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Paracetamol degradation in water by non-thermal plasma and heterogeneous catalysis coupling

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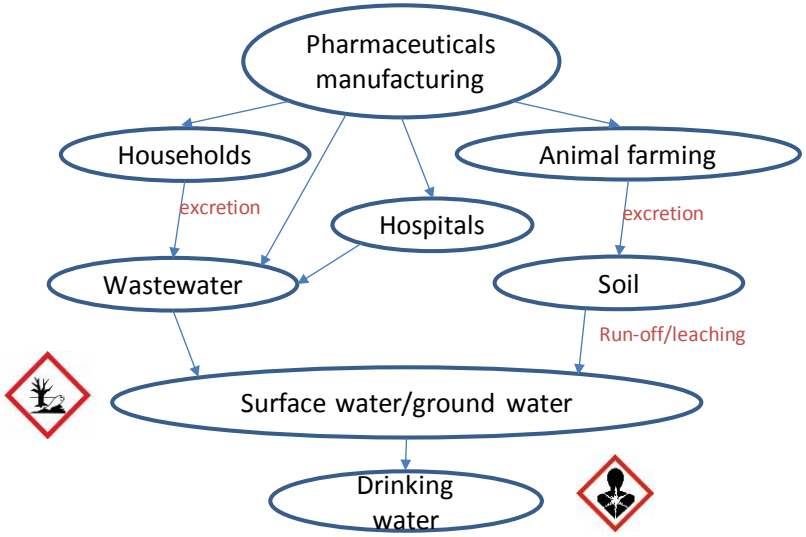
Introduction

Presence of **pharmaceutical molecules** in rivers, lakes… and **water tap**.

conventional wastewater plants are not efficient

Pharmaceutical drugs are a serious problem for environmental and for Human health

Emitting points of pharmaceutical compounds in environment



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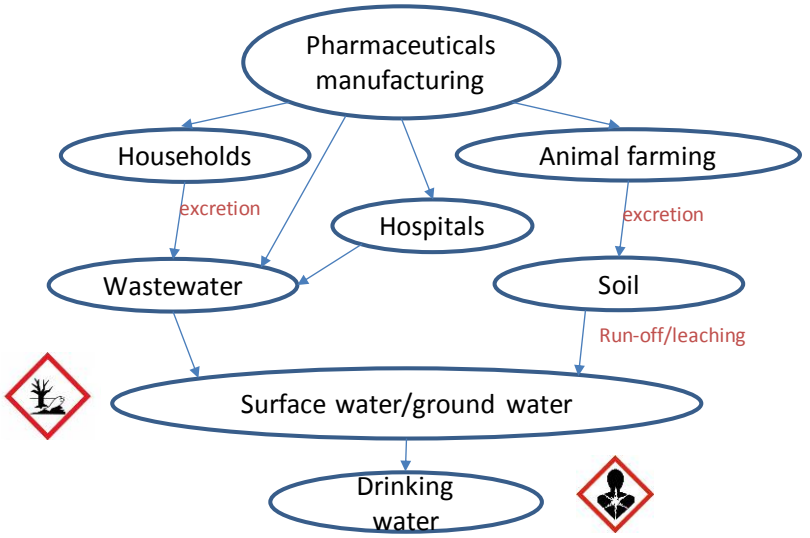
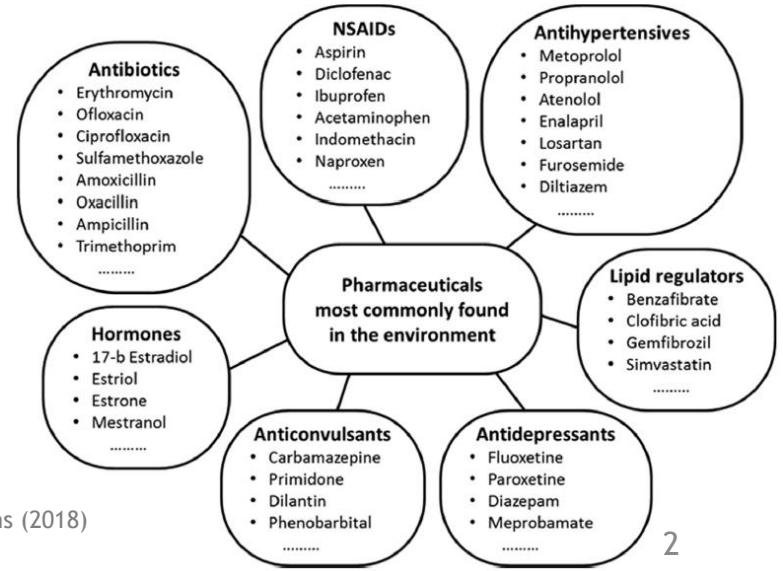


A lot of pharmaceutical molecules!



