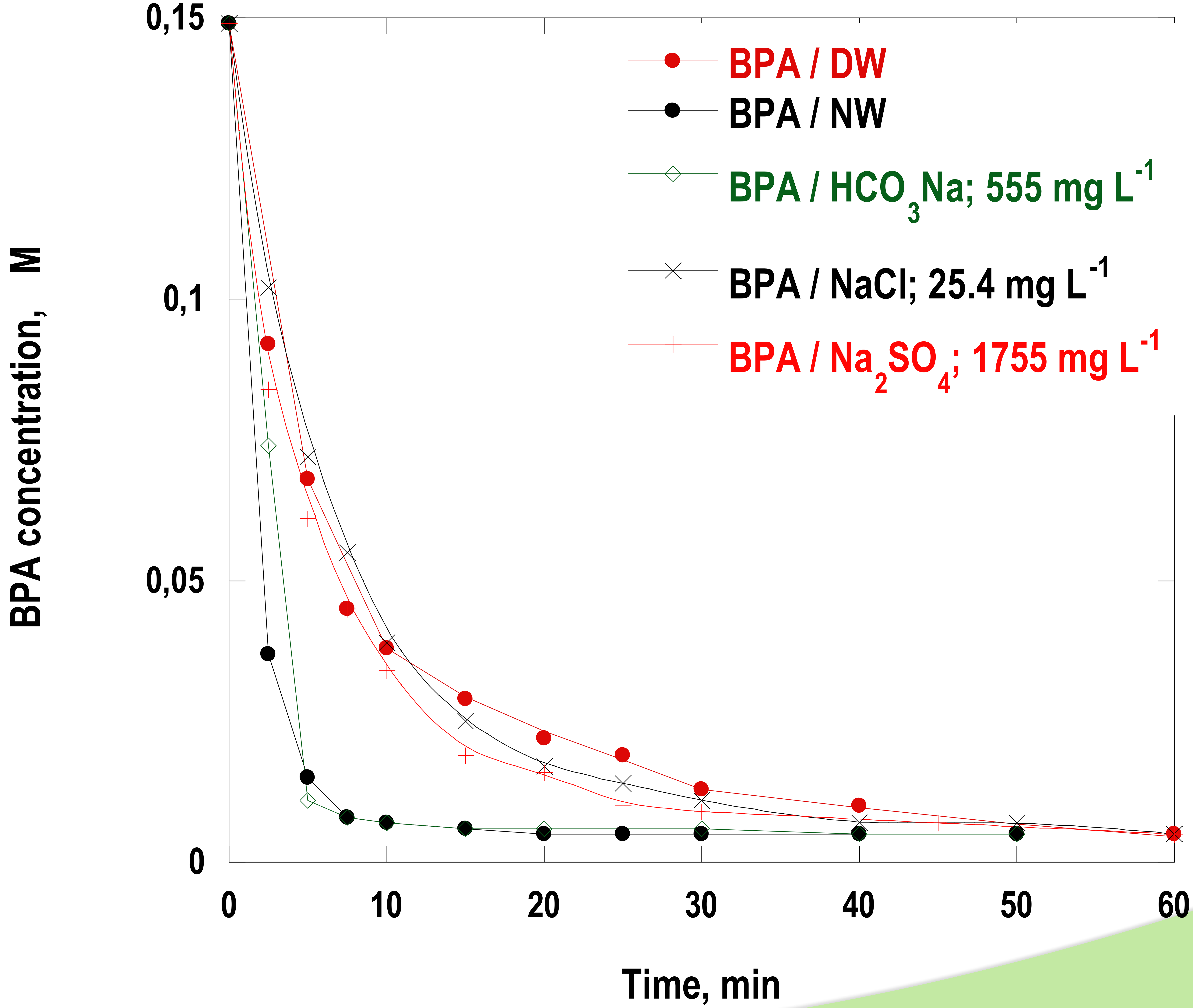
Sonochemical elimination of BPA in natural water

