Sonolytic treatment of water for removal of pollutants

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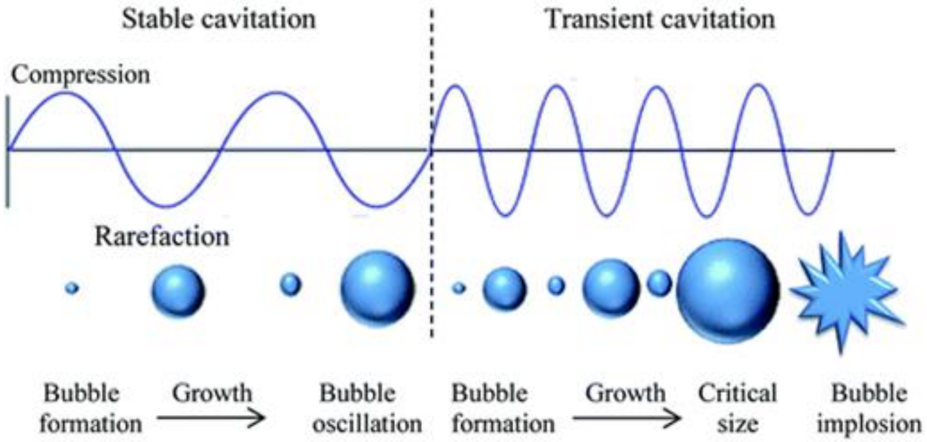
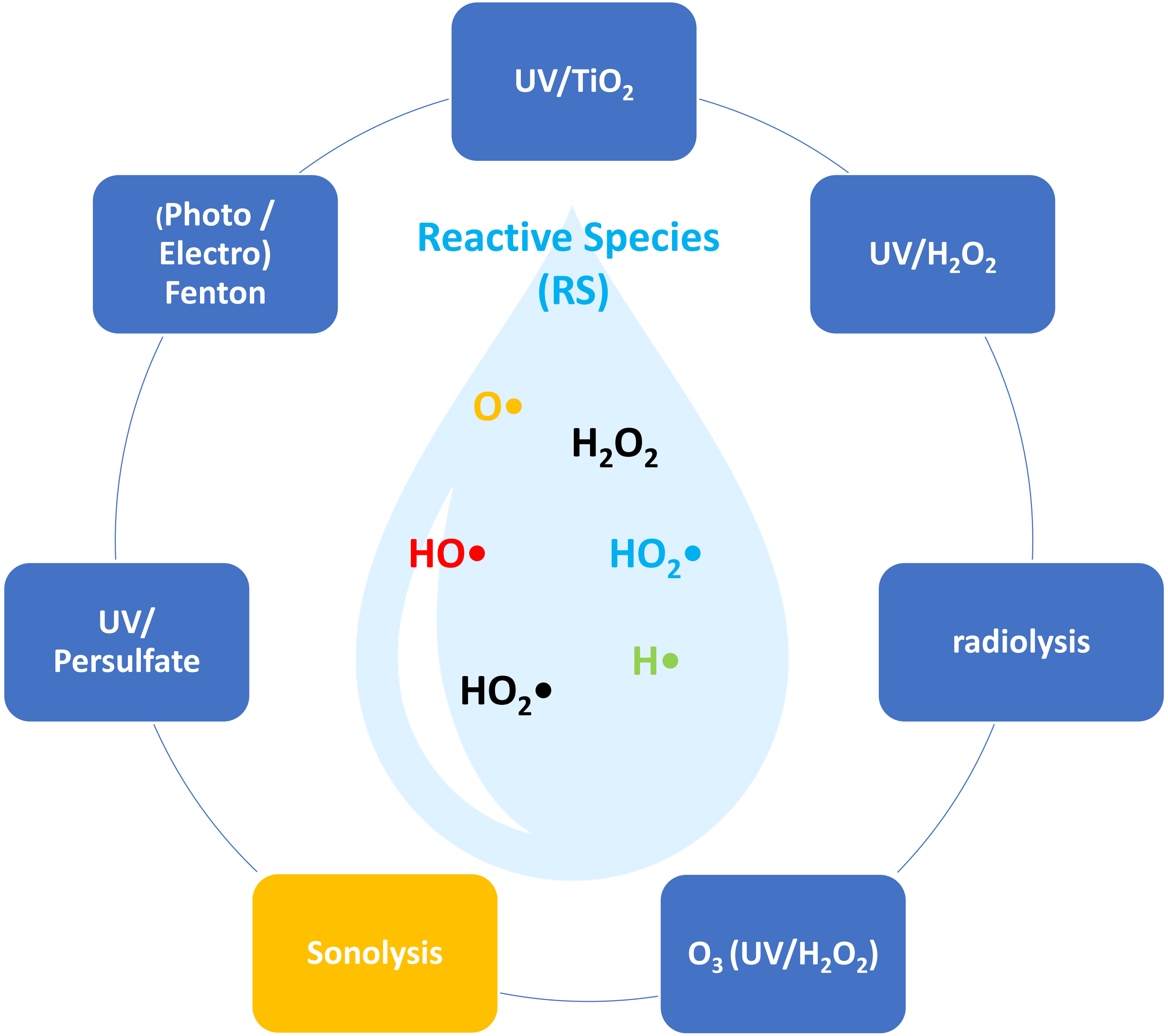


Training School “AOPs for water T&O”
5-9 Sep 2022, Athens, Greece

Advanced Oxidation Processes (AOPs) for water treatment



UV/TiO_2

UV/H_2O_2

radiolysis

O_3 (UV/H_2O_2)

Sonolysis

UV/ Persulfate

(Photo / Electro) Fenton

Reactive Species (RS)

O•

H_2O_2

HO•

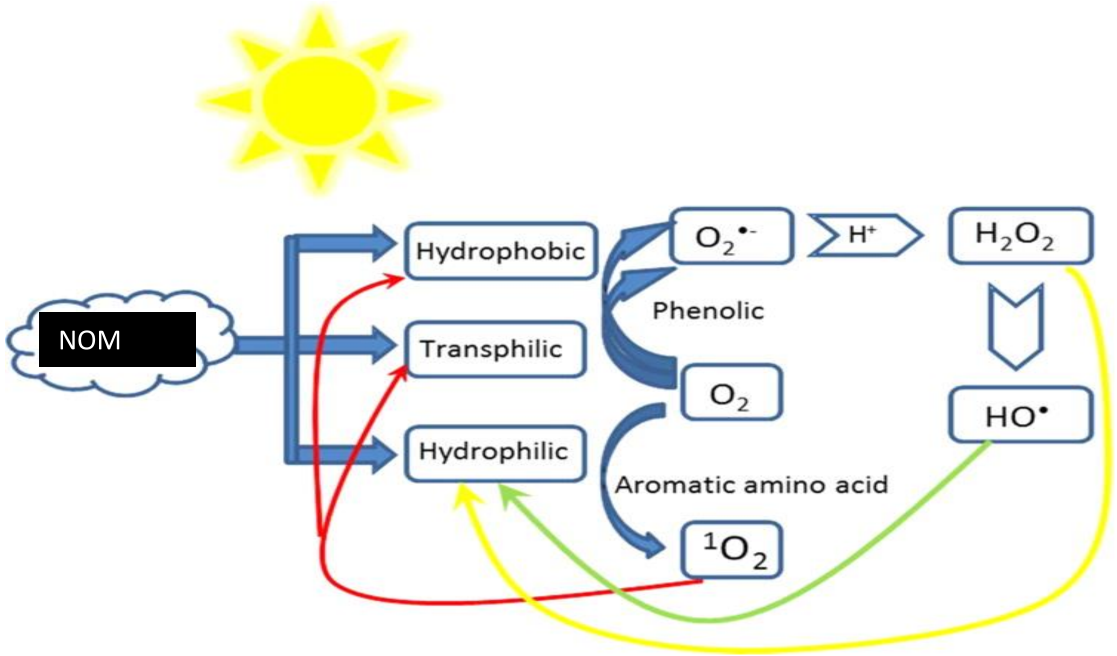
HO_2•

H•

HO_2•

reactive species in natural systems

Interaction of sunlight with naturally occurring organic matter, leads to the formation of Reactive Oxygen Species (ROS), capable of transforming organic pollutants.



Zhang et al. (2014) ES&T 48 (21), pp 12645–12653
Cottrell et. al. (2013) Water Research 47(14), pp. 5189-5199
Zafiriou et. Al. (1984) ES&T 18(12), pp. 358A-371A

Advanced Oxidation Processes (AOPs)

Selective ROS production

Pollutant degradation & transformation products (TPs)

Simulation of natural processes

Theory

sonochemistry in general

- ☐ Sonochemistry is the field of chemistry that uses ultrasound to enhance the rates or alter chemical reactions.
- ☐ Ultrasound (US) refers to frequency higher than the audible frequency of the human ear. Typically, 20 kHz to 10 MHz.
  - ☐ 20-100 kHz - Low frequency US
  - ☐ 200-1000 kHz – High frequency US
  - ☐ 5000-10000 kHz – Very high frequency US [1]
- ☐ 4 types of sonochemical applications are known:
  - ☐ cceleration of conventional reactions (initiates reactions surpassing energy barriers/changes reaction pathway/accelerates rates)
  - ☐ redox processes in aqueous solutions via production of reactive species (RS)
  - ☐ degradation of polymers
  - ☐ decomposition of organic solvents [2]

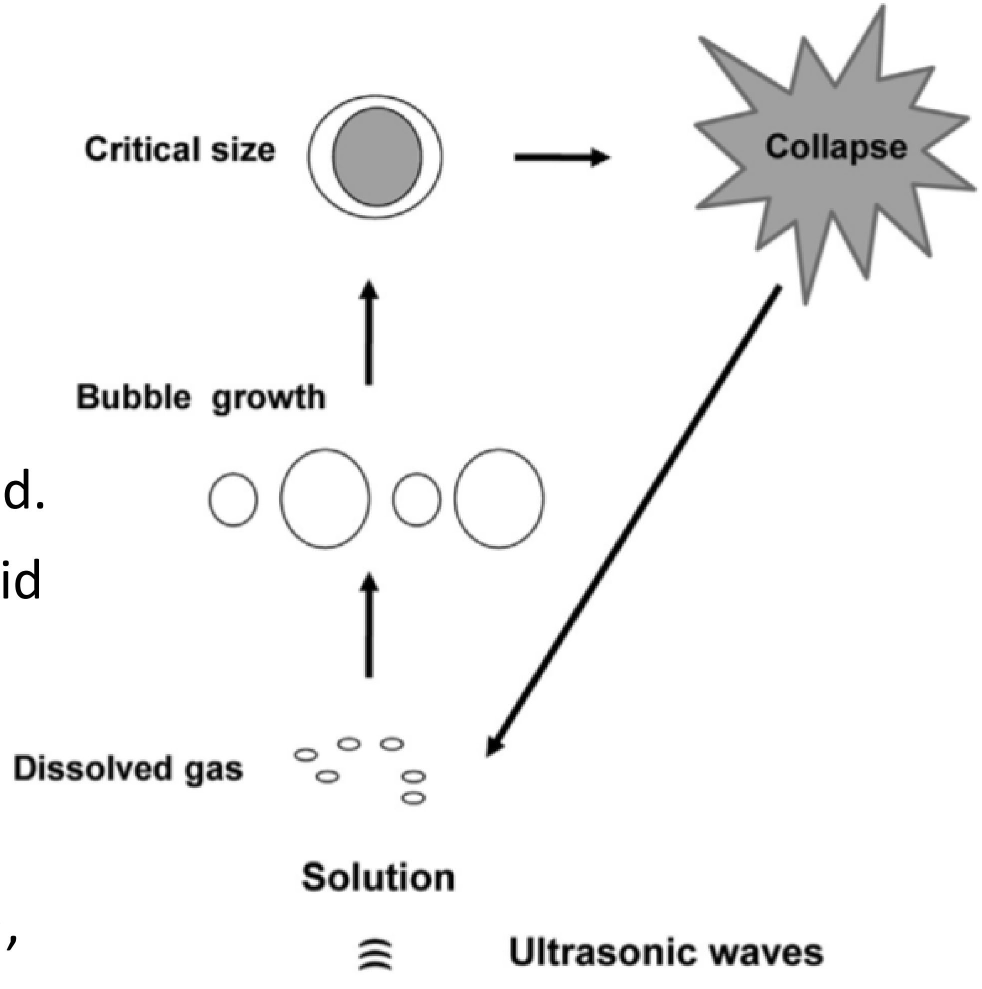
[1] S. Pilli, P. Bhunia, S. Yan, R. J. LeBlanc, R. D. Tyagi, and R. Y. Surampalli, “Ultrasonic pretreatment of sludge: A review,” *Ultrason. Sonochem.*, vol. 18, no. 1, pp. 1–18, 2011

[2] Henglein, A. (1987). "Sonochemistry: Historical developments and modern aspects." Ultrasonics **25**(1): 6-16

Principle of Sonolysis)))

Theory of hot-spots

- **Sonolysis** is the use of ultrasound for the degradation of a wide variety of organic pollutants through the formation of ROS.
- **Acoustic cavitation** is the formation, growth and implosive collapse of small gas bubbles in liquids exposed to ultrasound.
- **Hot spot theory** postulates that bubbles collapsing in a liquid medium, create a localized “hot-spot”, which reach temperatures of ~5000K and pressures of ~500-1000 atm.
- These conditions induce the **rupture of water molecules (homolytic bond cleavage)** and **thermal dissociation of oxygen**, generating various reactive radical species (HO•, H•, O•, and HO_2•), with the subsequent formation of hydrogen peroxide (H_2O_2).