Magureanu et al. Water Research, 81, 124, 2015

Introduction

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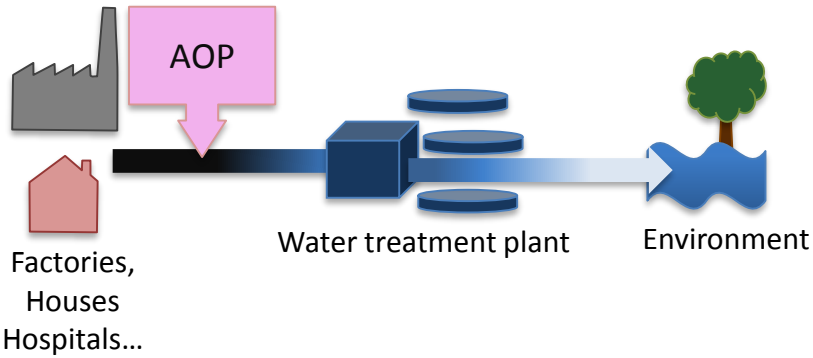
Pharmaceutical drugs are a serious problem for environmental and for Human health

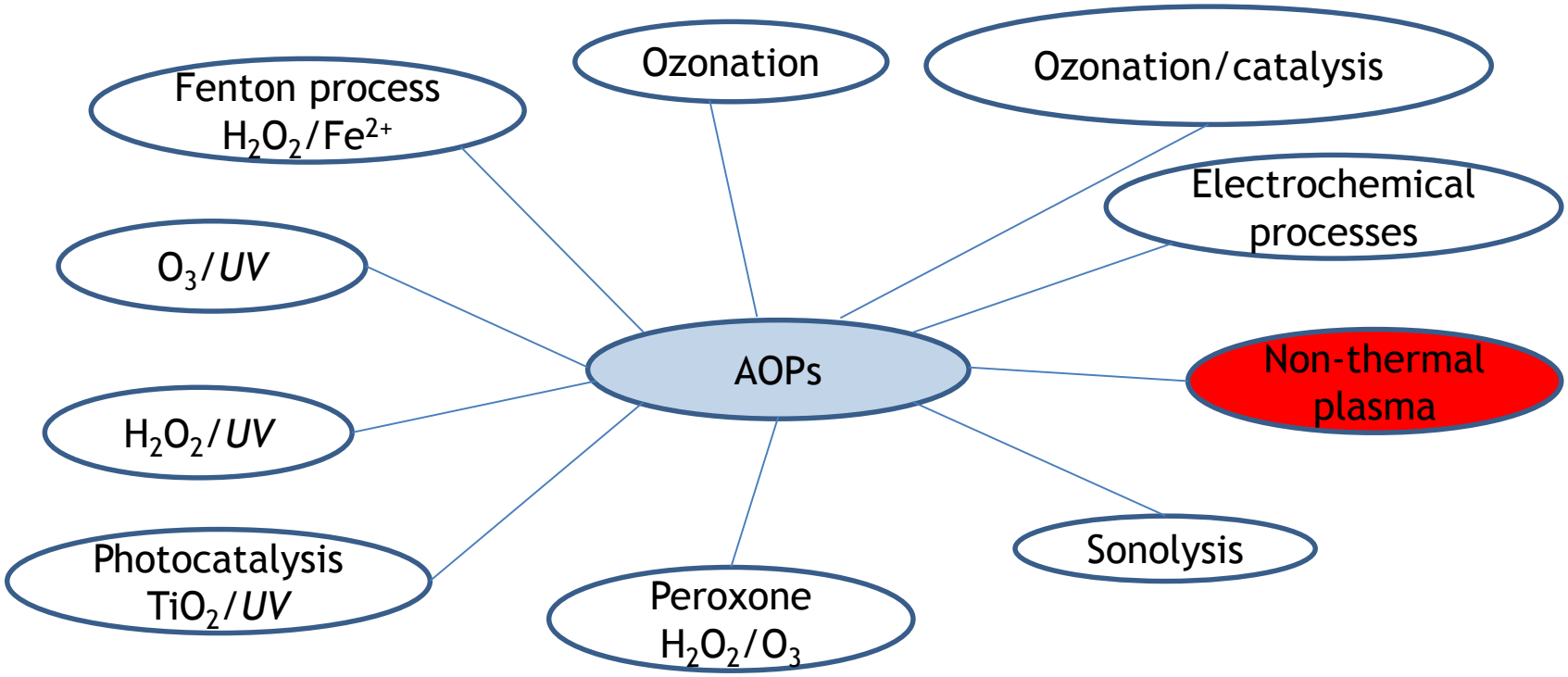
Develop innovative treatment processes at the upstream of the wastewater treatments