BPA: 0.15 μM (34.2 μg L^{-1}) ; 300 mL
Frequency: 300 kHz; Power: 80 W



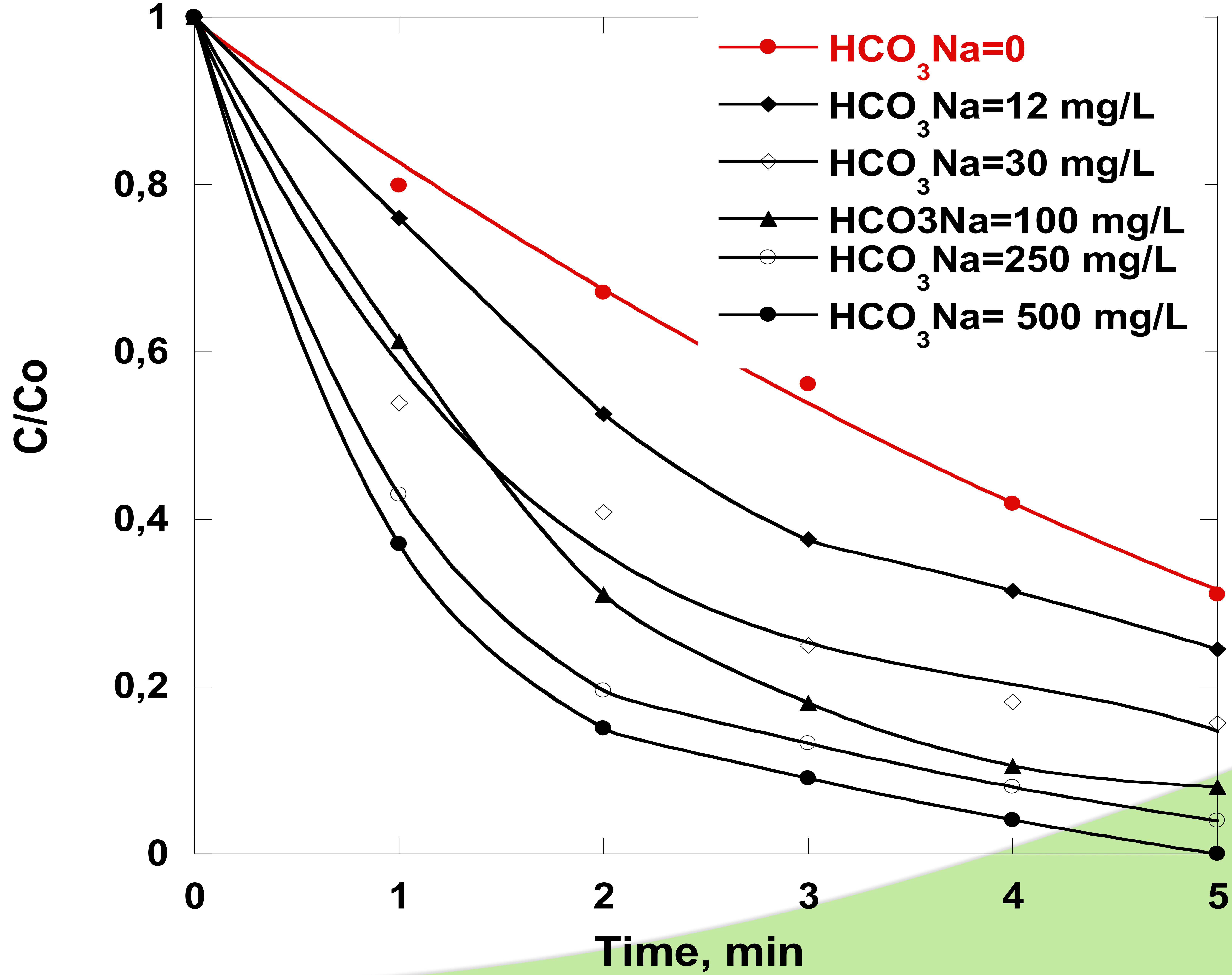
Sonochemical elimination of BPA

Influence of anions
BPA concentration: 0.15 μM



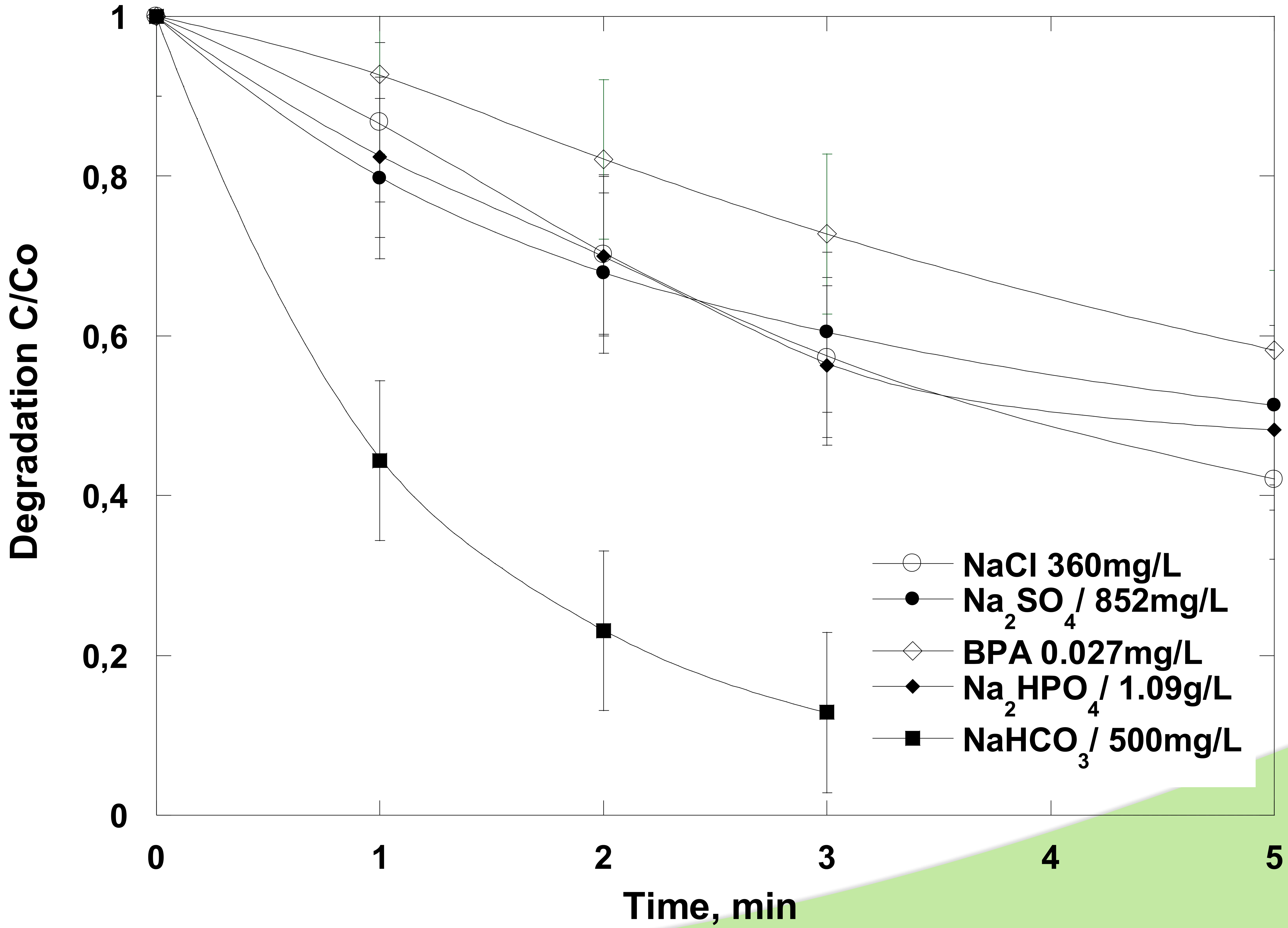
BPA (0.12 µM, 27 µg/L) elimination upon ultrasonic irradiation in water for different sodium bicarbonate concentrations (pH= 8.3)

Ultrasound: 300 kHz, 80 W, 500 mL



BPA (0.12 μM, 27 μg/L) elimination upon ultrasonic irradiation in water containing different anions (pH= 8.3)

Ultrasound: 300 kHz, 80 W, 500 mL.



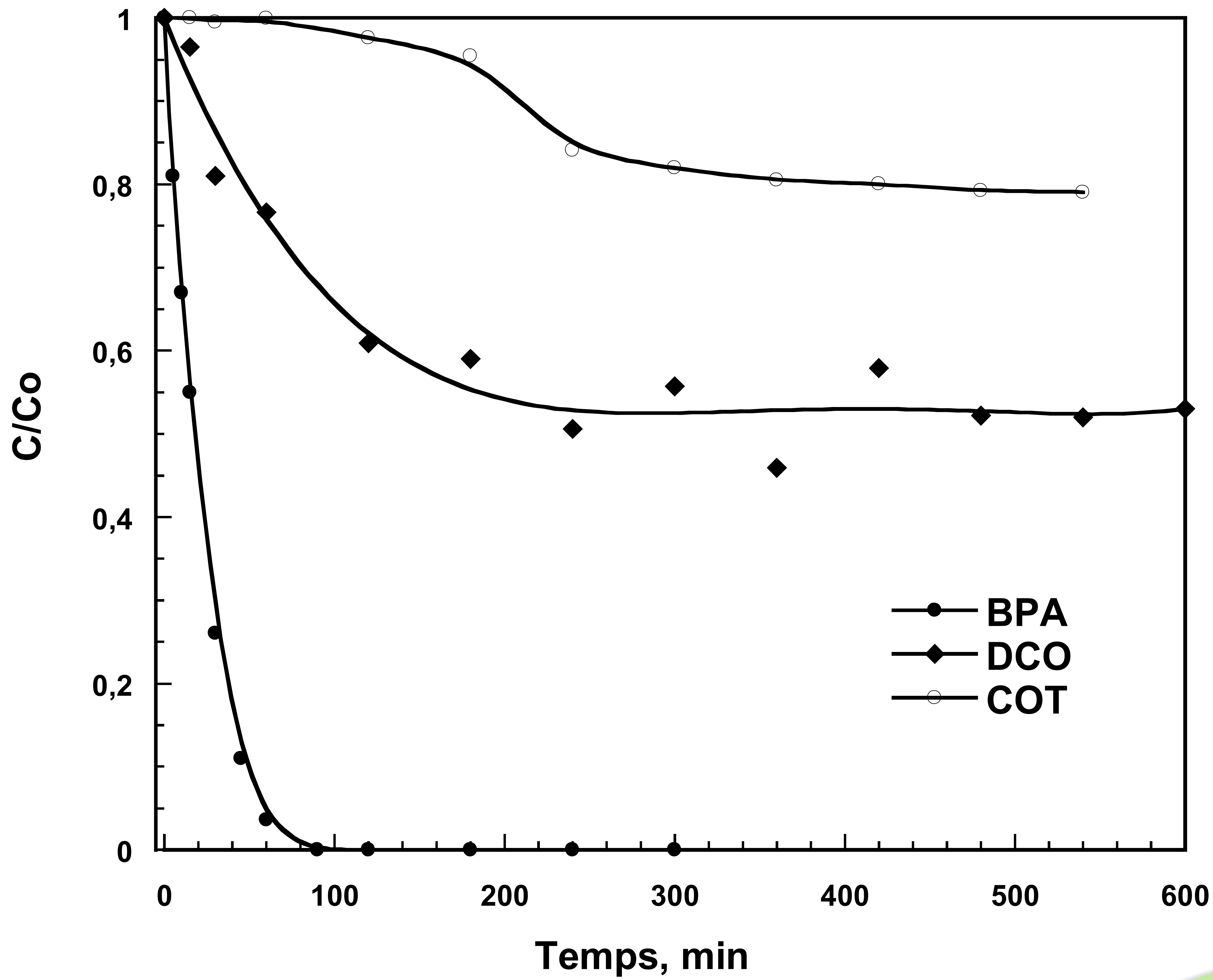
Enhancement of the BPA degradation rates would involve carbonate and bicarbonate ions

$HO^{\circ} + HCO_3^{-} \rightarrow H_2O + CO_3^{-\circ}$ $[k = 8.5 \times 10^{6}\ M^{-1}\ s^{-1}]$

$HO^{\circ} + CO_3^{2-} \rightarrow HO^{-} + CO_3^{-\circ}$ $[k = 3.9 \times 10^{8}\ M^{-1}\ s^{-1}]$