R. A. Torres-Palma and E. A. Serna-Galvis, “Chapter 7 - Sonolysis,” S. C. Ameta and R. B. T.-A. O. P. for W. W. T. Ameta, Eds. Academic Press, 2018, pp. 177–213.

Hot spot theory reactions

Rupture of water molecule

$$H_2O +)))) \rightarrow HO\bullet + H\bullet \tag{2.1}$$

Thermal dissociation of oxygen

$$O_2 +)))) \rightarrow O\bullet \tag{2.2}$$

$$HO\bullet + O\bullet \rightarrow HO_2\bullet \tag{2.3}$$

$$O\bullet + H_2O \rightarrow 2\,HO\bullet \tag{2.4}$$

$$H\bullet + O_2 \rightarrow HO_2\bullet \tag{2.5}$$

$$HO\bullet + H\bullet \rightarrow H_2O \tag{2.6}$$

$$2\,HO\bullet \rightarrow H_2O + O\bullet \tag{2.7}$$

$$HO_2\bullet + HO\bullet \rightarrow O_2 + H_2O \tag{2.8}$$

$$2\,HO_2\bullet \rightarrow H_2O_2 + O_2 \tag{2.9}$$

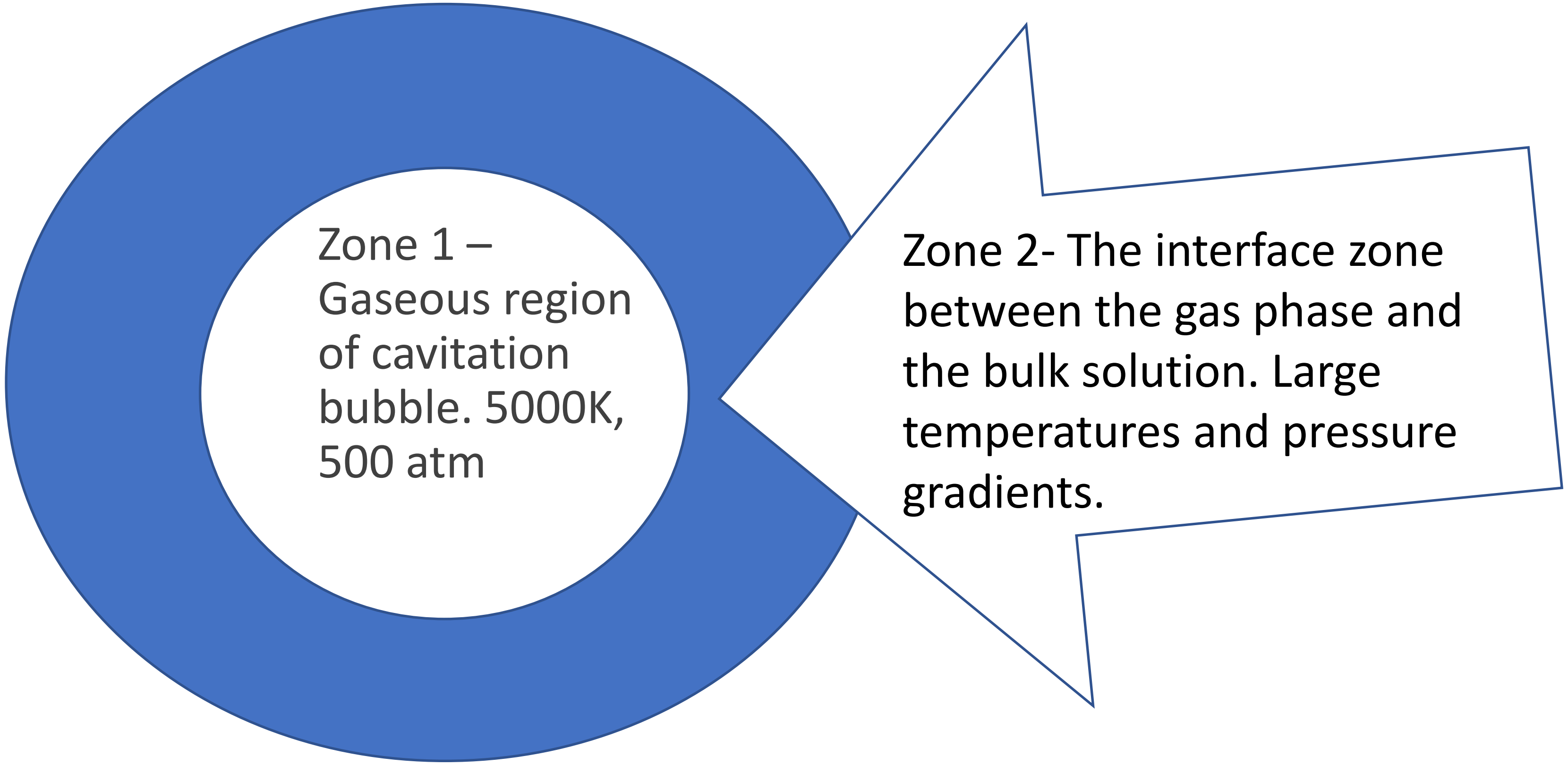
$$H\bullet + H_2O_2 \rightarrow HO\bullet + H_2O \tag{2.10}$$

$$HO\bullet + H_2O_2 \rightarrow HO_2\bullet + H_2O \tag{2.11}$$

$$2\,H\bullet \rightarrow H_2 \tag{2.12}$$

Sonolysis

Reaction zones



Zone 1 – Gaseous region of cavitation bubble. 5000K, 500 atm

Zone 2- The interface zone between the gas phase and the bulk solution. Large temperatures and pressure gradients.

Zone 3- Bulk solution. Ambient temperature and pressure.

Sonolysis

Operational parameters and ROS yield

- **ultrasound frequencies** usually increase the number of free radicals because there are more cavitational events that consequently lead to an increase of pollutant degradation, up to an optimum frequency
- **power intensity** increases the acoustic pressure, thus inducing more violent cavitational collapse, up to an optimum point above which, scattering of the he sound waves takes place, thus lowering the energy dissipated in the liquid
- Higher **temperature** facilitates the bubble formation and allows the pollutant molecules to move faster into the cavitation bubbles. Beyond the optimum temperature, a loss of cavitation energy is observed and the cavitation bubble escapes more easily
- **solution pH** is significant, since it is related to the state of the target compound (ionic or molecule) and the degree of protonation of the molecule, which could affect the accumulation of the target compound on the liquid-bubble interface
- the **presence of inorganic constituents** like chloride (Cl^-), sulfate ($SO_4^=$), and bicarbonate (HCO_3^-) ions
  - they can accelerate the sonolysis of organic substances by a "salting-out" effect (the presence of anions pushes the organics toward the bubble interface leading to an enhancement of the pollutants degradation)
  - The bicarbonate anion has a dual behavior that is determined by the relative concentrations of both the pollutant and anion

Advantages

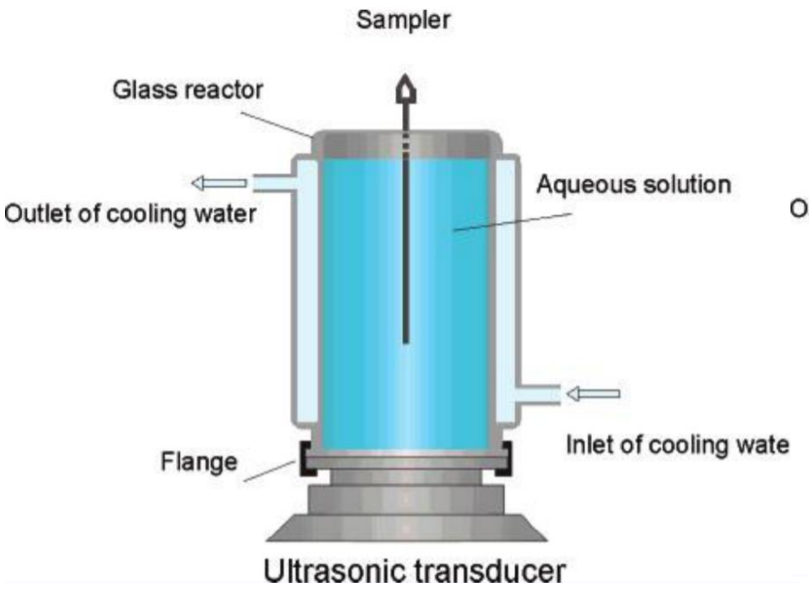
Sonolysis

- does not require addition of oxidants or catalyst
- does not generate additional waste streams, as compared to other treatment processes.
- is not affected by the toxicity of the target pollutants or the low biodegradability of compounds.
- **is in favor of the twelve principles of green chemistry**, especially when better yields, reduced reaction times, new reactivity and use of water as solvent, are achieved

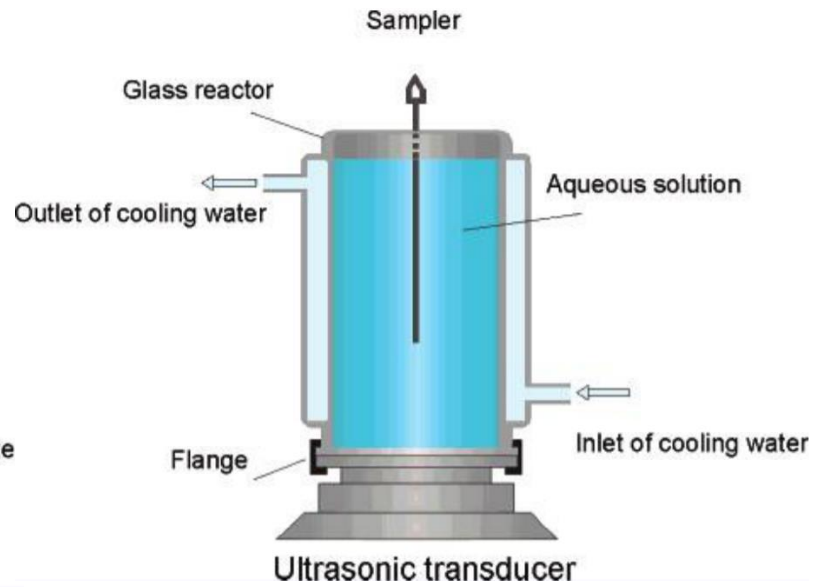
Apparatus for ultrasonic irradiation

Ultrasound generator K 80, Transducer E/805/T & Ultrasound Bath 5/1575

Working with big volumes:
500mL device



Working with small volumes:
Immersed glass tube
5-20 mL



Optimization of the small volume tube

- x,y,z position to transducer
- Ultrasound energy per cm^3

Experimental

Device

transducer E/805/T connected to an Ultrasound Generator K 80

- 850kHz
- maximum 100W
- 500 mL Ultrasound bath (5/1575 model)
- 5 mL tube for expensive compounds

Working with small volumes

Glass tube experiments

- A small tube is immersed in the water of the device.
- With this addition it is possible to degrade expensive compounds in water solutions of small volume (5 or 10 mL).
- It is also possible to use extreme pH as the transducer will not be directly to the acidic solution.
- Optimizing setup:
  - The optimal x,y,z position for this tube(vertical and horizontal position)
  - The material of the tube (plastic or glass)
  - Ultrasound energy per cm^3

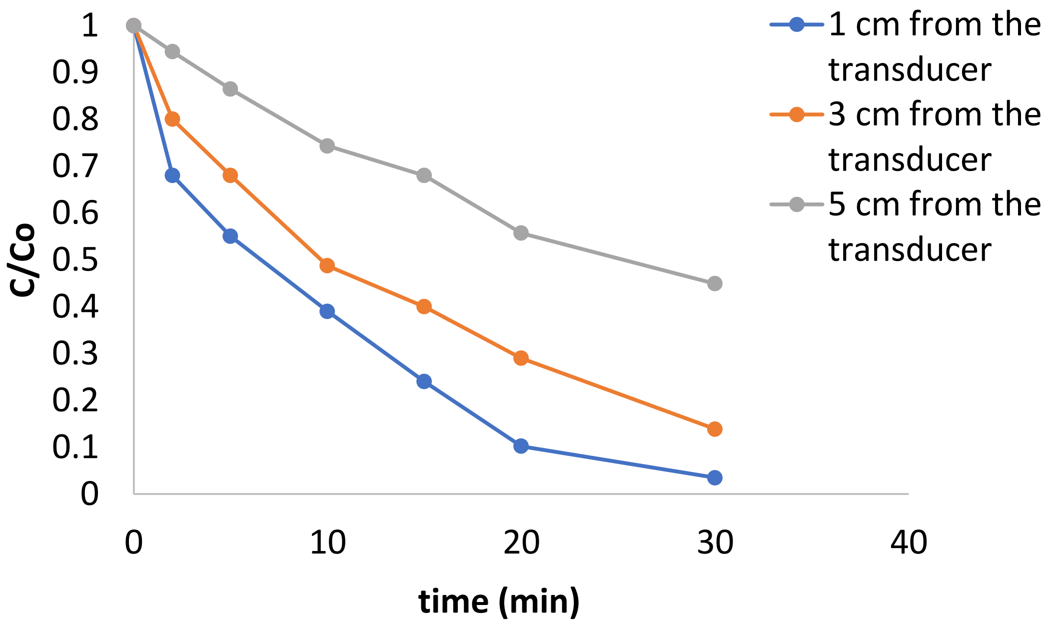
Optimizing the Glass Tube location (z axis)

A. Distance from the transducer

(z axis)

- The experiments were conducted using 10 mL 1mM 2.4-DCP .