Advanced Oxidative Processes to produce oxidative species ($OH^{\bullet}$, $O^{\bullet}$, O_3, H_2O_2…) which can react with pharmaceutical molecules



Advanced Oxidative Processes

Non Thermal plasma = combination of Advanced Oxidative Processes to produce $OH^{\bullet}$, $O^{\bullet}$, O_3, H_2O_2…



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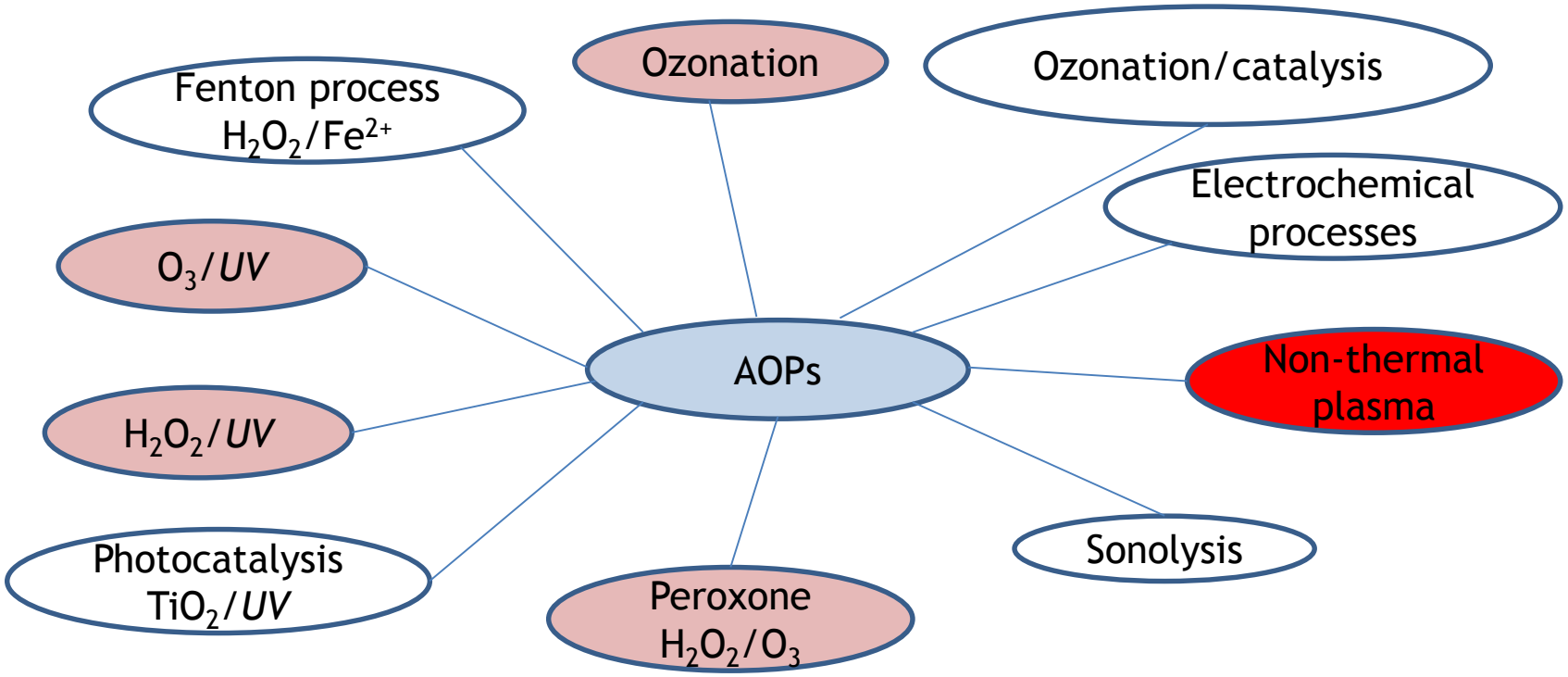
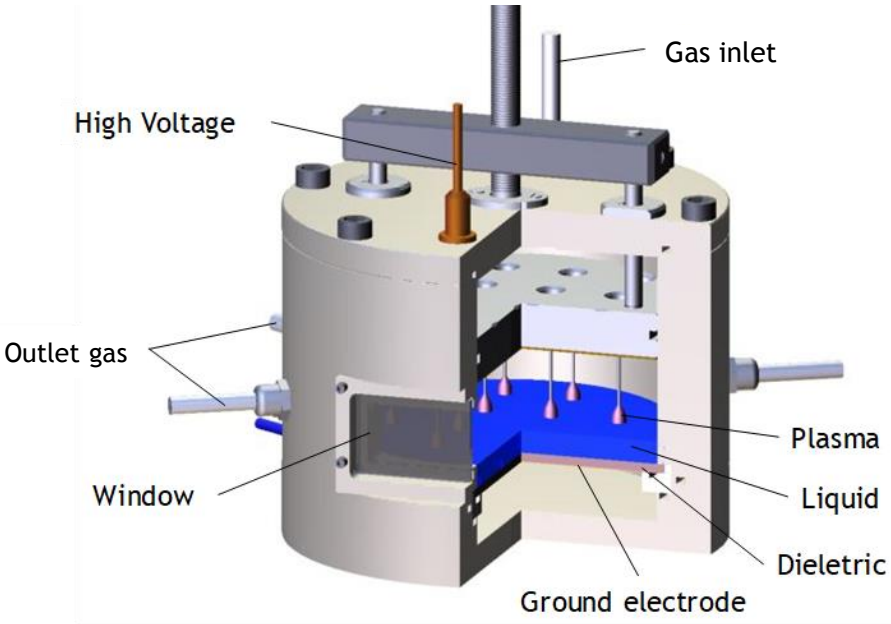