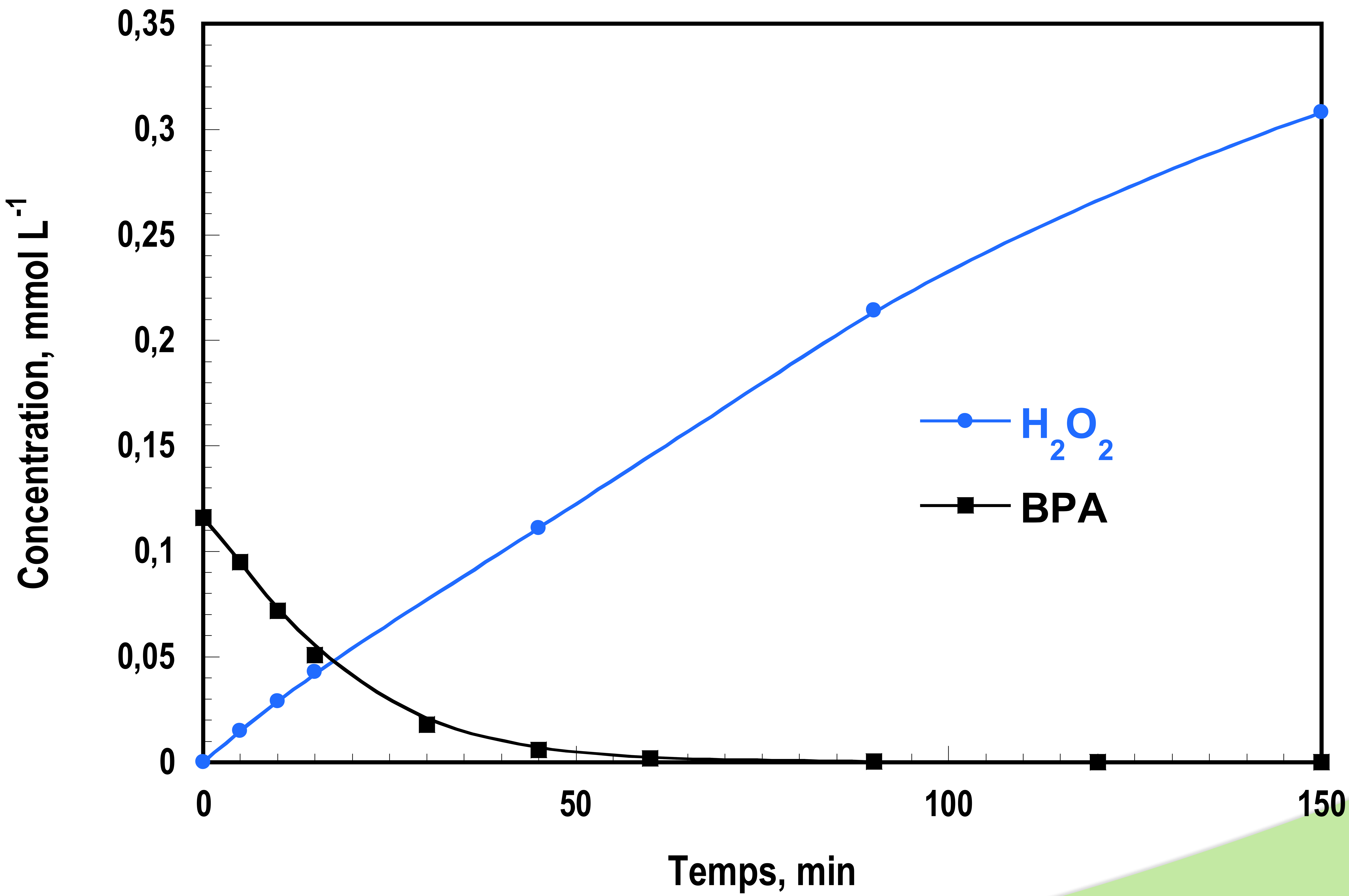
$CO_3^{-\circ} + M \rightarrow CO_3^{2-} + Mox$ $[10^{5} < k < 10^{9}\ M^{-1}\ s^{-1}]$

It is possible to enhance the efficiency of ultrasound action ?



Frecuencia: 300 kHz; potencia: 80 W; volumen: 300 mL;
gas: oxigeno; BPA: 118 μmol L^{-1}

It is possible to enhance the efficiency of ultrasound action ?