Tube distanse from the transducer



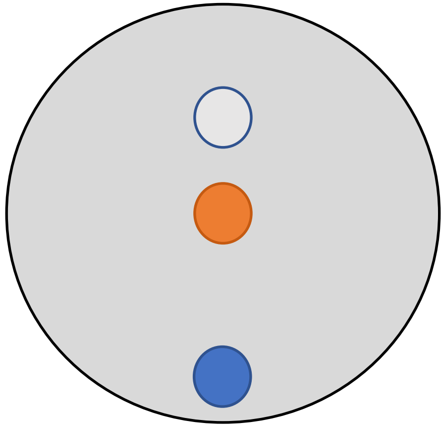
- When the tube is closer to the transducer the degradation is greater.
- The 1 cm distance was selected for the rest experiments.

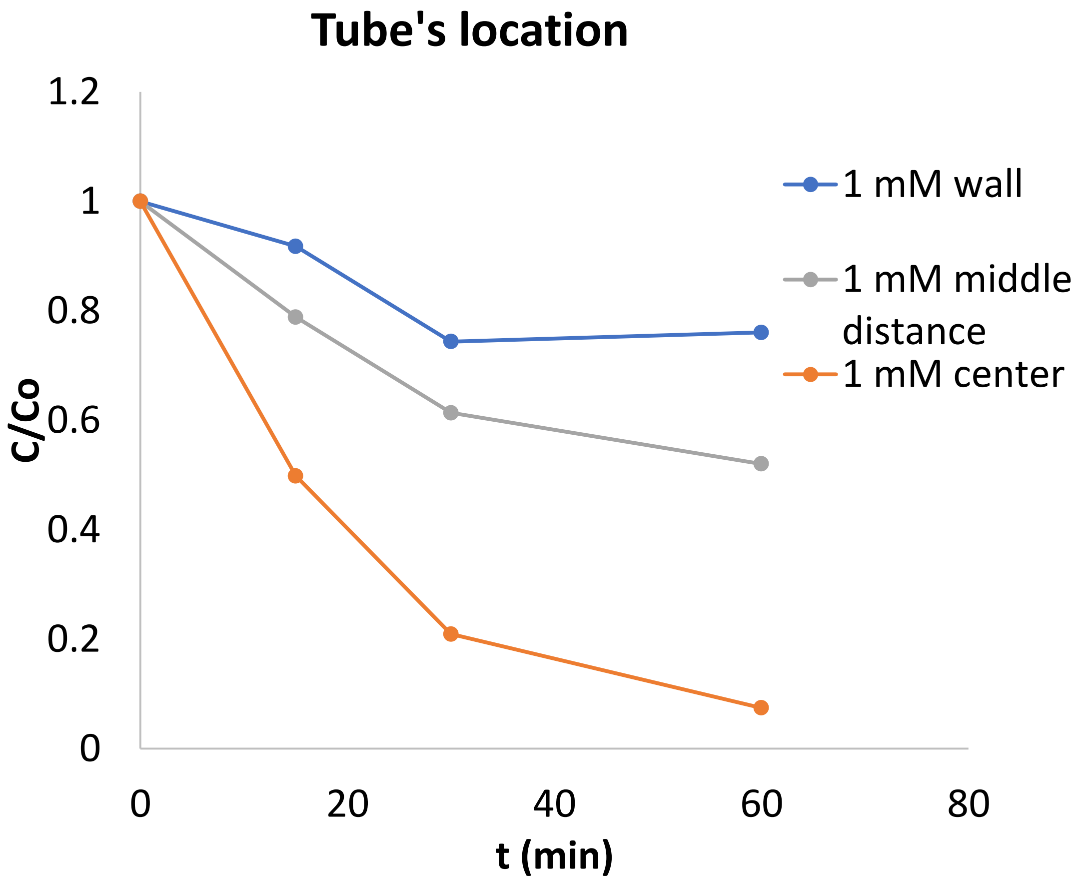
Distance	5 min	10 min	20 min	30 min
1 cm	0.55	0.39	0.10	0.03
3 cm	0.68	0.49	0.29	0.14
5 cm	0.86	0.74	0.56	0.45

Tube location optimization (x,y axis)

B. Tube’s Location (x,y axis)

- The ideal location of the tube was also examined.
- The selected positions are shown in the sketch.





- When the tube was adjusted at the center there was greater degradation.
- The tube was located at the center for the rest experiments.

Measuring the oxidative capacity of the system

Chemical Dosimetry

- ❑ Monitoring and quantifying the radicals formed is important in understanding the mechanism and applicability of such processes
- ❑ We relate the sonochemical radical formation in our system to the time period that ultrasound is applied and therefore to the incident energy used to produce them.
- ❑ In our studies, the Fricke and coumarin dosimeters are used.
- ❑ The influence of several operation parameters
  - ❑ acoustic power
  - ❑ water volume and
  - ❑ tube’s position

Fricke Dosimetry

Fricke dosimeter monitors all the produced ROS through the production of Fe^{3+} which was monitored using a spectrophotometer at 305 nm

☐ Fricke solution:

- $FeSO_4$ 0.001 M
- H_2SO_4 0.4 M
- NaCl 0.001 M

☐ This dosimetry technique depends on the oxidation of ferrous ions (Fe^{2+}) to ferric ions (Fe^{3+}).

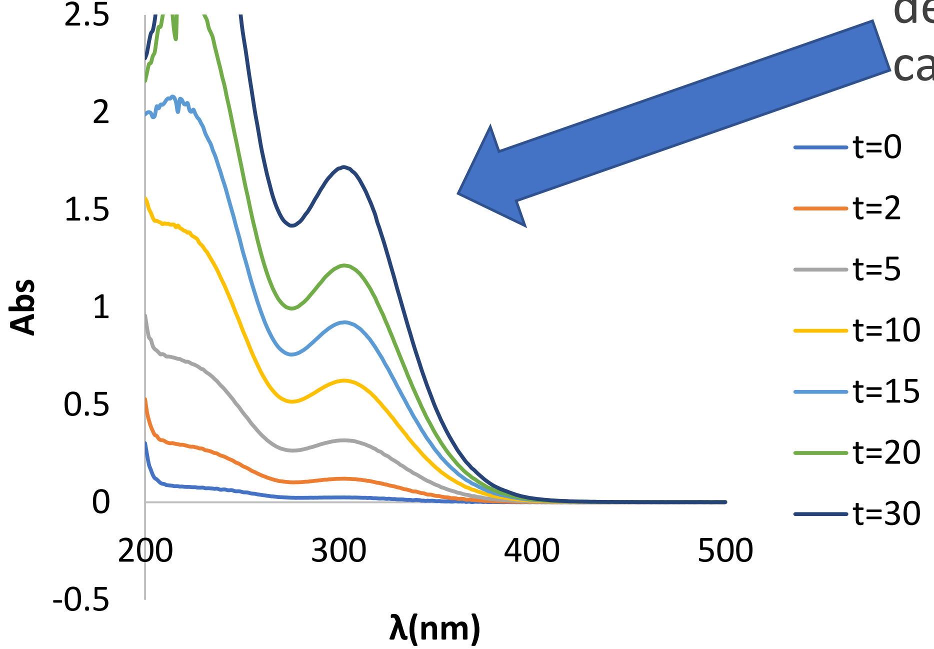
☐ Oxidizing agents: $HO\bullet$, H_2O_2, $HO_2\bullet$.

☐ Reactions:

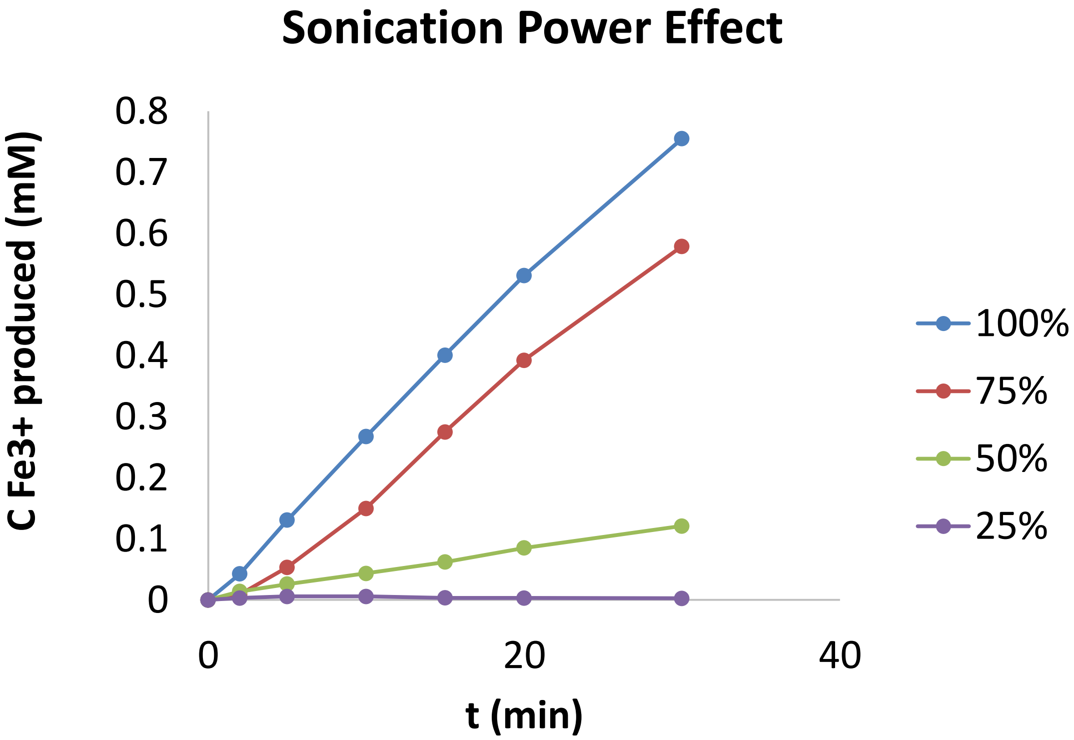
- $Fe^{2+} + HO\bullet + H^+ \rightarrow Fe^{3+} + H_2O$
- $Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + H_2O + HO\bullet$
- $H\bullet + O_2 \rightarrow HO_2\bullet$
- $Fe^{2+} + HO_2\bullet + H^+ \rightarrow Fe^{3+} + H_2O_2$

Fricke dosimeter
Ultrasonication power effect

The Fe^{3+} concentration at several degradation times was calculated using a calibration curve at the maximum of 305 nm.

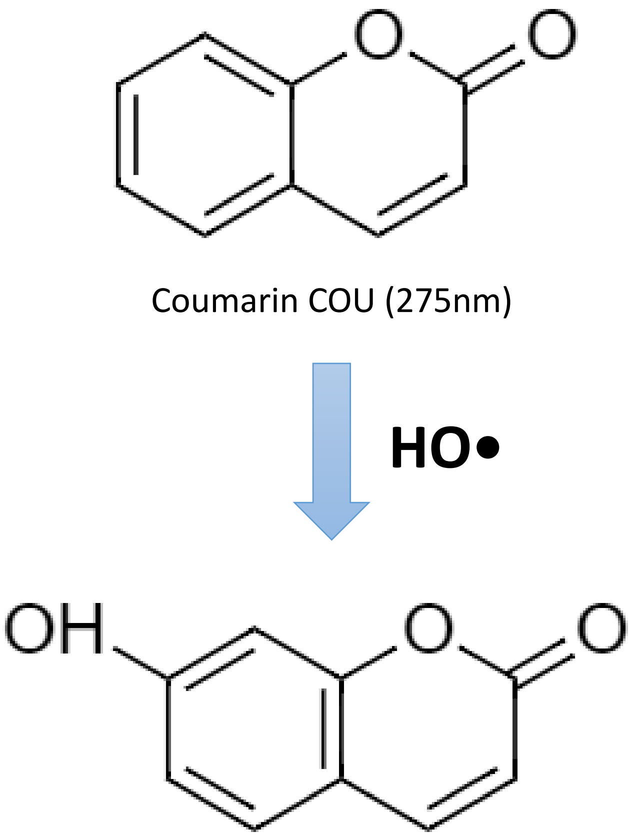


The concentration at 305 nm is calculated using the calibration curve.



Coumarin as a probe (1)

- Coumarin is an organic compound that **reacts with HO• radicals** to form several hydroxyl isomers.
- Along them **7-hydroxycoumarin is a fluorescent molecule** .
- Coumarin is an important dosimeter because it reacts selectively with OH radicals.
- The drawback is that there is **no clear correlation between the amount of HO•** produced by the device and the amount used to produce 7-hydroxycoumarin.
- The decreased concentration of coumarin was measured spectrophotometrically at 275 nm.
- The 7-hydroxycoumarin produced was monitored fluorespectrophotometrically. The excitation λ is 332nm and the luminescence intensity was measured at 456 nm.