Various NTP configurations:
- post-discharge treatment = ozonation (reaction with long life-time species)
- *in-situ* treatement (direct contact between liquid and the discharge)

➔ effects of short life-time reactive species ($OH^{\bullet}$, $O^{\bullet}$…)

Experimental set-up: Plasma reactor

Direct liquid-discharge contact treatement:
DBD reactor with a multiple needles-to-plate

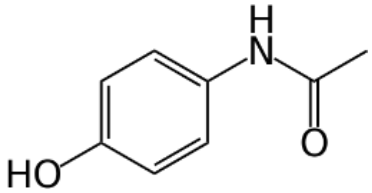


Electrical parameters:
AC high voltage, square waveform
500 Hz

Distance between the tip of the needles and the surface of the liquid : 5 mm

Gas: air, Ar+O_2, Ar+air, Ar, N_2...
Gas flow rate: 100 sccm

[paracetamol] = 25 mg.L^{-1} in pure water



$C_8H_9NO_2$ - M=151 g/mol

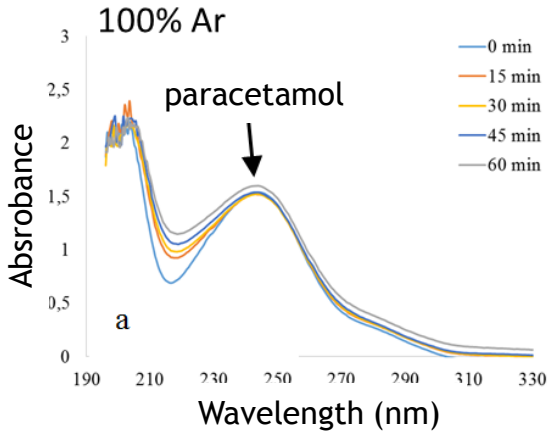
Liquid volume treated = 40 mL
Liquid height: 4 mm

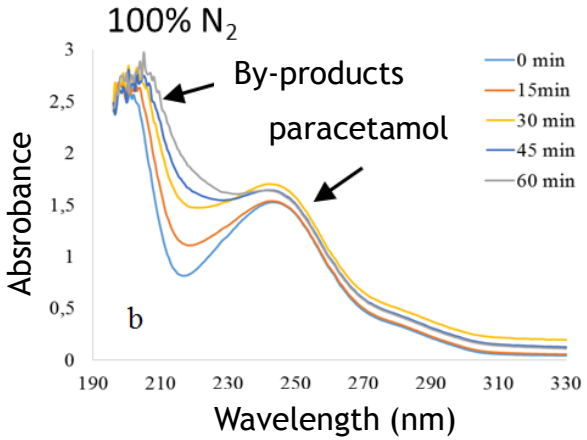
Paracetamol degradation by plasma alone: effects of the input gas