Frecuencia: 300 kHz; potencia: 80 W; volumen: 300 mL;
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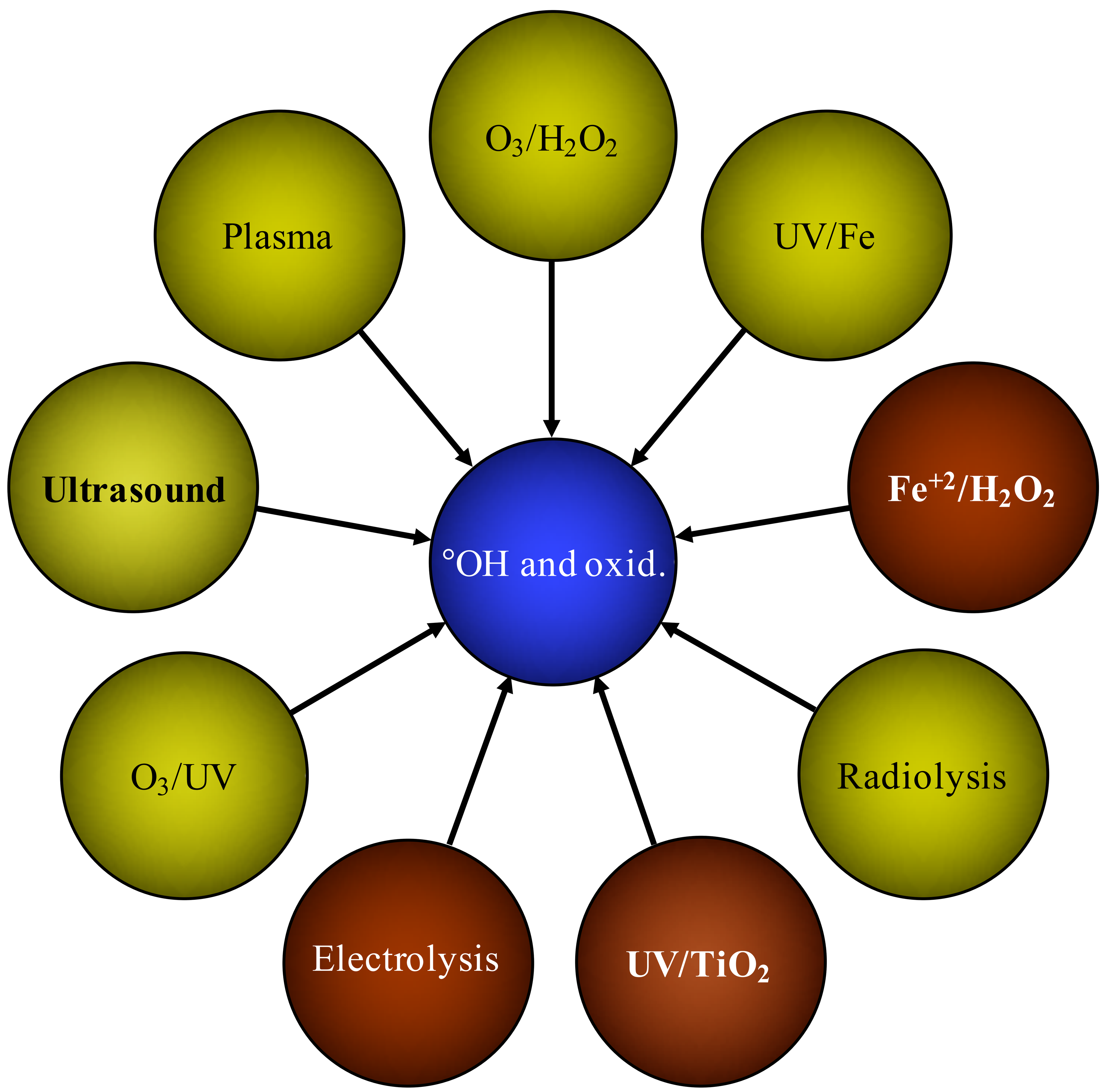
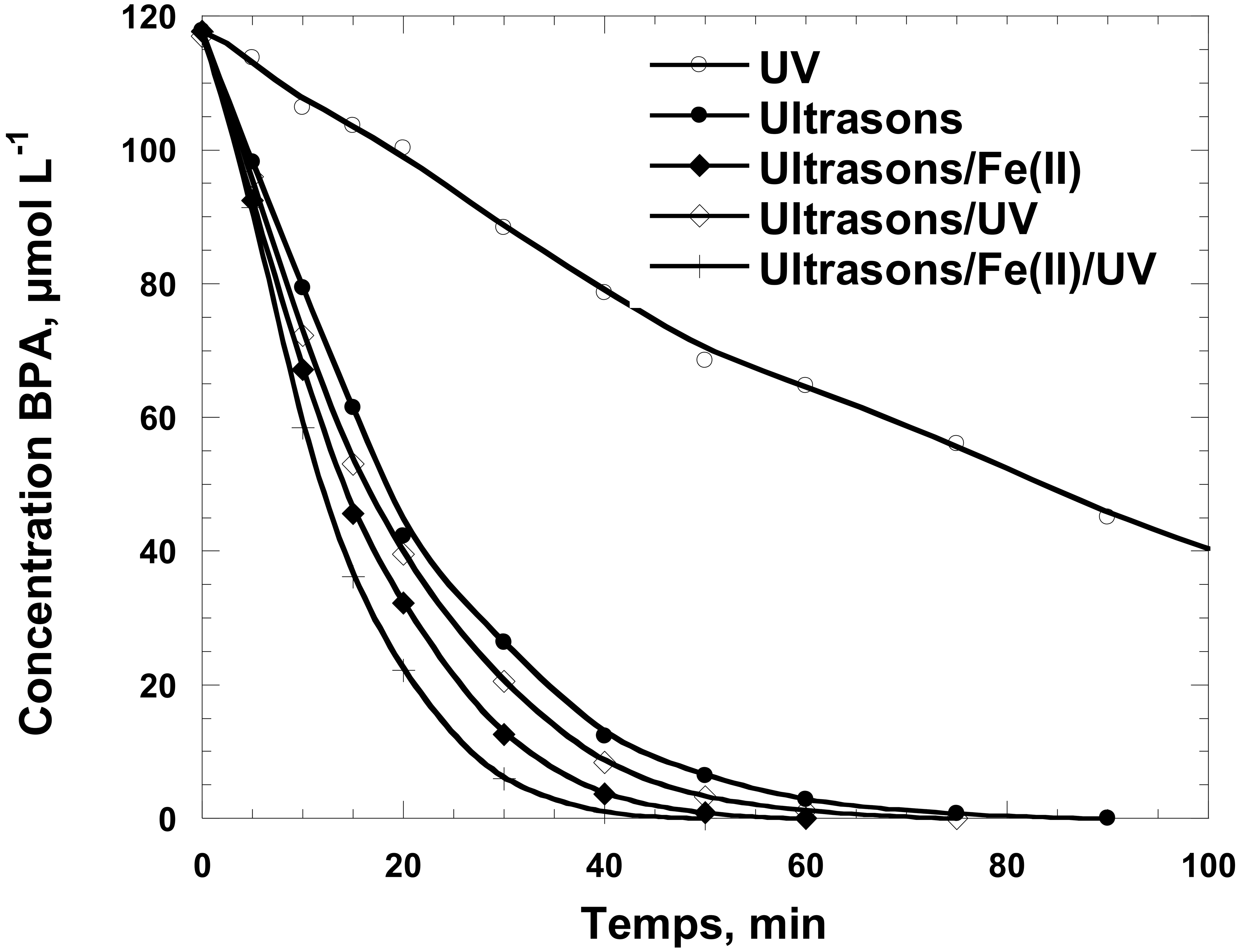
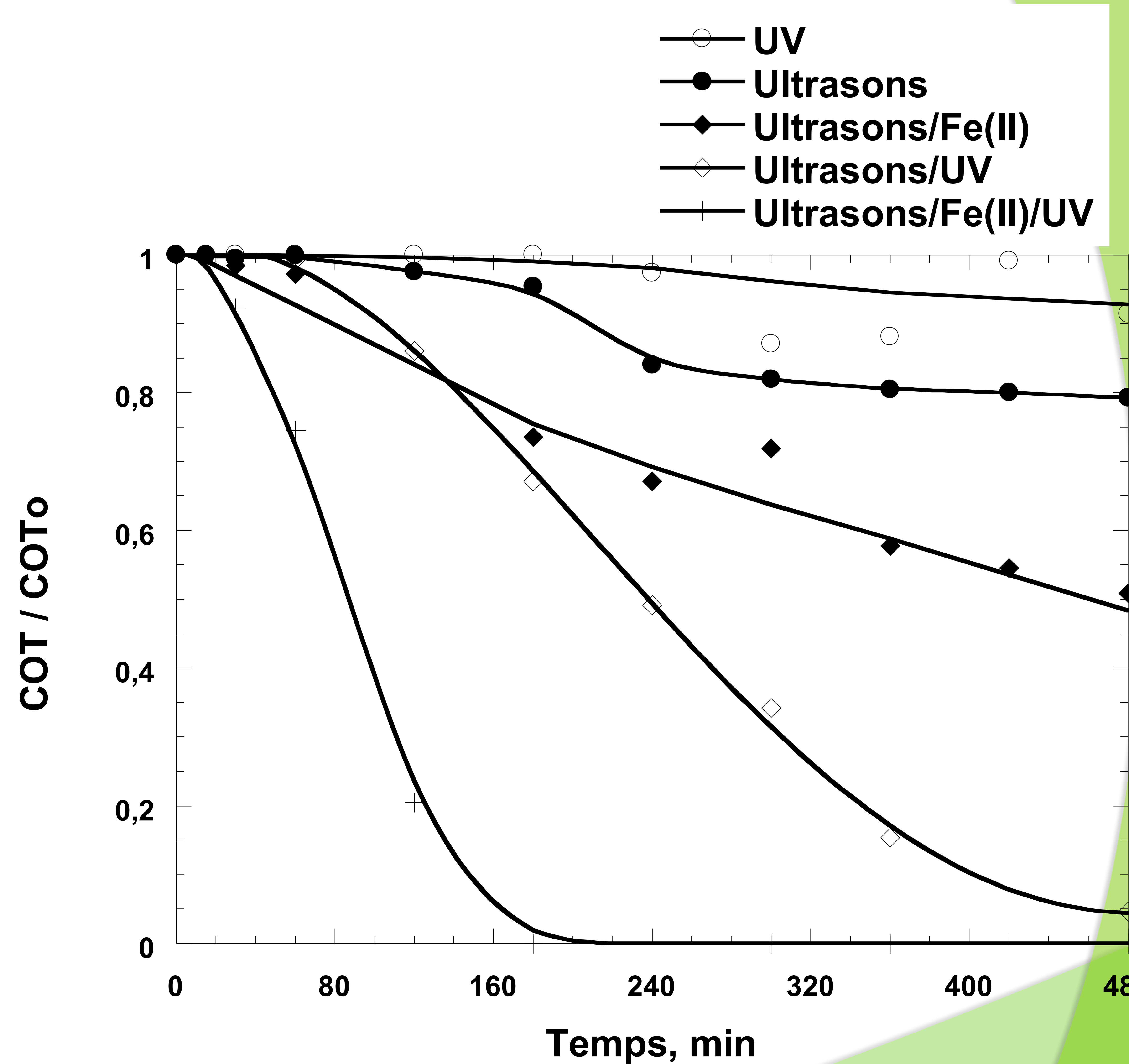
Advanced Oxidation Processes