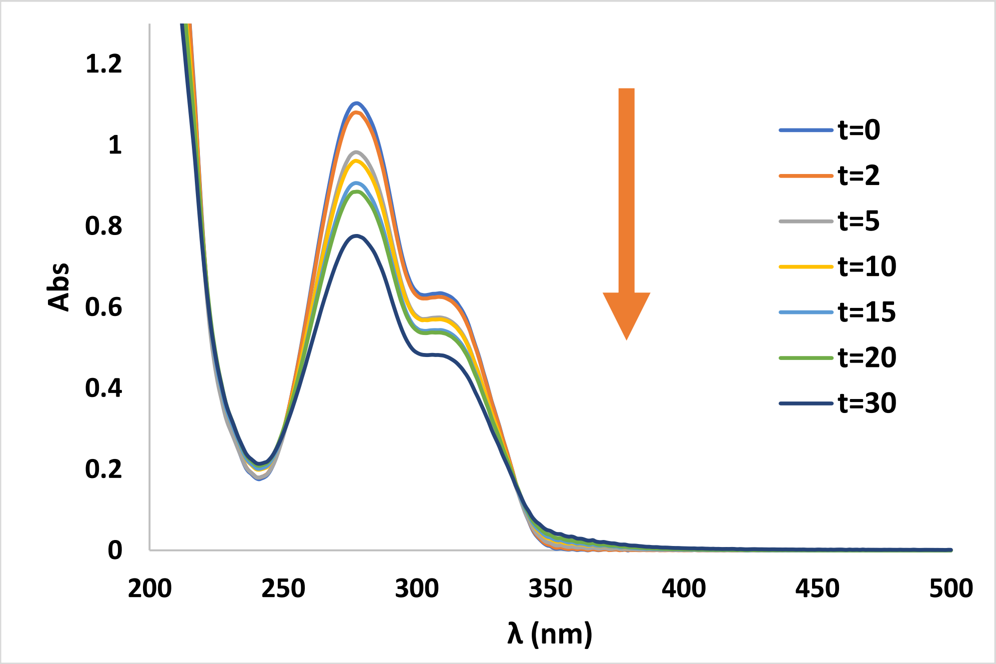


Coumarin COU (275nm)

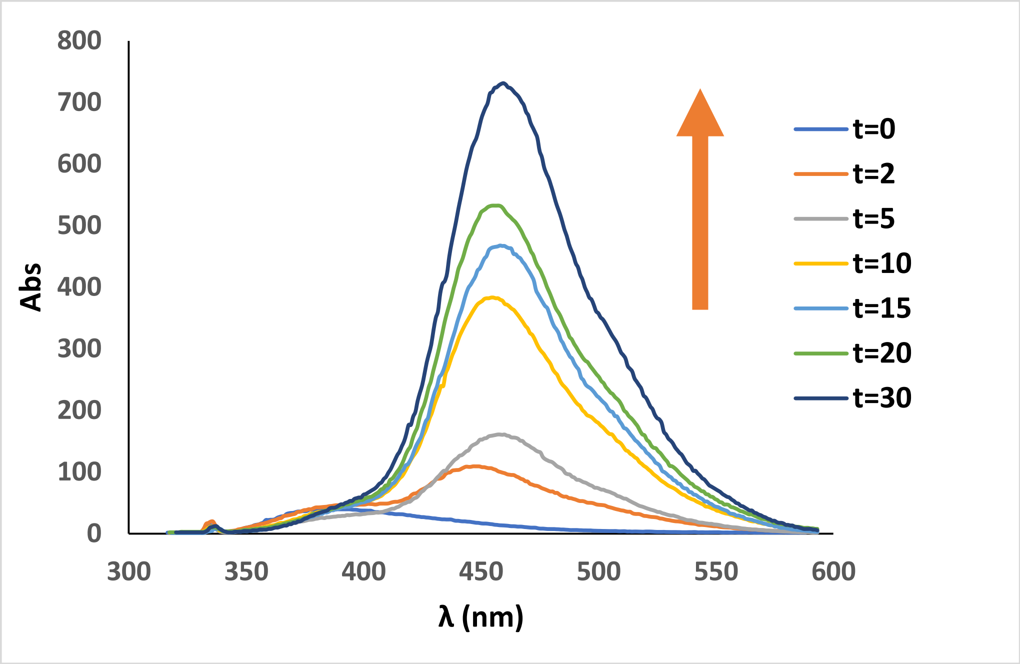
7-hydroxycoumarin 7HCOU
excitation: 332nm -> luminescence 456nm

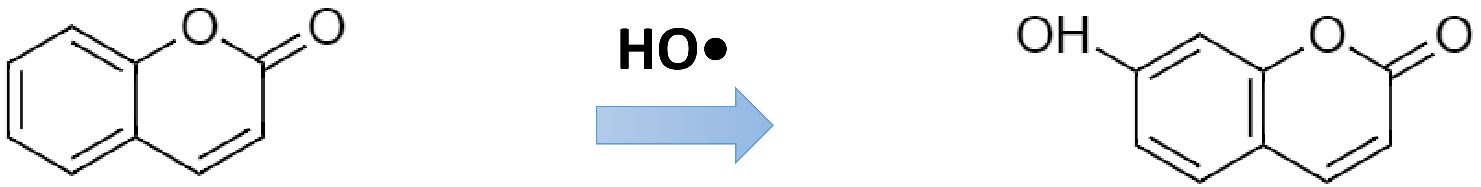
Coumarin as a probe (2)

Coumarin degradation spectrum



7-hydroxycoumarin production spectrum





Sonolysis and cyanobacteria

sonolysis has been proposed and applied for the control of cyanobacterial blooms in surface water

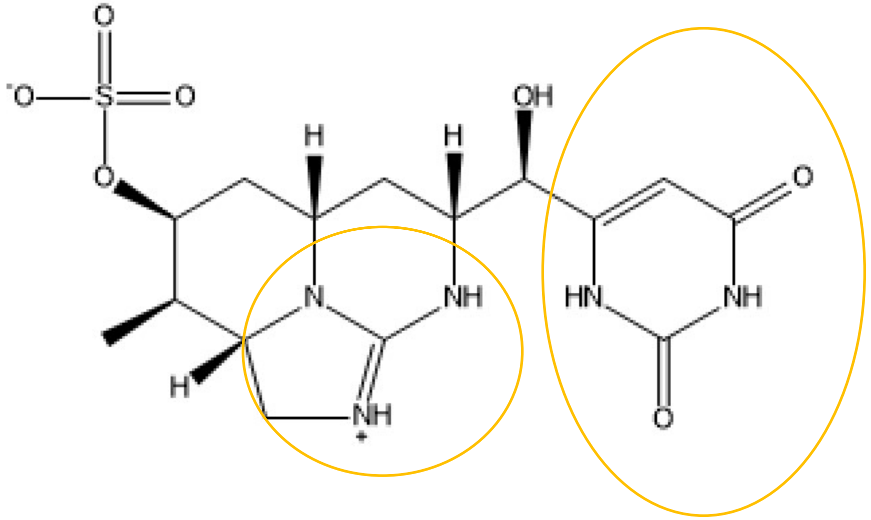
As a prevention measure

- reducing the growth rate of cyanobacteria by structural or functional destruction of algal cells
  - disruption of their gas vesicles, which destroys buoyancy of algae leading to sedimentation on the bottom of lakes
  - destruction of the cell membrane (i.e. lysis)
  - prevention of photosynthesis
- Ultrasound has found extensive application in lakes and surface water reservoirs worldwide, with projects in Australia, China, UK and USA.
- The application of ultrasound is critical to be applied at an early stage of cyanobacterial life cycle, before the formation of cyanobacterial bloom, which could lead to the release of CTs in the water

As a treatment method

- Degradation of cyanotoxins

Cyanotoxins – Cylindrospermopsin (CYN)



- Cyanotoxins may be produced by cyanobacteria that may form blooms due to their exponential growth.
- Cylindrospermopsin (CYN) is a polycyclic uracil derivative containing guanidino and sulfate groups.
- CYN was first isolated from *C. raciborskii* and it has been identified as hepatotoxic, dermatotoxic and cytotoxic.
- The uracil group and more specifically the –OH attached on C-7 has been considered responsible for CYN's toxicity. [1]
- CYN is effectively degraded using Advances Oxidation Processes (AOPs) (radiolysis, TiO_2 photocatalysis and ozonolysis).

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[1] C. Cartmell *et al.*, "Synthetic analogues of cyanobacterial alkaloid cylindrospermopsin and their toxicological activity," *Toxicol. Vitr.*, vol. 44, pp. 172–181, 2017, doi: https://doi.org/10.1016/j.tiv.2017.07.007.

Sonolytical degradation of CYN

- CYN solutions were prepared by diluting solid CYN’s standard in ultrapure water.
- CYN was degraded under several parameters:
  - Ultrasonication power
  - Initial pH
  - Initial concentration
- CYN was monitored using an HPLC-PDA operating at 262 nm.
- The kinetic model was calculated for each reaction.

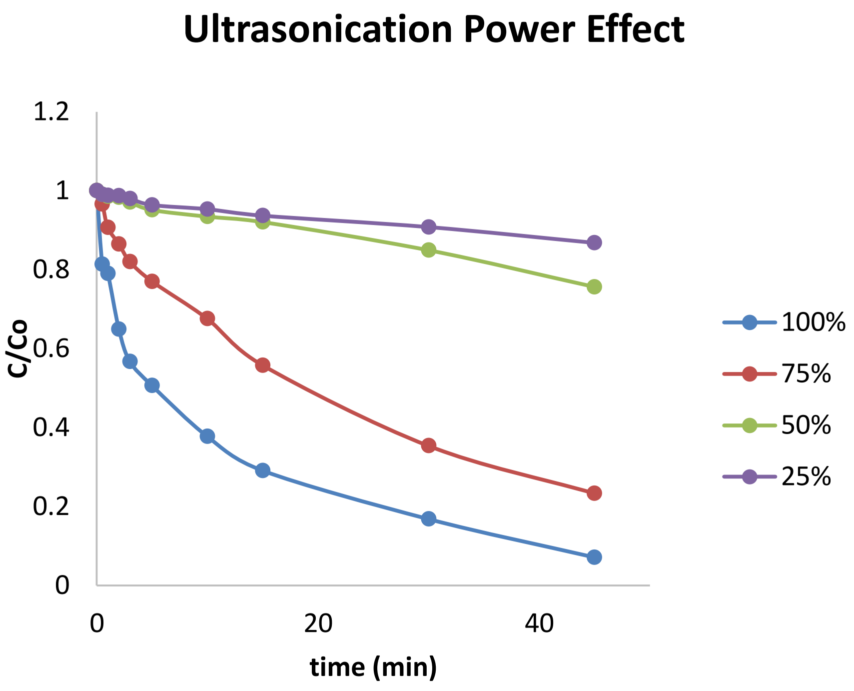
- The most important experimental parameters are explored in the following slides.

CYN degradation

Effect of ultrasonication power

Parameters:

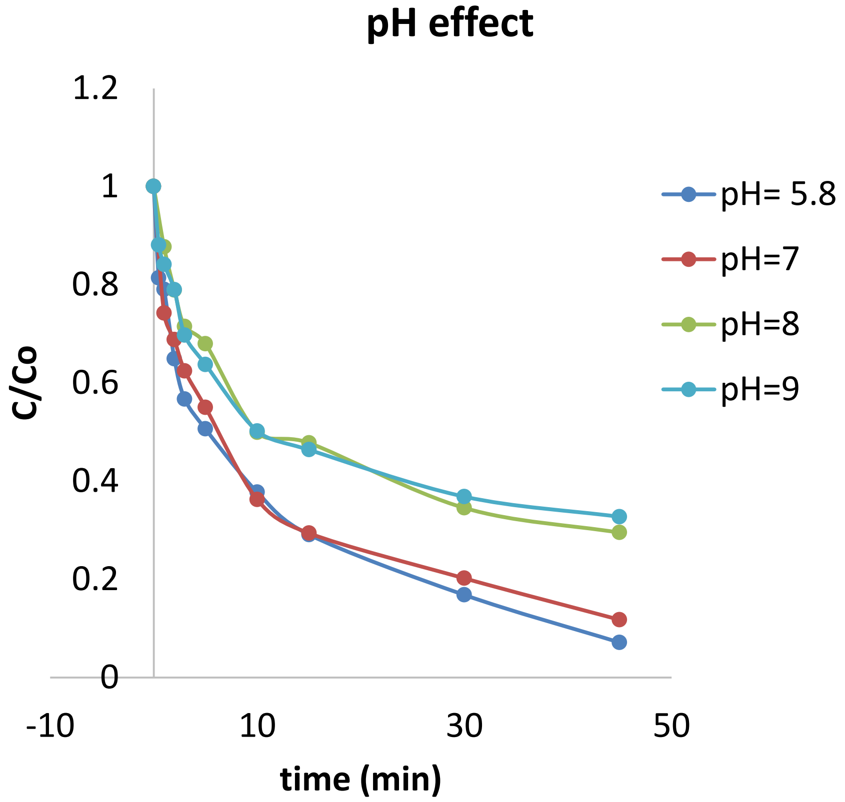
- 5 mL CYN's solution 1 mg/L
- 250 mL surrounding H_2O
- 1 cm distance from the transducer
- pH 5.8 (pH without adjustment)



- CYN is degraded more efficiently applying higher nominal ultrasonication power.
- At 100% nominal ultrasonication power (110 W) CYN is fully degraded after 45 minutes.