Paracetamol degradation by plasma alone: effects of the input gas

Paracetamol degradation can be followed by Absorption spectroscopy

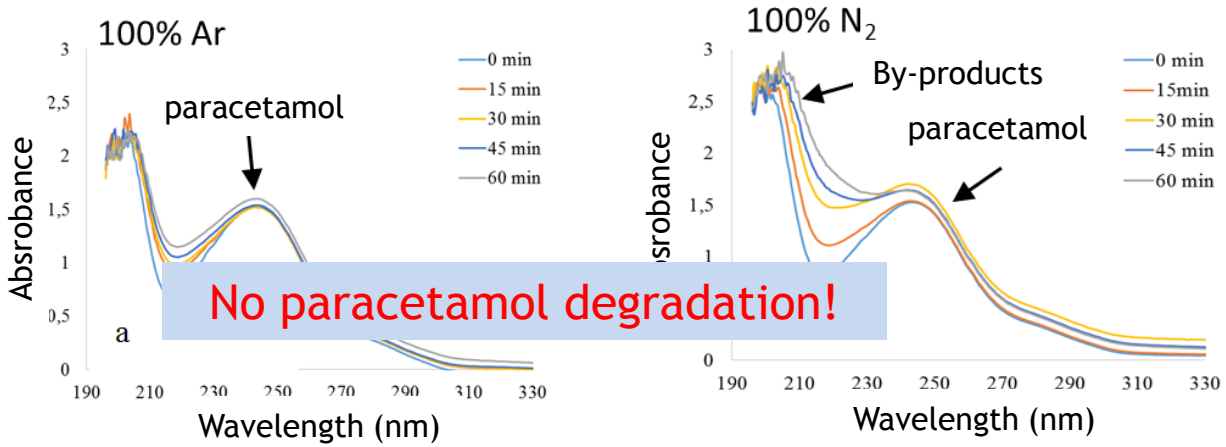
In pure Ar or N_2





Paracetamol degradation by plasma alone: effects of the input gas

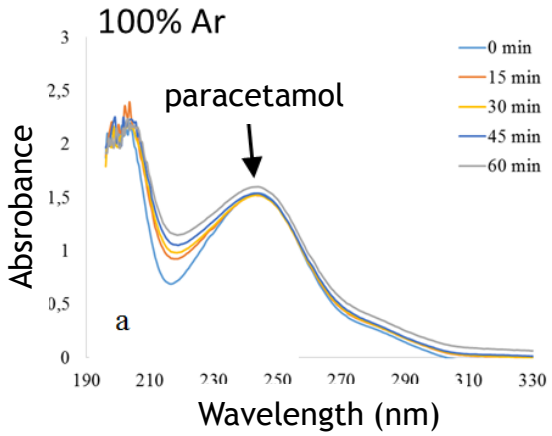
In pure Ar or N_2

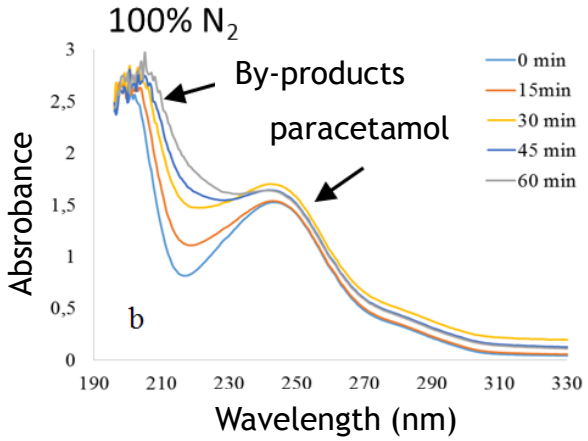


No paracetamol degradation!

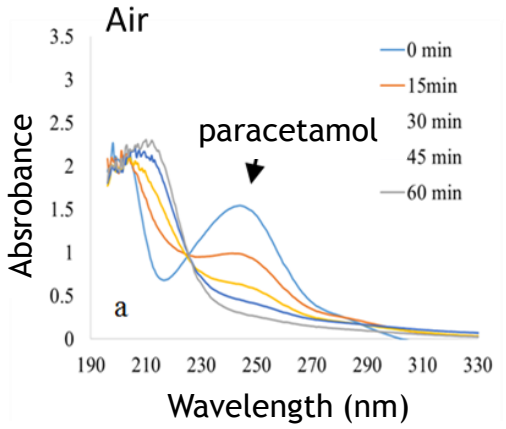
Paracetamol degradation by plasma alone: effects of the input gas