Ultrasound/Fe(II)/UV

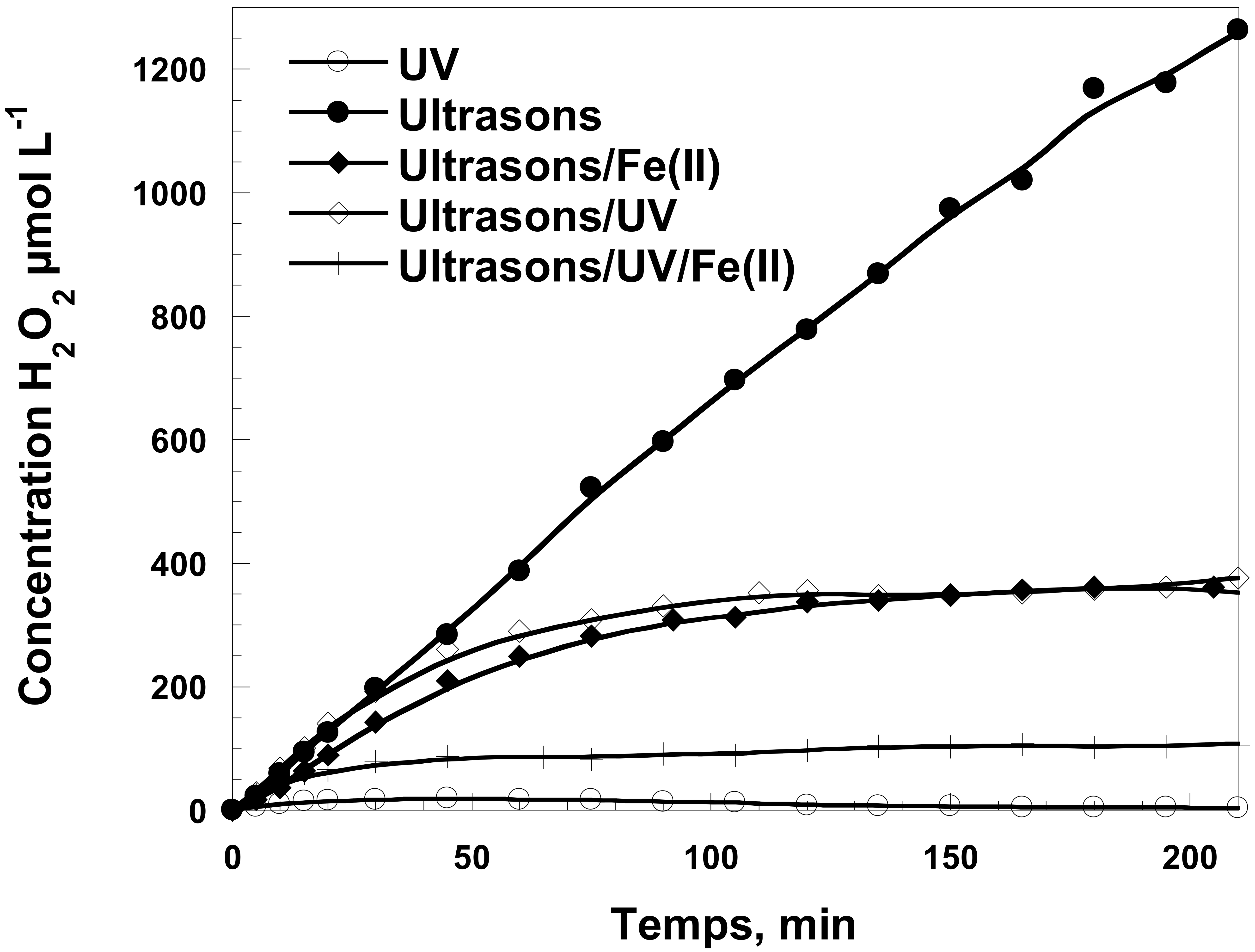
Evolution of BPA and TOC





Ultrasound/Fe(II)/UV

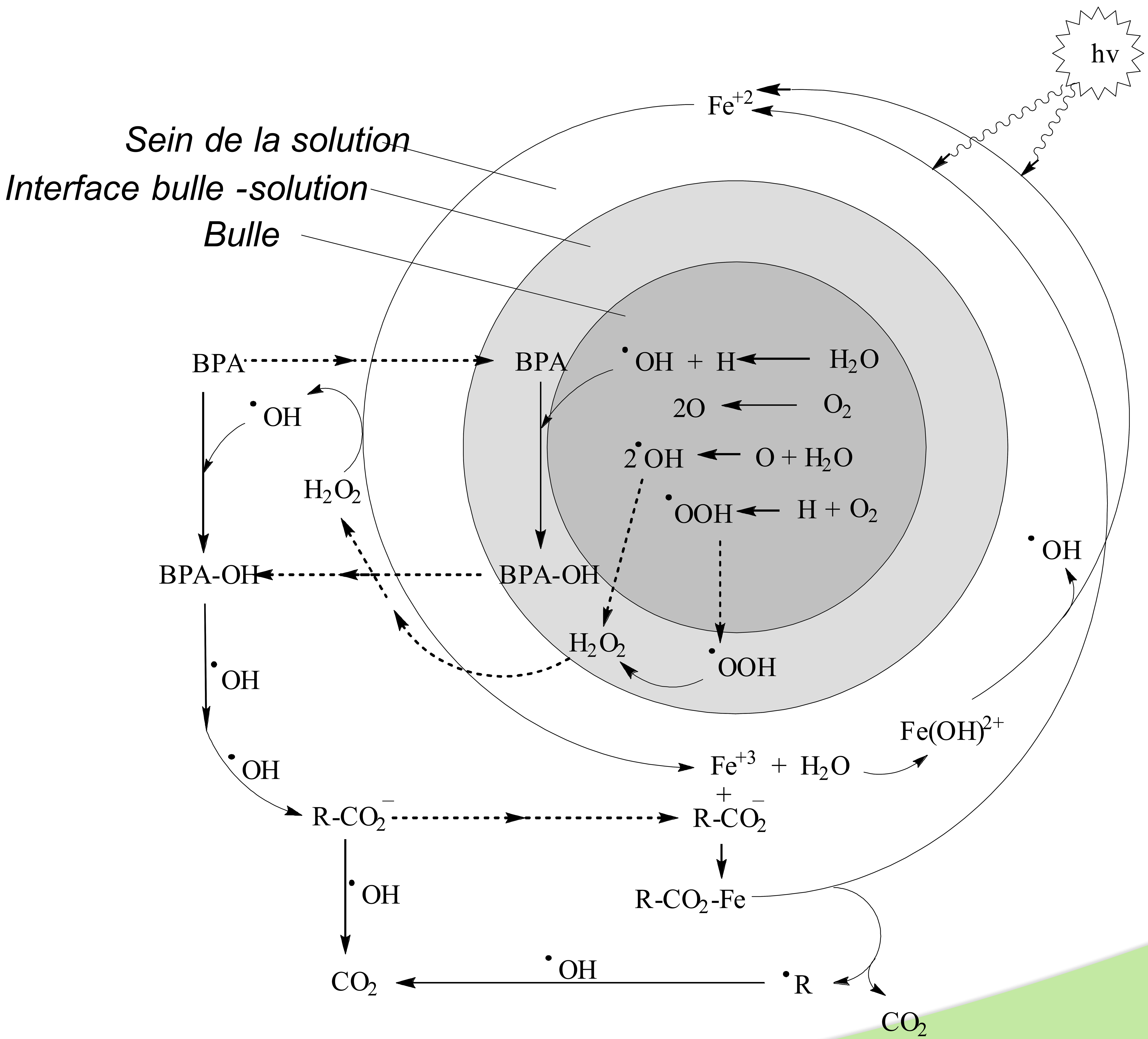
Hydrogen peroxide evolution



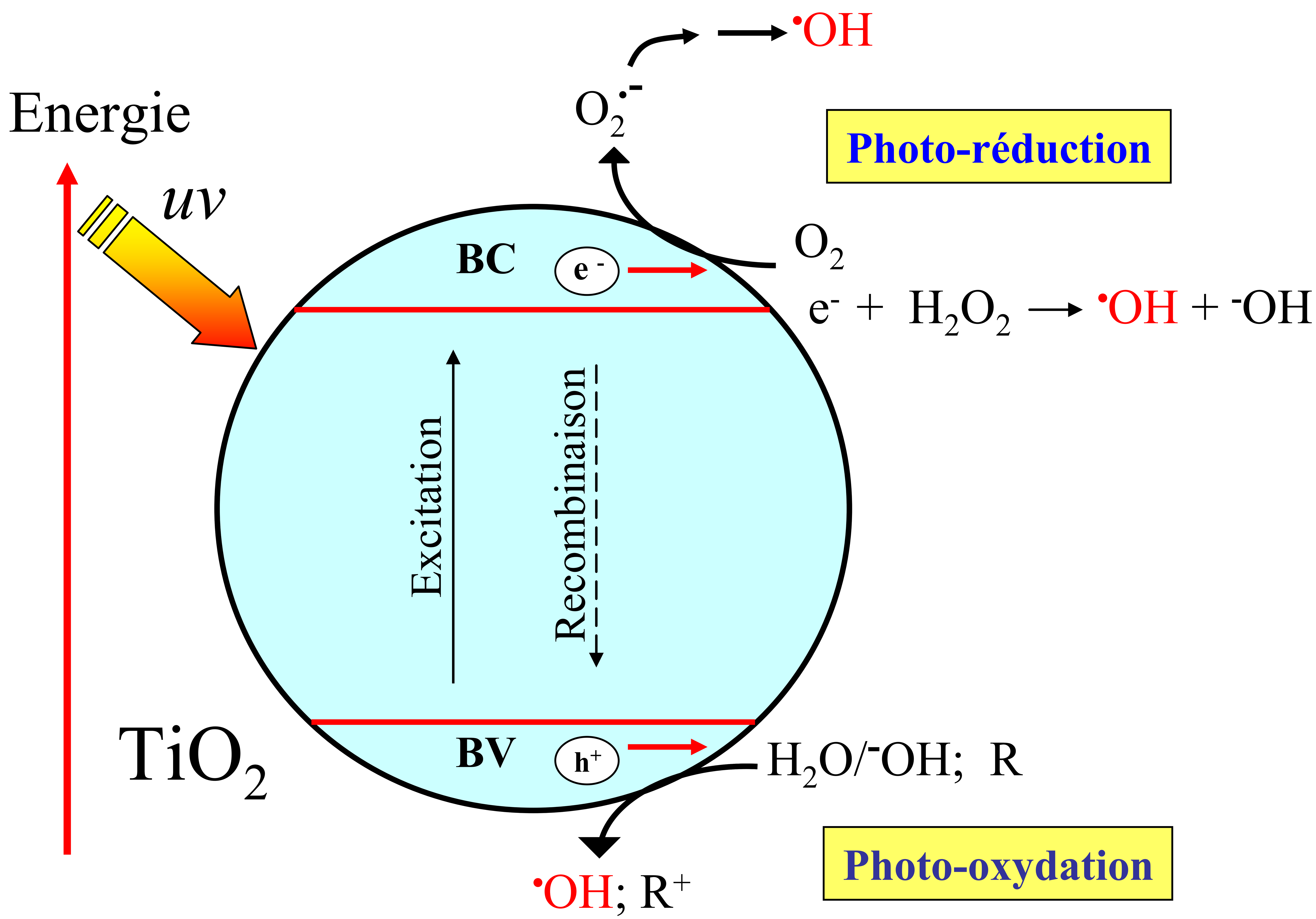
$$H_2O_2 + h\nu \rightarrow 2°OH$$

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + °OH + OH^-$$

Ultrasound/Fe(II)/UV



Combining ultrasound with TiO_2 photocatalysis



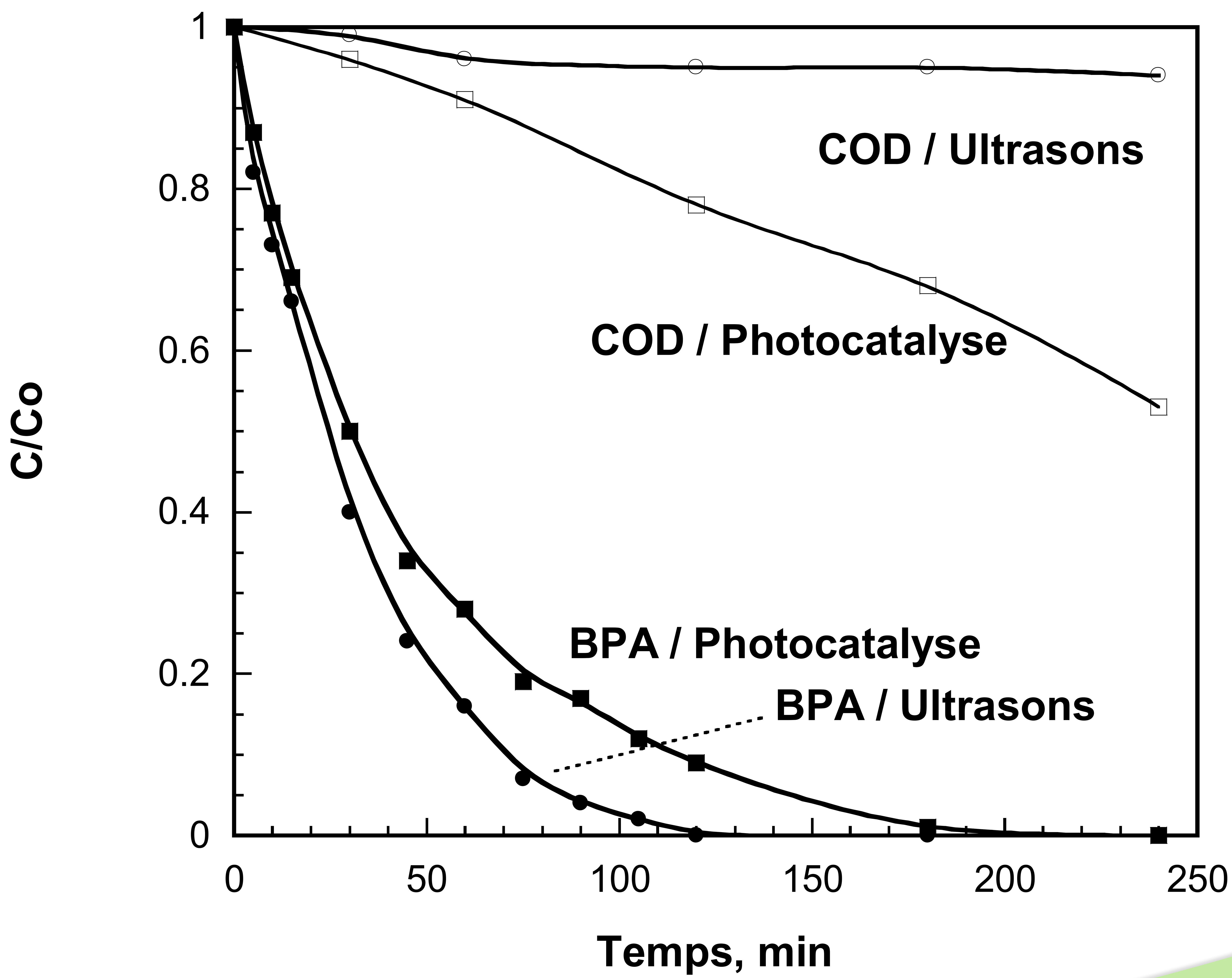