CYN degradation

Effect of pH

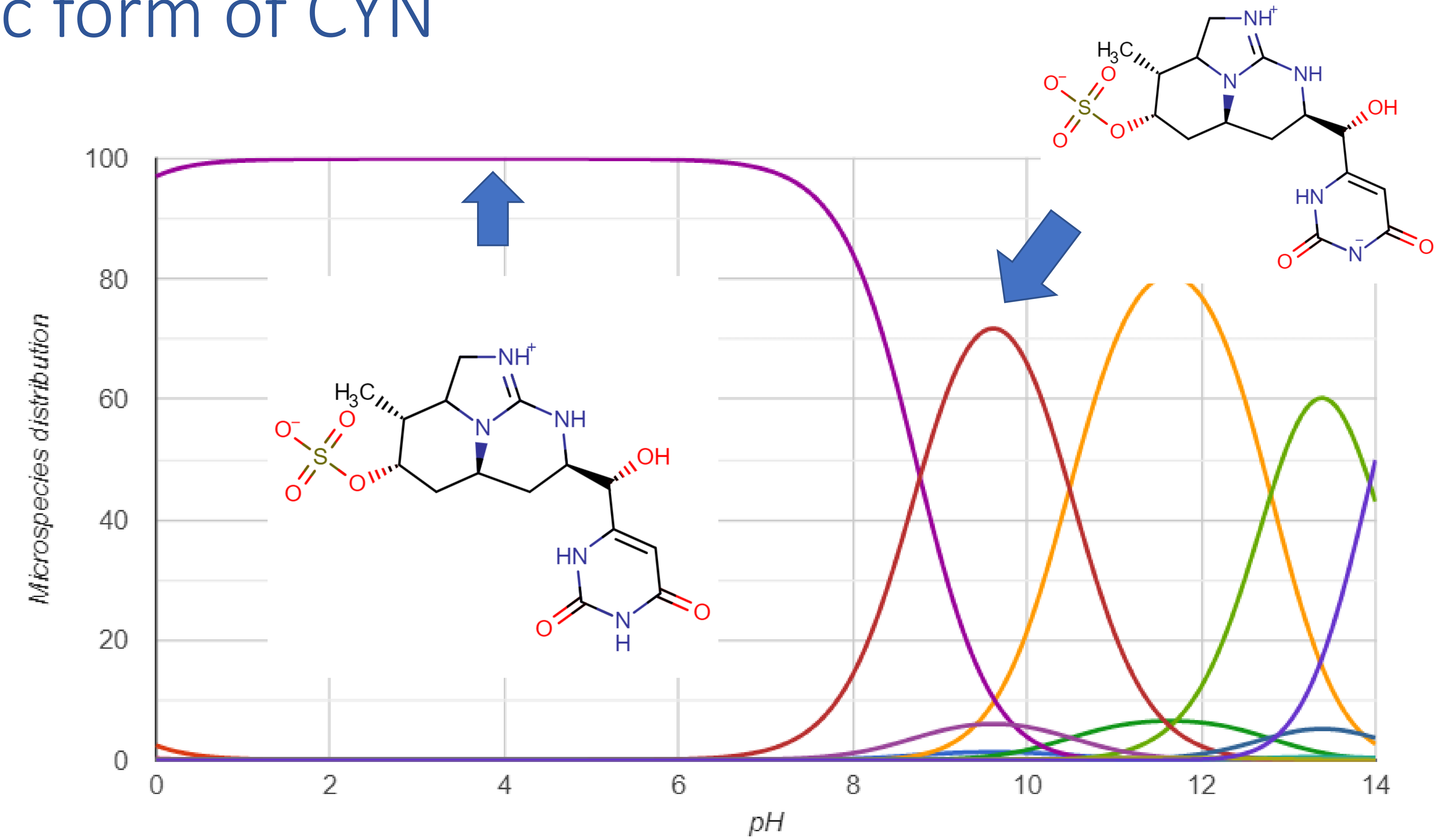


- pH affects the degradation because CYN has different ionic form at pH <8 and at pH >8
- CYN is degraded more efficiently at pH <8.

Parameters:

- 5 mL CYN's solution 1 mg/L
- 250 mL surrounding H_2O
- 1 cm distance from the transducer
- 100 % nominal ultrasonication power

Ionic form of CYN



Degradation kinetic parameters

	Pseudo-First Order		
Effect of ultrasonication Power	k (s^{-1})	R^2	r_0 (µmol L^{-1} s^{-1})
100%	0.0009	0.926	0.0033
75%	0.0006	0.989	0.0022
50%	9.00E-05	0.981	0.0003
25%	5.00E-05	0.949	0.0002
pH effect	k (s^{-1})	R^2	r_0 (mmol L^{-1} s^{-1})
pH=5.8	0.0009	0.926	0.0033
pH=7	0.0008	0.895	0.0029
pH=8	0.0006	0.894	0.0022
pH=9	0.0005	0.860	0.0018
Effect of initial concentration	k (s^{-1})	R^2	r_0 (mmol L^{-1} s^{-1})
Co=0.5 mg/L	0.0014	0.878	0.0025
Co=1 mg/L	0.0009	0.926	0.0033
Co=2 mg/L	0.0006	0.980	0.0043

The sonolytical degradation reaction best fits the pseudo-first order kinetic model.

- ☐ Degradation rate constant calculated based on: $\ln[C/C_0] = -kt$
- ☐ Initial degradation rate calculated for initial 5min of reaction

CYN sonolysis

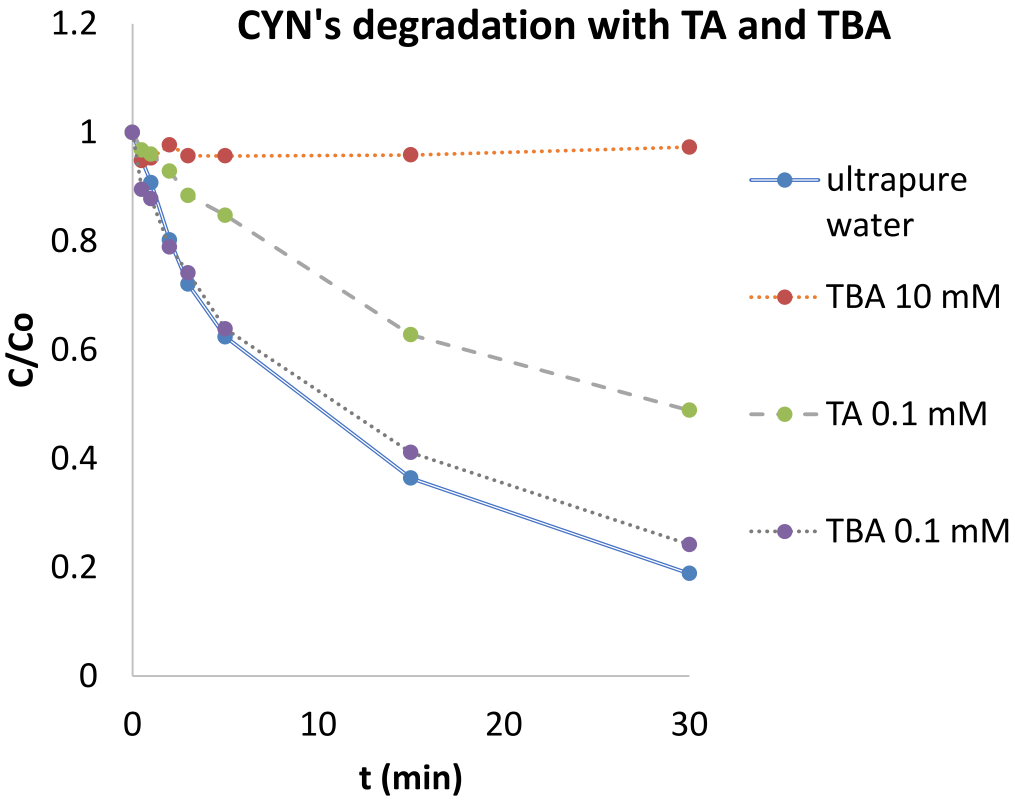
Reaction zone

- We use two different HO• scavengers: one volatile semi water-soluble (tert-butyl alcohol TBA) and one water-soluble (terephthalic acid TA)
- TBA is expected to scavenge HO• mainly in the inside of the bubble and the gas/liquid interface
- TA is expected to scavenge HO• mainly in the bulk region[1]

[1]W. Song, T. Teshiba, K. Rein, and K. E. O'Shea, "Ultrasonically Induced Degradation and Detoxification of Microcystin-LR (Cyanobacterial Toxin)," Environ. Sci. Technol., vol. 39, no. 16, pp. 6300–6305, Aug. 2005, doi: 10.1021/es048350z.

CYN sonolysis

Reaction zone



	First order kinetic model		
	k (s^{-1})	R^2	r_0 (mmol L^{-1} s^{-1})
No scavenger/ultrapure water	9.00E-04	0.9804	0.64
TBA (0.1 mM)	8.00E-04	0.9746	0.54
TA (0.1 mM)	4.00E-04	0.9809	0.27

CYN sonolysis

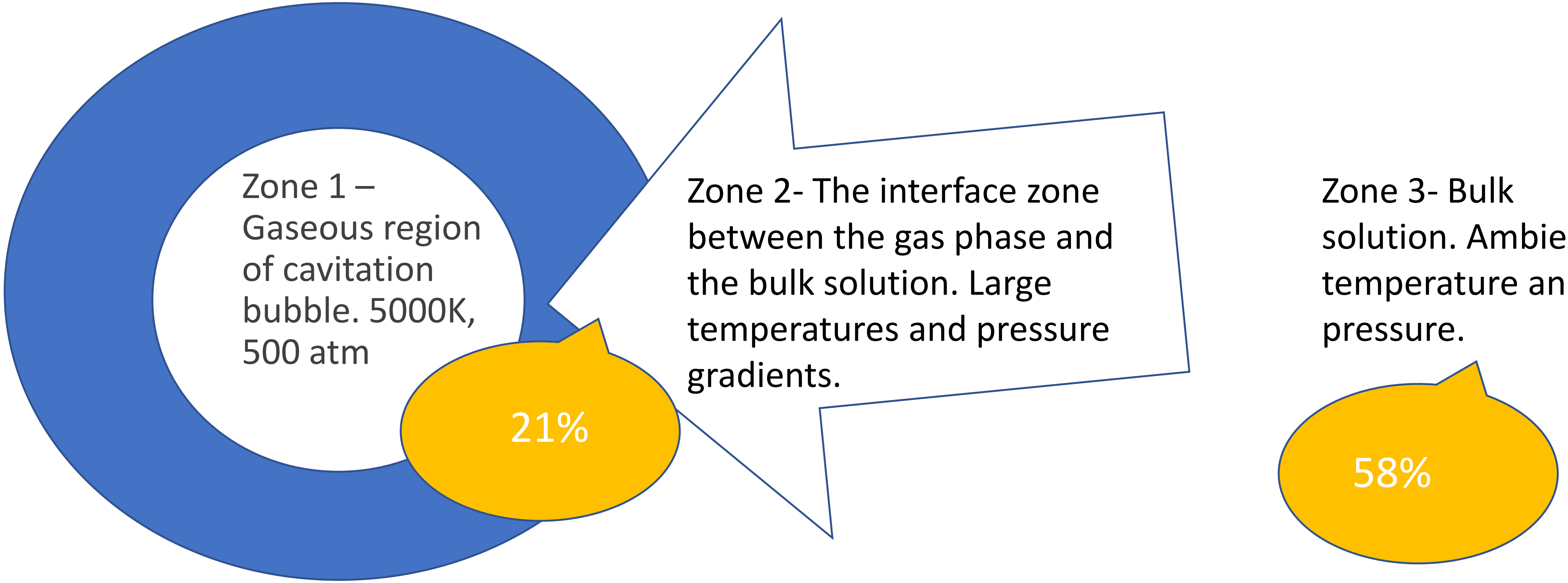
Reaction zone

- With TA: r_0 = 0.27 mmol L^{-1} s^{-1}
- With TBA: r_0 = 0.54 mmol L^{-1} s^{-1} .
- With no scavenger r_0 = 0.64 mmol L^{-1} s^{-1}.

- % degradation $_{\text{(in bulk)}}$ = $\frac{0.64 - 0.27}{0.64} \times 100$ = 58 %
- % degradation $_{\text{(in bubble/interface)}}$ = $\frac{0.64 - 0.54}{0.64} \times 100$ = 21 %
- The rest 21% due to pyrolysis/hydrolysis

CYN Sonolysis

Reaction zones



Zone 1 – Gaseous region of cavitation bubble. 5000K, 500 atm

21%

Zone 2- The interface zone between the gas phase and the bulk solution. Large temperatures and pressure gradients.

Zone 3- Bulk solution. Ambient temperature and pressure.

58%

CYN Sonolysis

Reaction zones

Targeted / suspect analysis

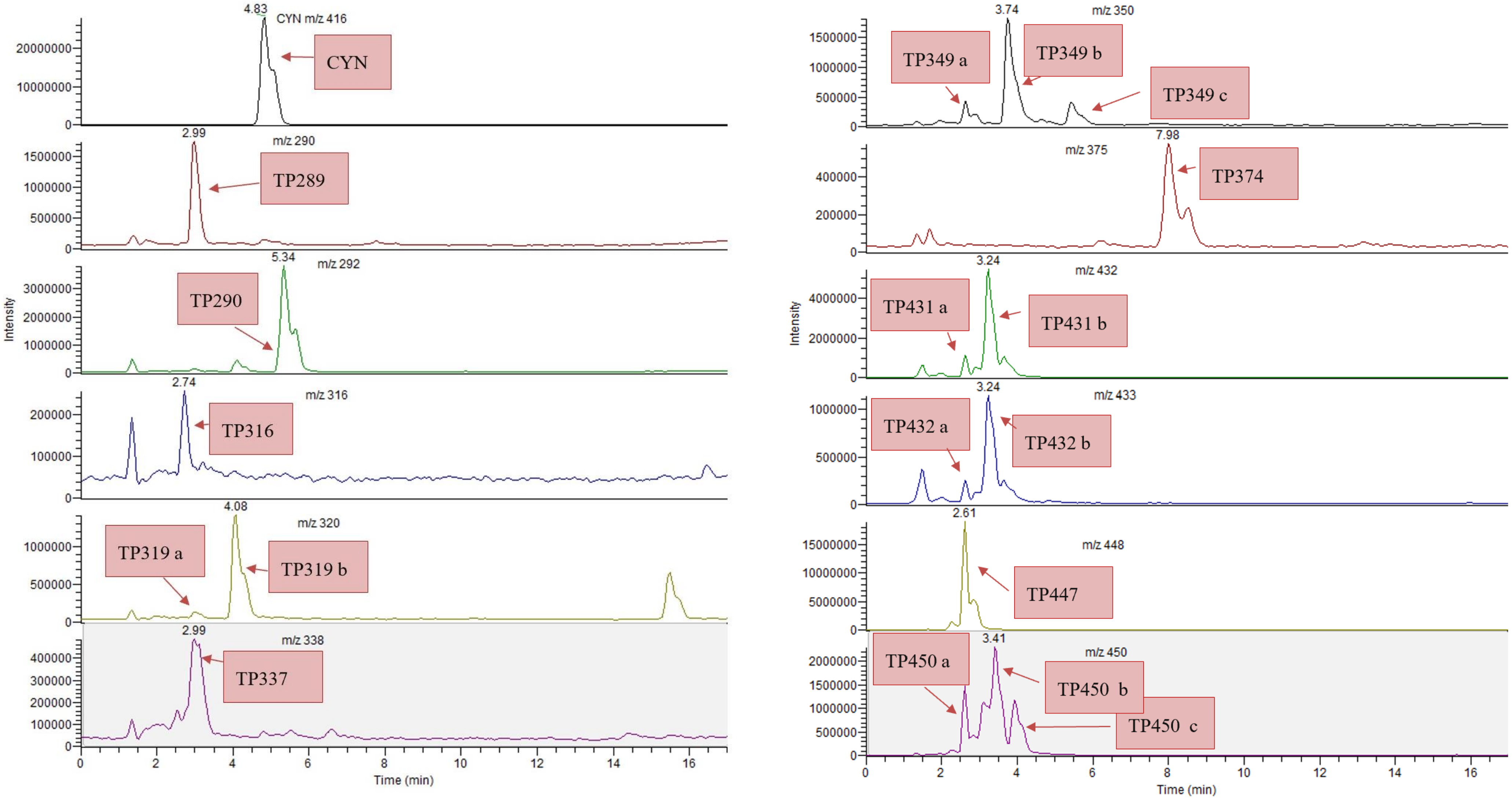
- Selection of *m/z* precursor (possible TPs) from past studies and bibliography
- SIM chromatograms of targeted/suspect *m/z* in different reaction times
- Comparison with chromatograms of t_0
- Integration of identified peaks for temporal changes in TP profile
- MS/MS fragmentation of selected TPs for structure elucidation