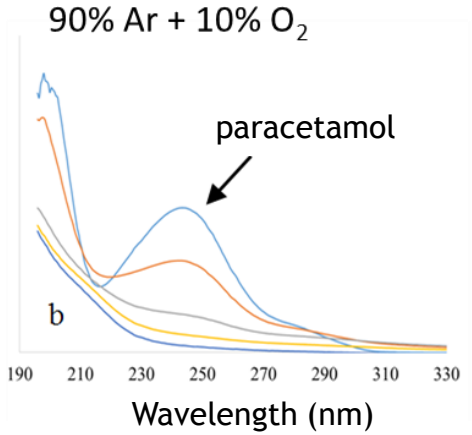
In pure Ar or N_2

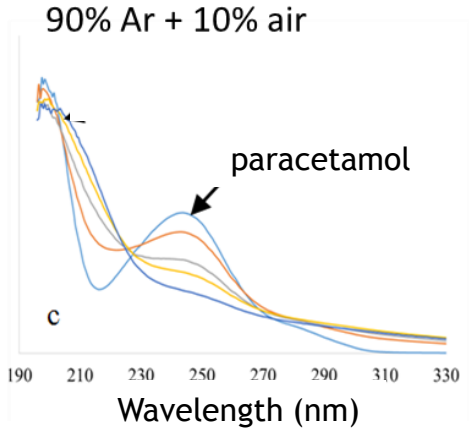




In O_2 mixture gases

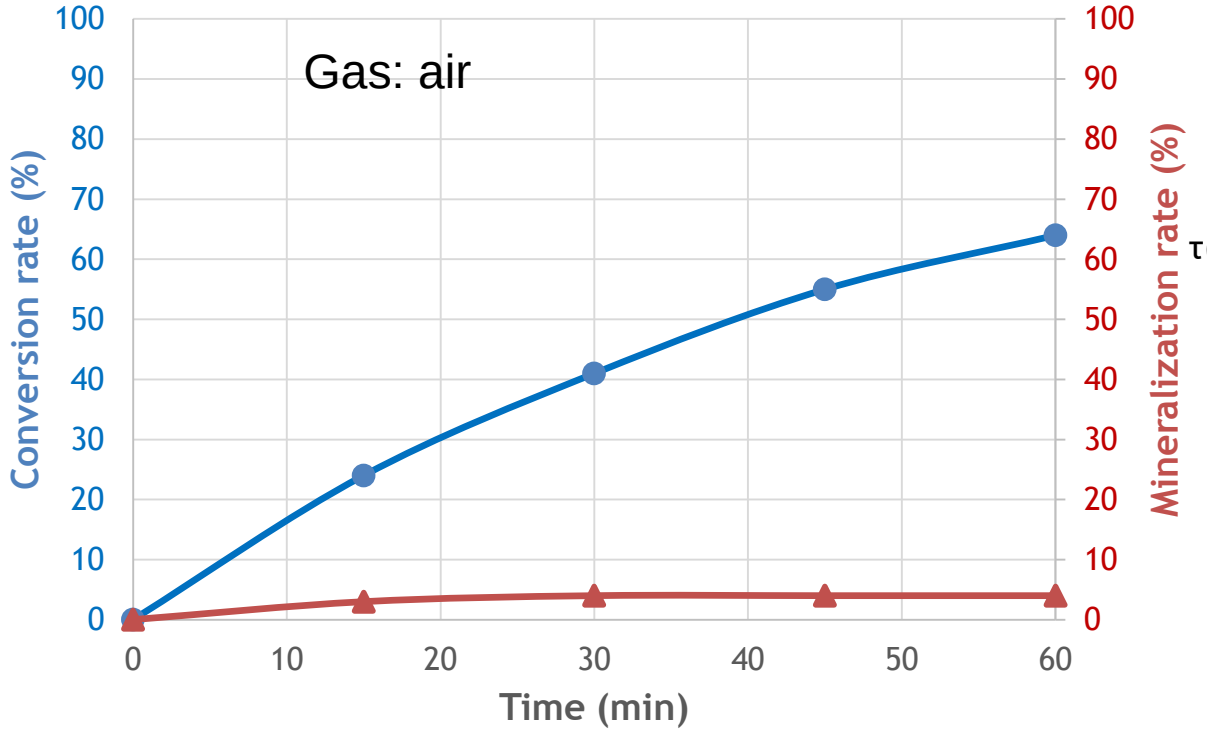






Degradation of paracetamol is observed only with oxydative gas

Paracetamol degradation by plasma alone: conversion & mineralization rates



Operating conditions:
Plasma: 500 Hz, 11.2 kV
[para] = 25 mg.L^{-1}
$V_{treated}$ = 40 mL