Experimental part

* Photocatalyse:
Suntest
TiO_2 P-25 0.01-1 g L^{-1}
* Ultrasons :
300 kHz, 80 W

600 mL BPA 118 μM,
pH 3, O_2
22 ± 2 °C

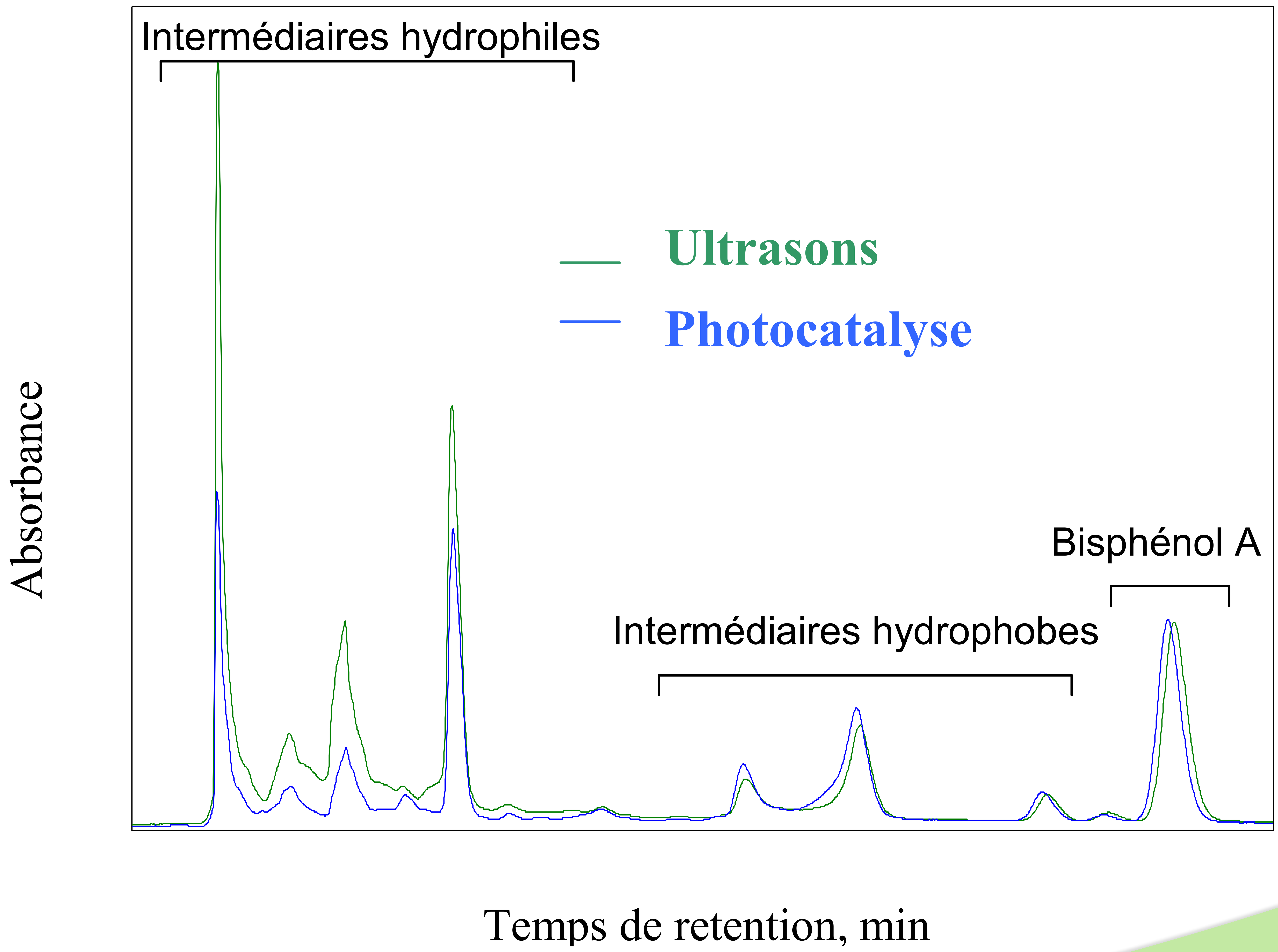
Analyses :
HPLC
COD
H_2O_2

Photocatalysis 1g L^{-1} TiO_2

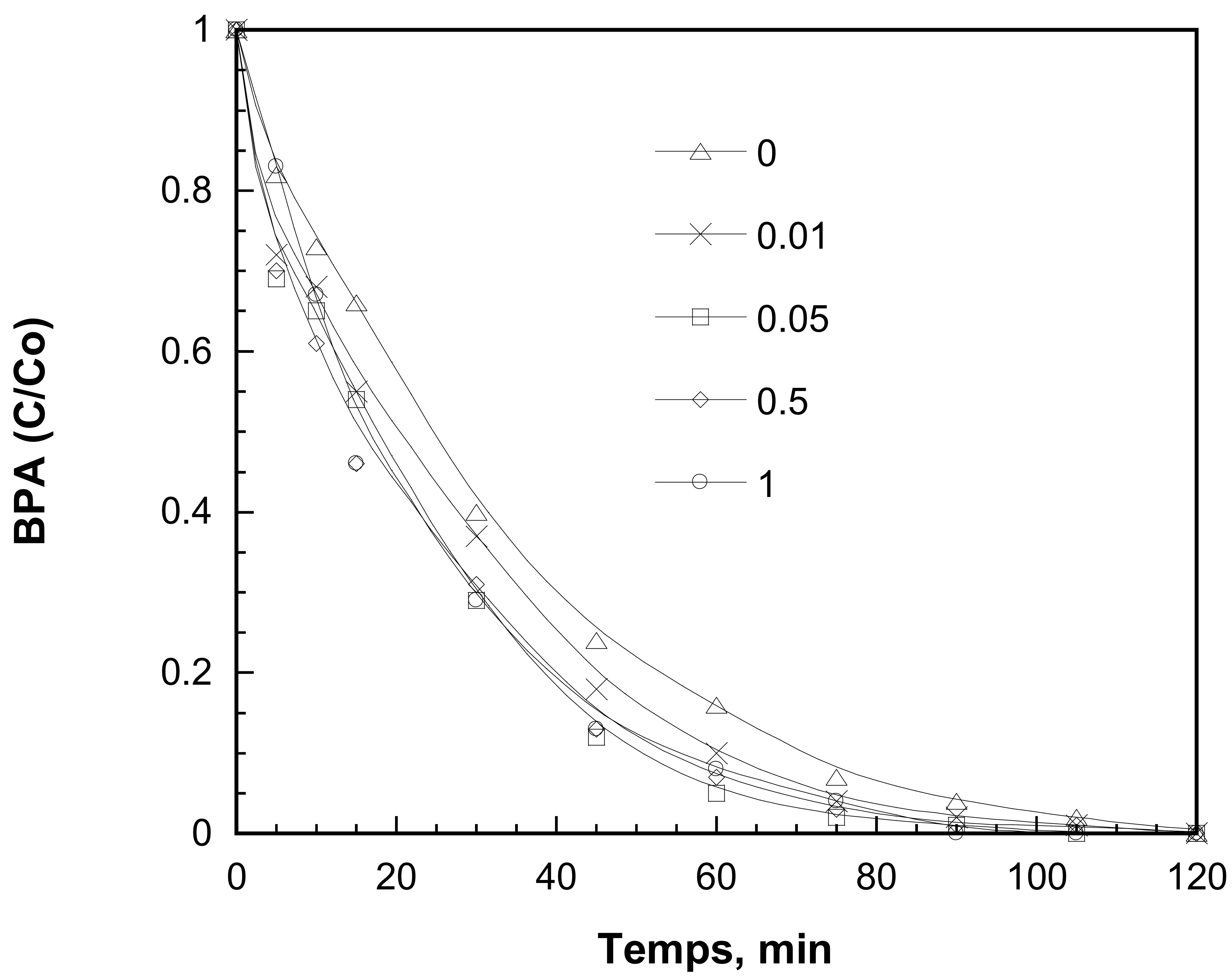


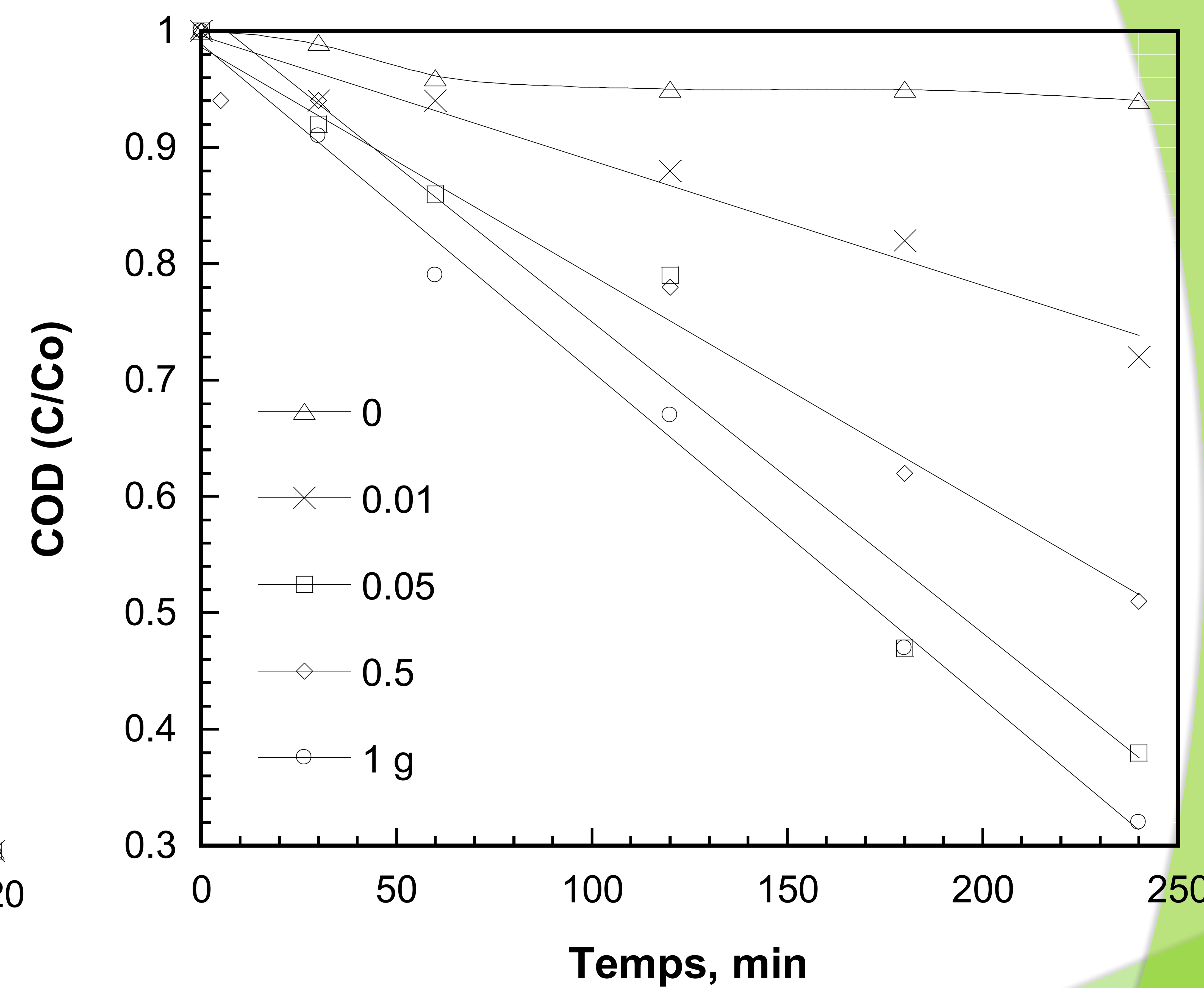
Ultrasons vs TiO_2 photocatalysis

50 % of BPA elimination

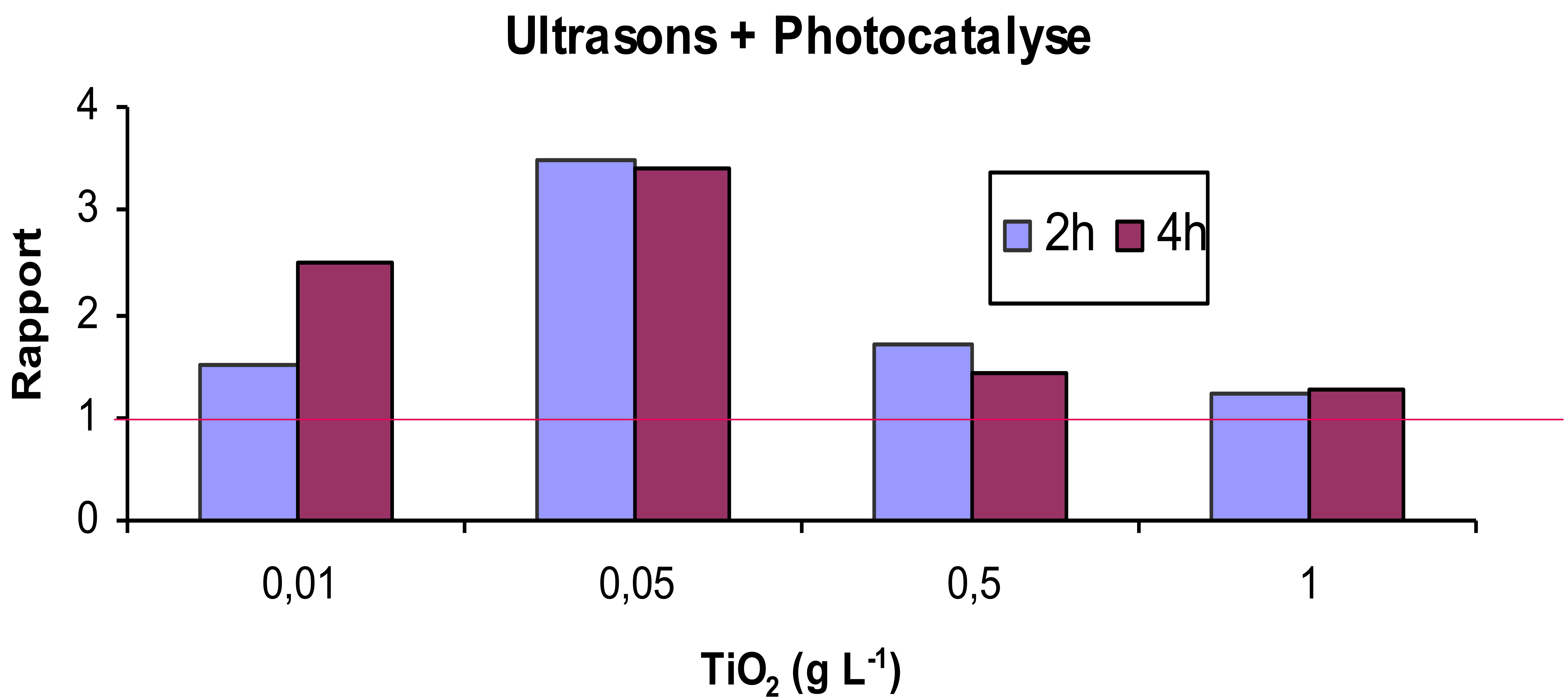