Non-targeted analysis

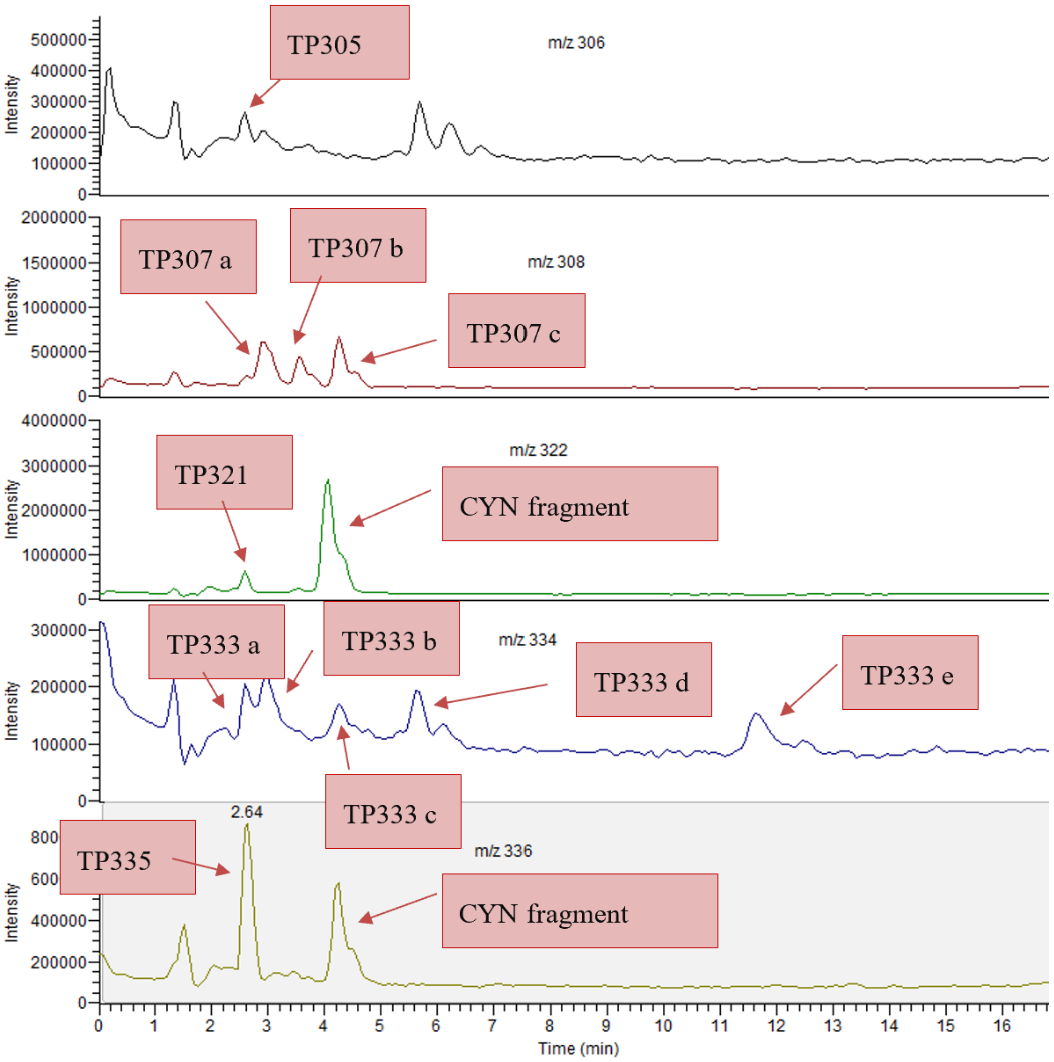
- Full MS chromatograms in different reaction times
- Peak picking: Selection of possible TP peaks not occuring in chromatogram of t_0
- Selection of main *m/z* from each unknown peak spectrum
- Check bibliography for unknown peak *m/z*
- Fragmentation MS/MS of *m/z*
- Structure elucidation