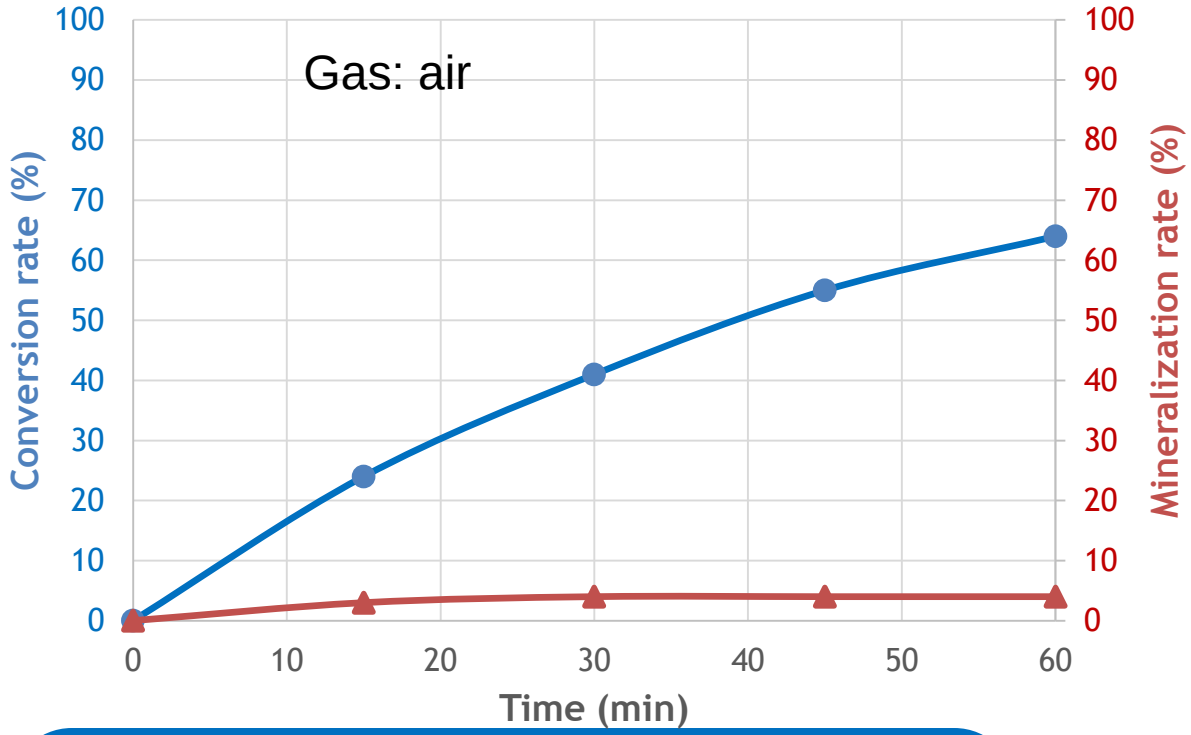
Conversion rate

$$\tau(\%)=\frac{[\text{paracetamol}]_0-[\text{paracetamol}]_t}{t}\times 100$$

Mineralization rate
TOC: total organic carbon

$$\text{mineralization}(\%)=\frac{[TOC]_0-[TOC]_t}{t}\times 100$$

Paracetamol degradation by plasma alone: conversion & mineralization rates



Operating conditions:
Plasma: 500 Hz, 11.2 kV
[para] = 25 $mg.L^{-1}$
$V_{treated}$ = 40 mL

Conversion rate still be low
A low mineralization to CO_2

HRMS analyses ➔ Organic molecules (carobxylic acids, aromatics…) [1,2]

Similar results with $Ar+O_2$ and Ar+air

Effects of the plasma-catalysis coupling on conversion, mieralization and produced species?

[1] Y. Baloul, O. Aubry, *et al*. Eur. Phys. J. Appl. Phys. (2017) 79: 30802.
[2] Y. Baloul, H. Rabat, *et al*. Int. J. of Plasma Environmental Science & Technology (2016) 10(2)

Plasma-catalysis coupling

Catalysts coupled to plasma in litteratures

Homogenous Fenton catalysts [3,4]

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

Activated carbons [5,6]

$O_3 + CA\text{-}OH \rightarrow OH^\bullet + CA\text{-}O_2^\bullet$

$AC + H_2O_2 \rightarrow OH^\bullet + OH^- + AC^-$

Photocatalyst TiO_2 [7,8]