Evolution of BPA and DOC



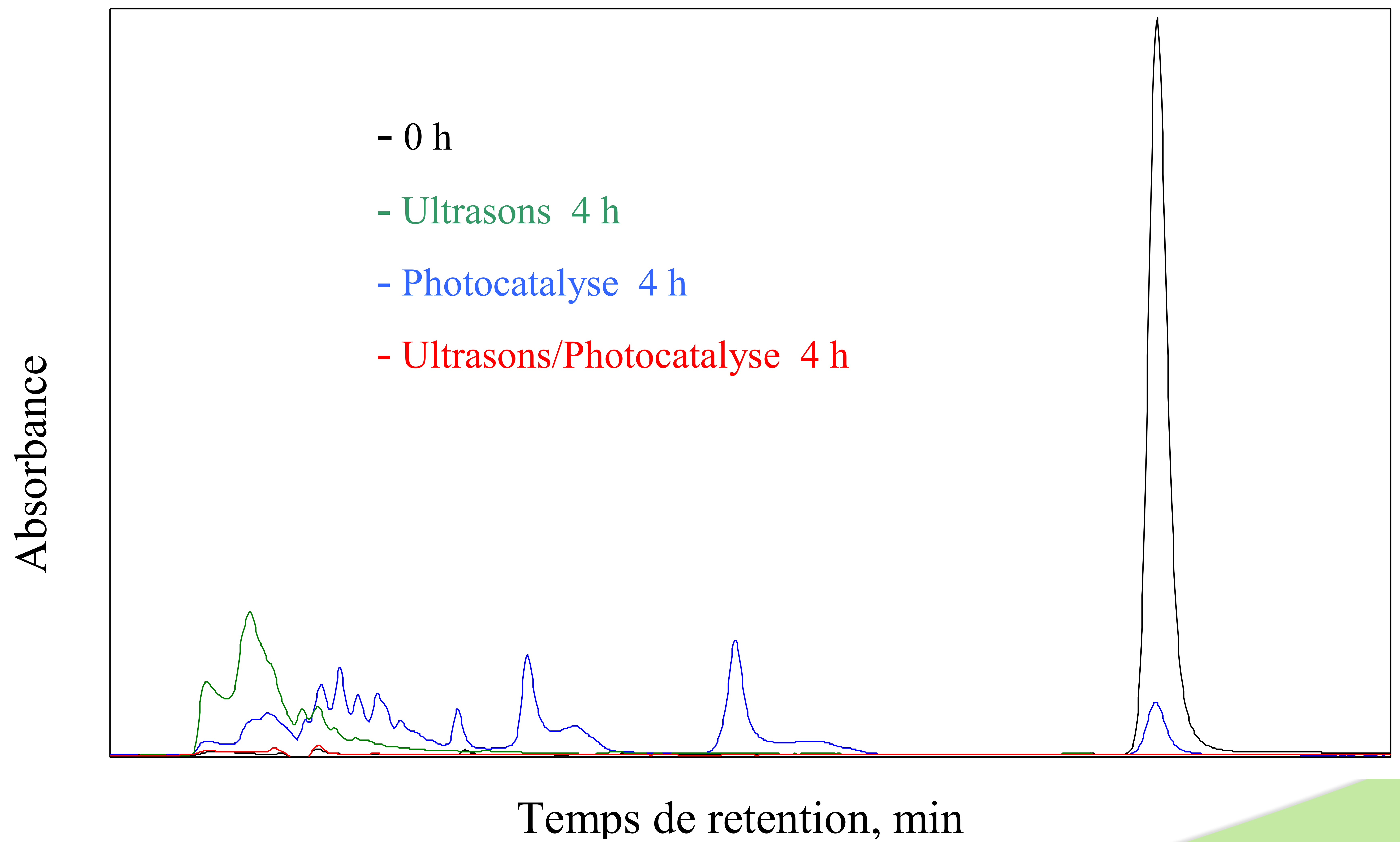


Combining ultrasound with TiO2 photocatalysis



Ultrasound/TiO_2/UV

After 4 h of BPA treatment
TiO_2 0,05 g L^{-1}



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Concluding remarks

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- Ultrasound can selectively remove antibiotics and its associated AA if matrix components have a more hydrophilic character.

- Combination of ultrasound with other AOPs can be a sinergistic alternative to the complete removal of organic pollutants

- Sonotreated water can be completely mineralized using a subsequent biological process.

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	COP	USD	COP	USD
Undergraduate students	$ 210.000	$ 81	$ 300.000	$ 115
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Thanks!!!

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