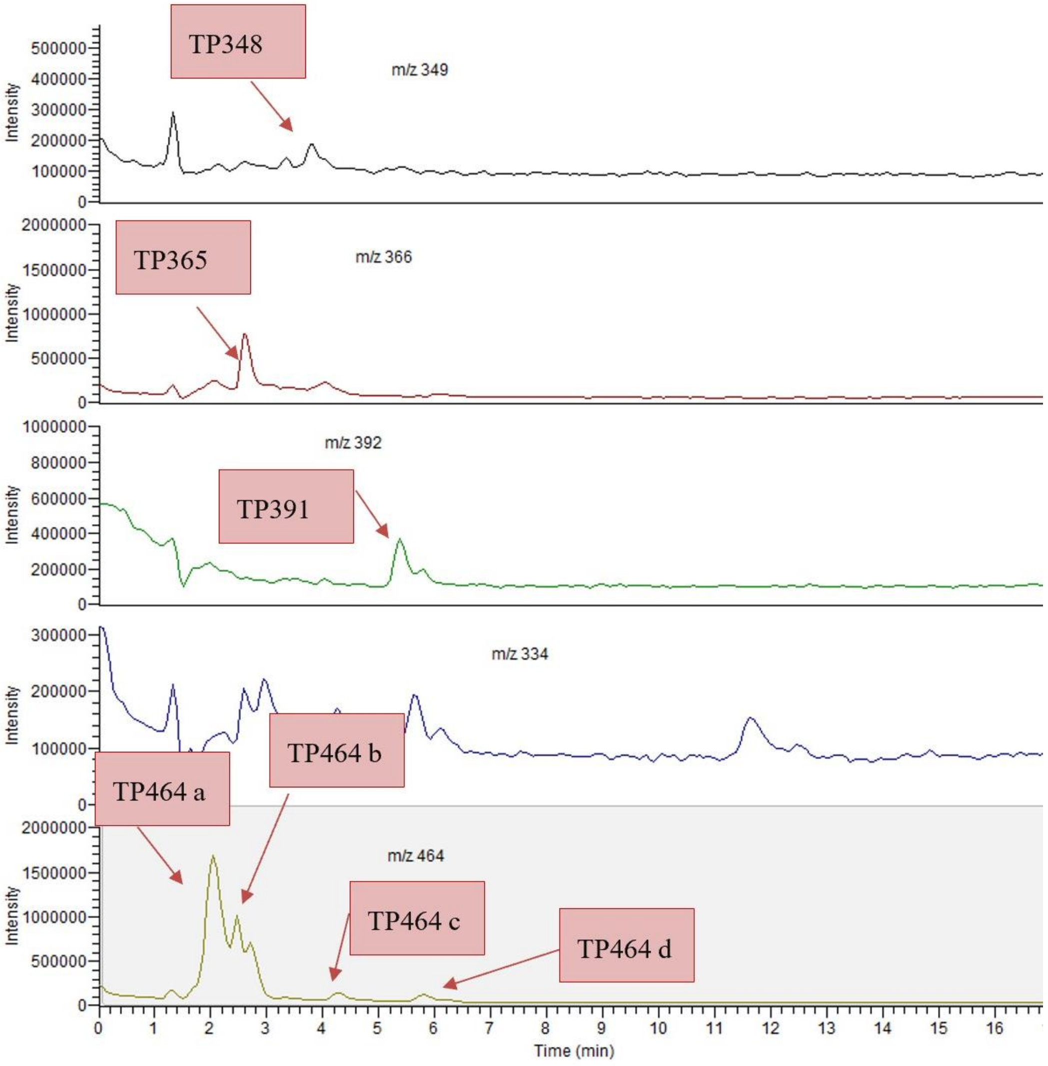
CYN Sonolysis

Reaction zones

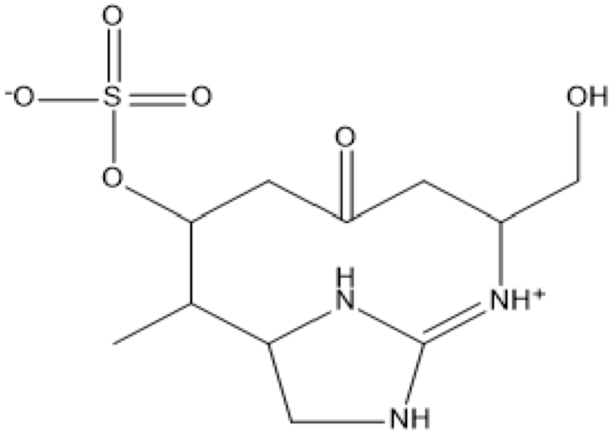


CYN Sonolysis
Reaction zones

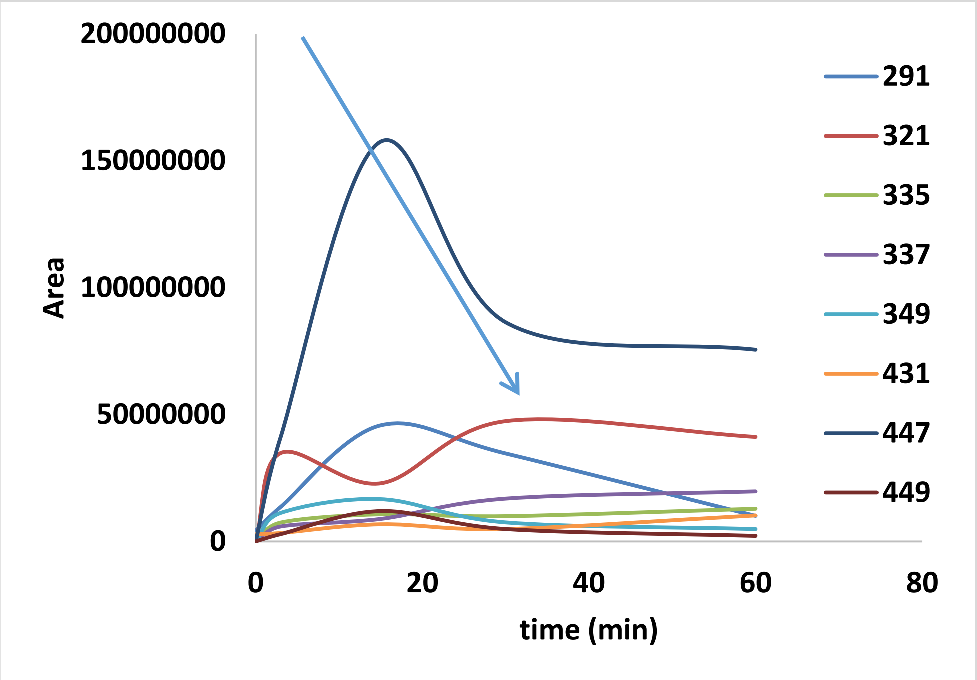




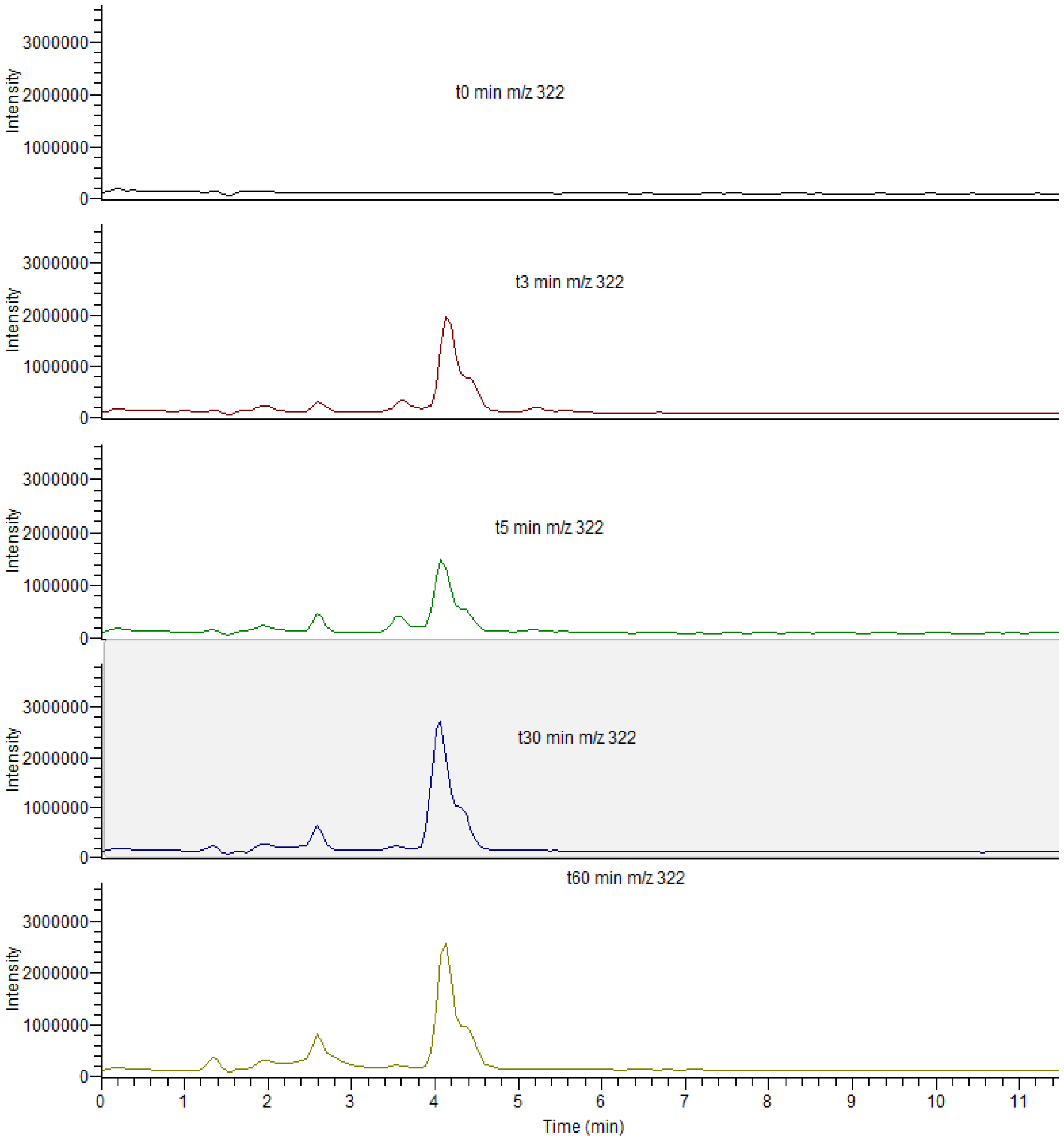
TP321



-O
S
O
O
O
O
OH
H
N
NH+
NH

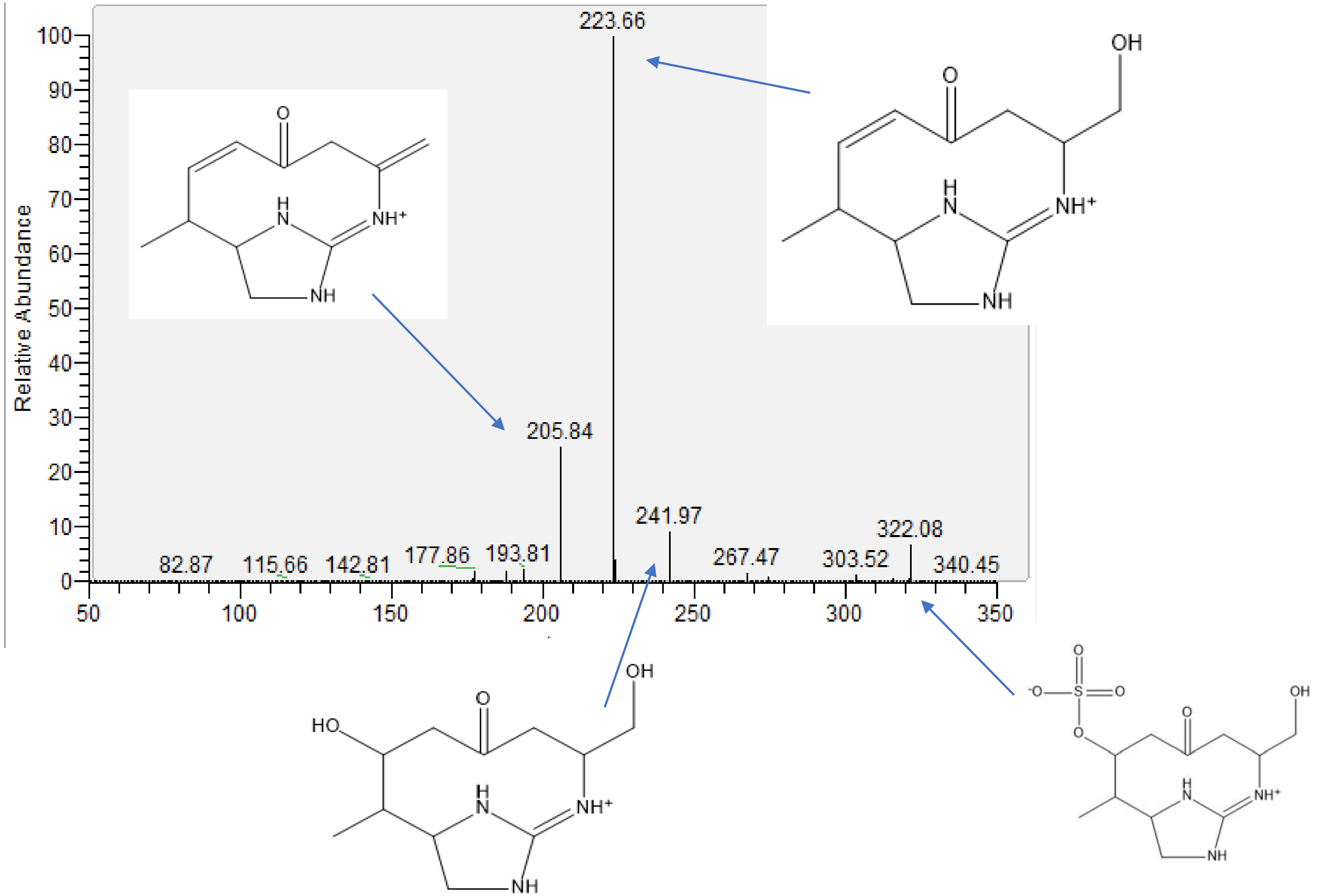


200000000
150000000
100000000
50000000
0
Area
0
20
40
60
80
time (min)
291
321
335
337
349
431
447
449

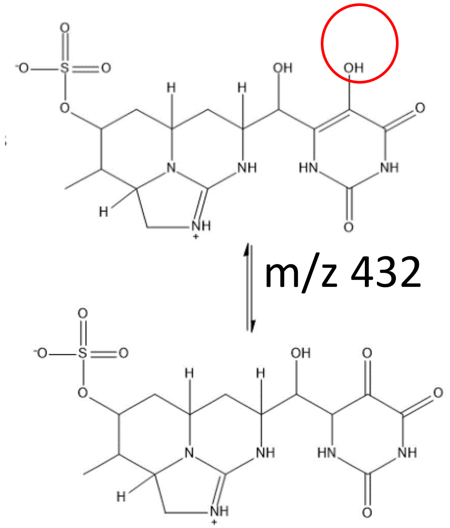


t0 min m/z 322
t3 min m/z 322
t5 min m/z 322
t30 min m/z 322
t60 min m/z 322
Intensity
3000000
2000000
1000000
0
0
1
2
3
4
5
6
7
8
9
10
11
Time (min)

MS/MS φάσμα του TP321

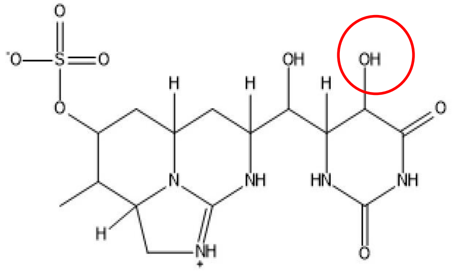


Hydroxylation



m/z 432

m/z 434



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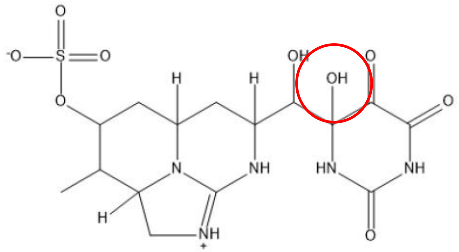

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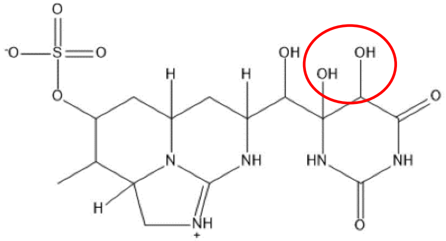
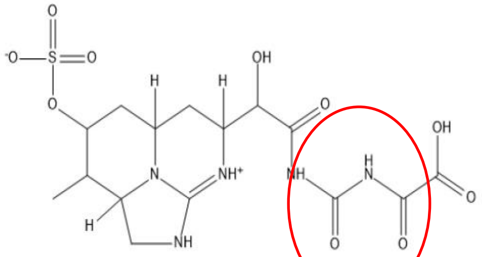


Ring D opening

m/z 464



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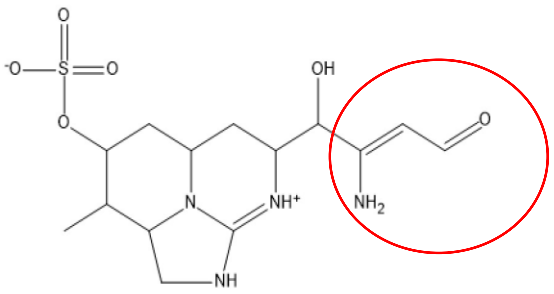
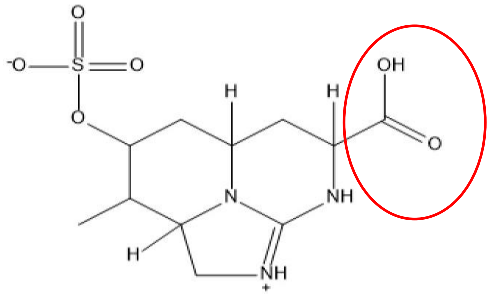
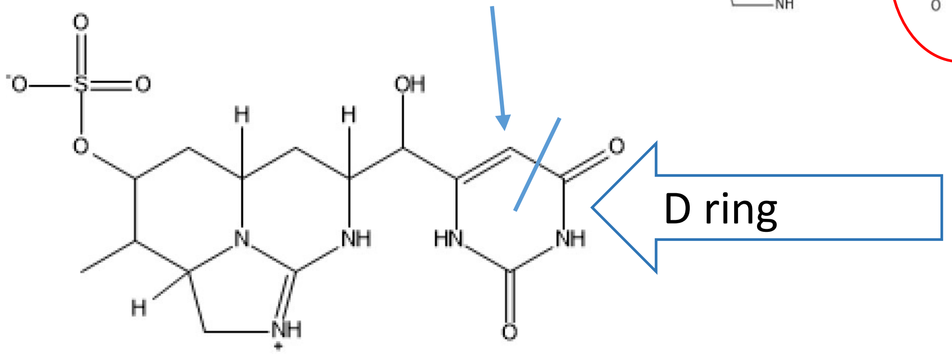


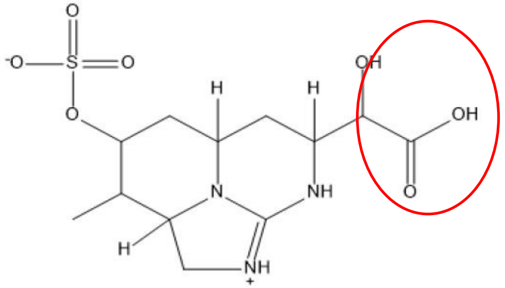
m/z 320





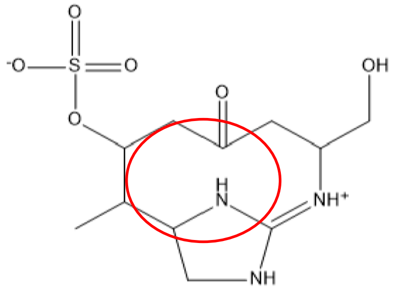
D ring

m/z 350

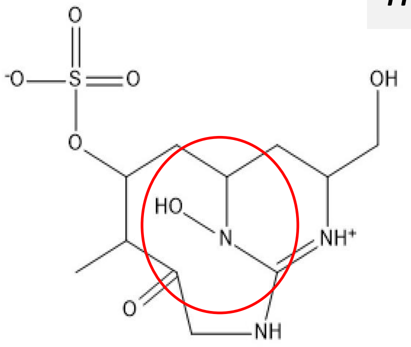


Ring D removal and tricyclic structure opening

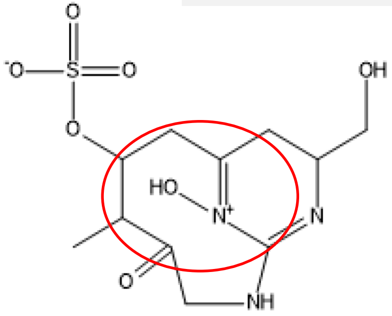
m/z 322



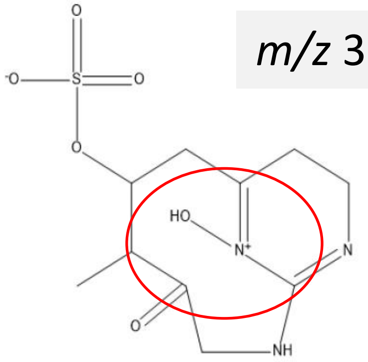
m/z 338

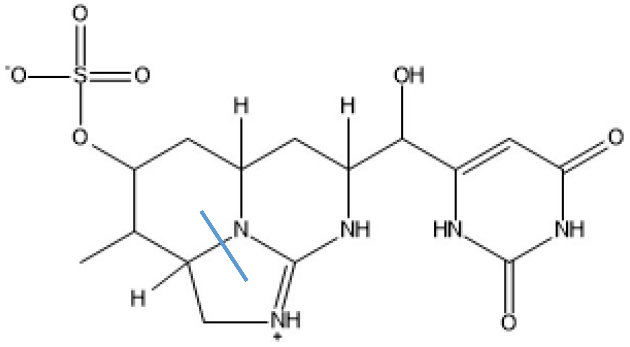


m/z 336



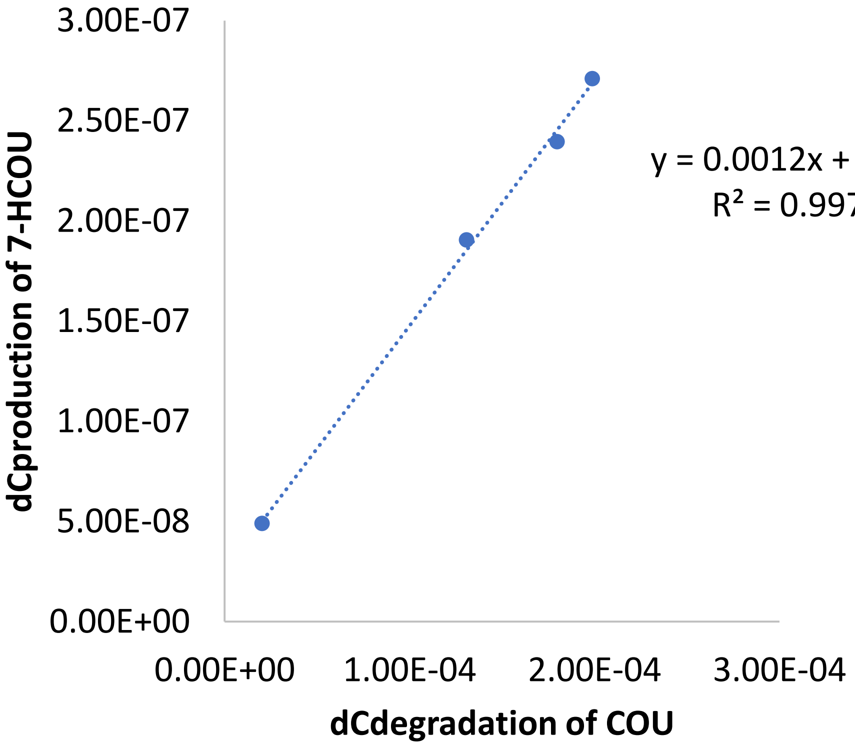
m/z 306





HO· quantitation problem

COU degradation vs 7-HCOU production



- 10 mL Coumarin solution 1mM
- 250 mL H_2O
- Intensity 100 % (110 W)
- 1 cm distance from the transducer

Under these specific conditions:

The ratio of 7-HCOU formed : COU degraded indicates that only ***1‰*** of the degraded COU turns to 7-HCOU.

Quantitation of HO•

The Problem

- COU reacts selectively with HO• and produces among others, 7-HCOU which can be fluorimetrically detected.
- They do not react 1:1
- We cannot quantitatively link 7-HCOU to the absolute concentration of HO•
- We need a calibration procedure to do that

The Solution

g-irradiation can produce HO• at an exact known rate. We use it as a tool to indirectly quantify HO• in sonolysis experiments

Manipulation of G irradiation in order to produce individual RS

G irradiation when applied to water produces several RS (i.e. e_{aq}^-, H· HO·)

Reaction of COU in the presence of different gasses/scavengers both in the G-Irradiation and the US system.

A steady state G radiolysis device ^{60}Co Gamma Chamber source was used.

G irradiation systems

- All Reactive species are produced
- Repeatable and steady production
- Manipulation of the RS produced
- Known yield

	G value (µmol of RS J^{-1})					
Prominent Reactive Species	**Experimental Conditions**					
	air	**N_2O**	**Deaerated/ TBA**	**Deaerated/ TBA pH 1**	**O_2**	**O_2/ HCOOH**
e_{aq}^-	***0.28***	0	***0.28***	0	0	0
$H^\bullet$	0.06	0.06	0.06	***0.34***	0	0
$HO^\bullet$	***0.28***	***0.56***	0	0	***0.28***	0
$O_2^{-\bullet}$ / $HO_2^\bullet$	0.0027	0.0027	0.0027	0.0027	***0.34***	***0.62***

Workflow of OH quantification

G- irradiation can be experimentally manipulated to produce certain RS at known yields (presence of air 0.28 µmol HO· J-1 L-1)

We monitored the formation of 7-HCOU with both sonolysis and steady-state gamma radiolysis.

G irradiation: We link the formation of 7-HCOU to the produced HO· through the known yield.

Ultrasonication: We back-calculate the produced HO· through the formation of 7-HCOU of the system.

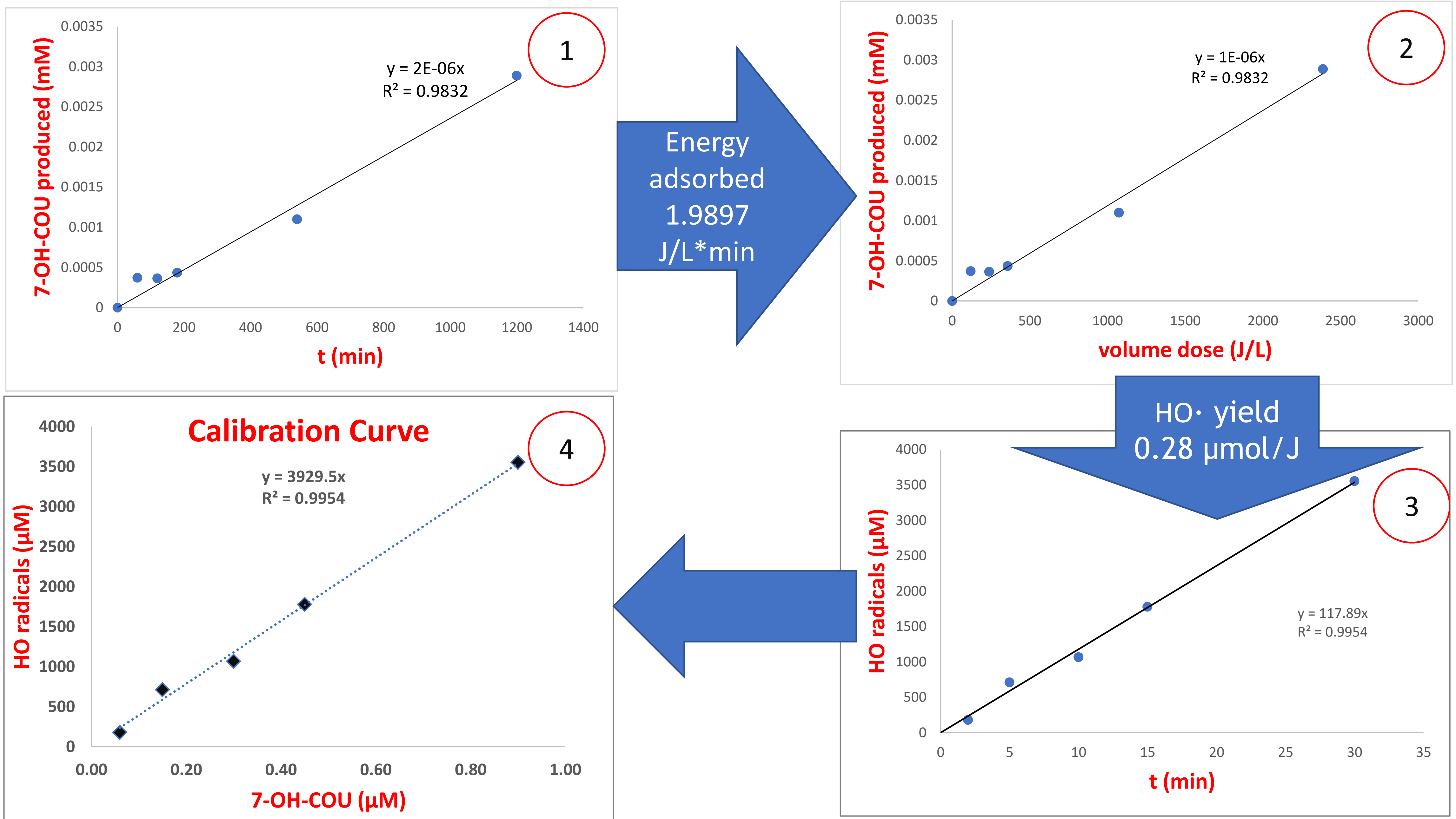
Basic Assumption

HO· react with the same stoichiometry with COU to produce 7-HCOU in both systems.

Proven

Other RS do not produce 7-HCOU

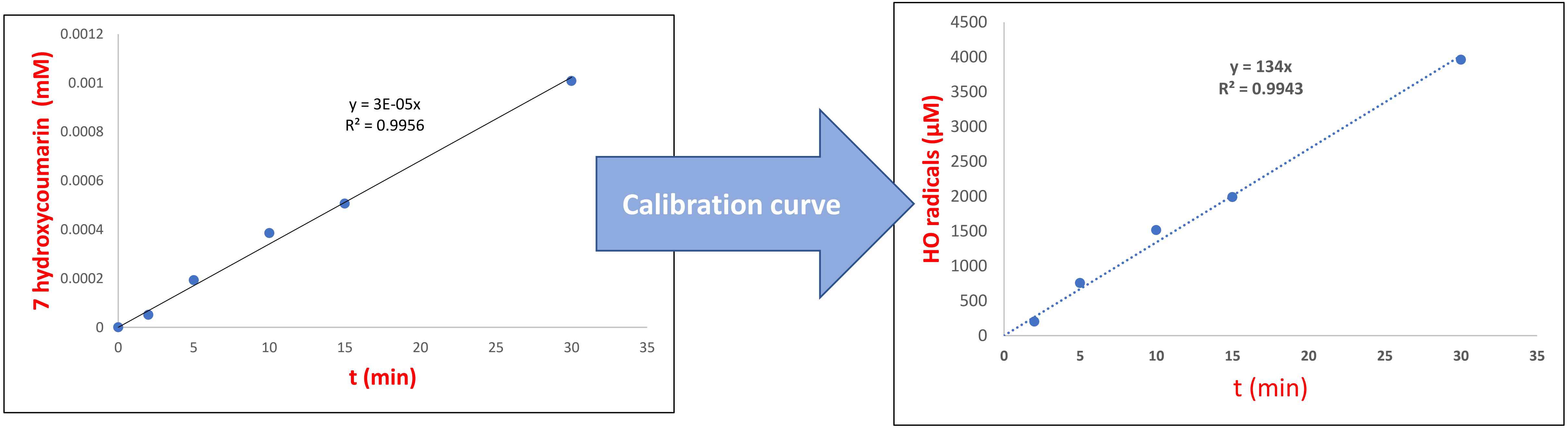
Workflow on G-irradiation system



Energy adsorbed 1.9897 J/L*min

HO· yield 0.28 µmol/J

Back calculation on US system



HO· production rate is 134 µM HO·/min = 2.23 µM HO·/s

For CYN degradation [CYN]/[HO·]= 0.0033/2.23 = 0.0015

Approximately 675 mol of HO· are used during the degradation of 1 mol CYN

The road to the future

combined / hybrid treatment techniques with other AOPs

- **ultrasound with UV photolysis (photosonolysis)** - considerable advantage by the formation of excess HO• upon photolysis of ultrasound-induced H_2O_2
- **sonophotocatalysis**, where sonolysis is combined with the application of UV irradiation in the presence of a photocatalyst. The results is a significant increase in the degradation efficiency of target pollutants due to the generation of enhanced HO• quantities [, since TiO_2 particles provide extra nuclei for cavitation bubble formation
- **ultrasound coupled with homogenous Fenton** (Fe^{2+}/H_2O_2). The resulting Fe^{3+} can react with H_2O_2 to generate an intermediate complex ($Fe–O_2H^{2+}$) which further dissociates into Fe^{2+} and under US irradiation. The isolated Fe^{2+} further reacts with H_2O_2 to produce HO• and the cycle continues.
- **Ultrasound coupled with heterogeous Fenton** ($Fe^0 + H_2O_2$) enhances iron corrosion in acid media (Fe^0 to Fe^{2+}) and the subsequent formation of increased HO• quantities, which are aided by the extra nuclei (iron particles) for cavitation bubble formation
- **Sonochemistry and persulfate or peroxymonosulfate** (sono sulfate) promote the formation of sulfate radical ($SO_4^{\bullet -}$), ($E^0 = 2.6$ V) which is able to degrade refractory substances through HO• (e.g., perfluoroalkyl compounds and cyanuric acid). Thus, the presence of radical $SO_4^{\bullet -}$, in addition to HO•, significantly increases the pollutants' degradation.

Thank you for the kind attention

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Refs in
https://www.dropbox.com/sh/yzm7zjyztesm5va/AACOQM1Z3Z_T5hVuZA_kNs_aa?dl=0