$TiO_2 + hv \rightarrow e^- + h^+$

$h^+ + H_2O \rightarrow OH^\bullet + H^+$

→ **Oxides based catalysts**

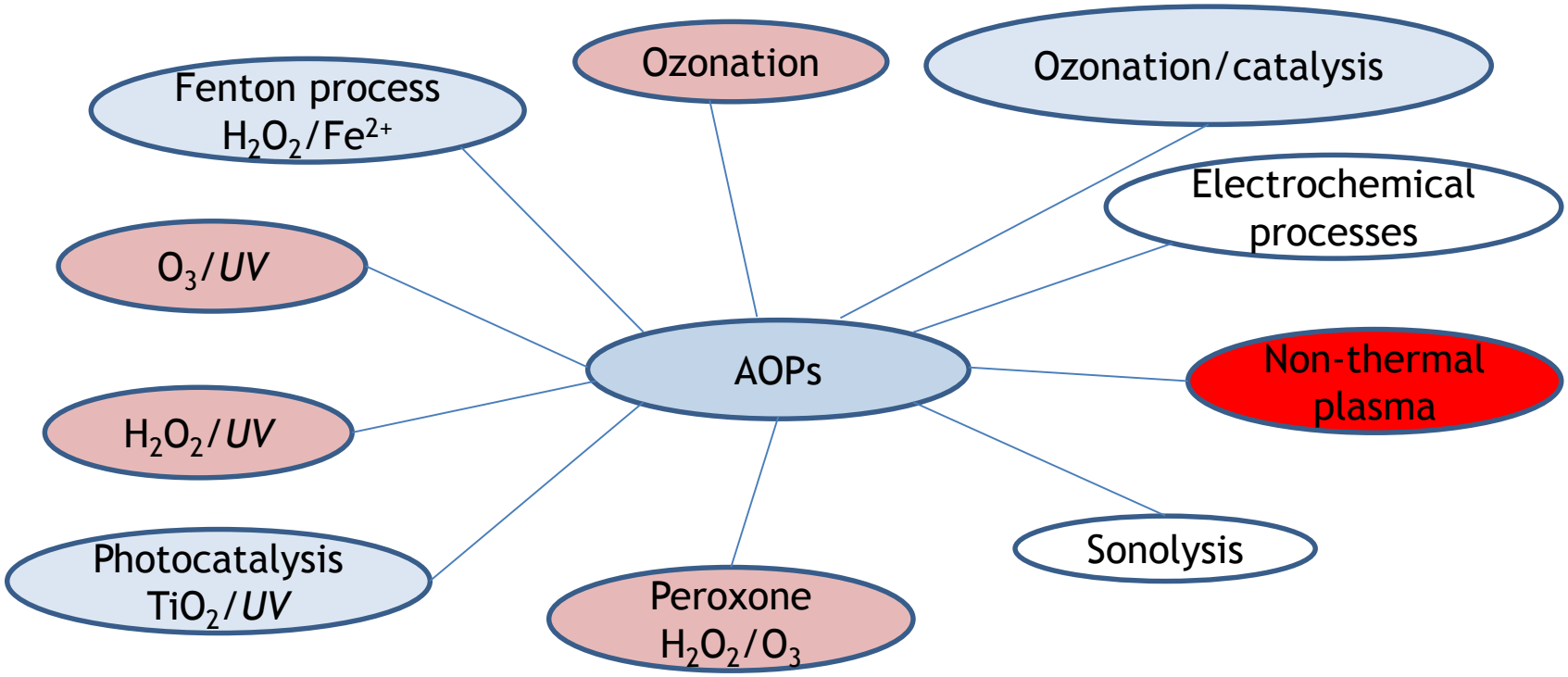
Fenton like catalysts

Ozone decomposition

[3] X. Hao, M. Zhou, Q. Xin, L. Lei, Chemosphere 66 (2007) 2185–2192.
[4] Y. Shen, L. Lei, X. Zhang, M. Zhou, Y. Zhang, J. Hazard. Mater. 150 (2008) 713–722.
[5] D.R. Grymonpré, W.C. Finney, B.R. Locke, Chem. Eng. Sci. 54 (1999) 3095–3105.
[6] N. Lu, J. Li, X. Wang, T. Wang, Y. Wu, Plasma Chem. Plasma Process. 32 (2012) 109–121.
[7] H.J. Wang, X.J. Chen, J. Hazard. Mater. 186 (2011) 1888–1892.
[8] K. Marouf-Khelifa, F. Abdelmalek, A. Khelifa, A. Addou, Chemosphere 70 (2008) 1995–2001.

Plasma-catalysis coupling

Non Thermal plasma + catalysts = combination of Advanced Oxidative Processes

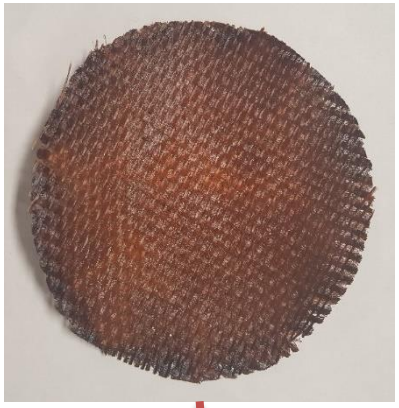


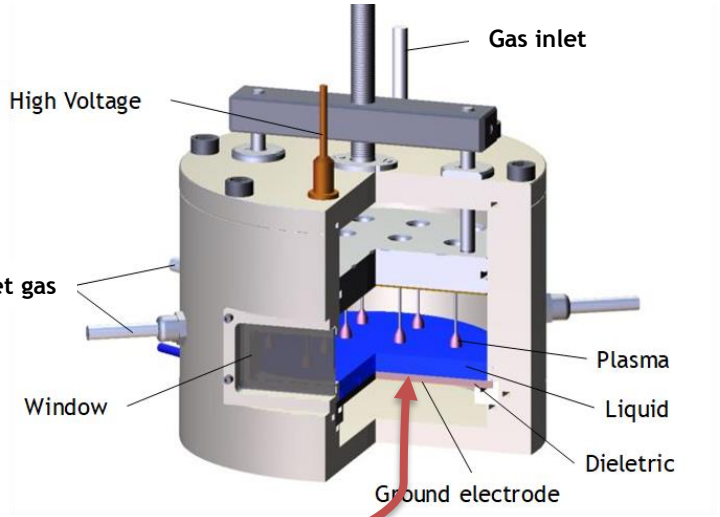
Plasma-catalysis coupling: nature of the studied catalysts

Home-made catalysts:

oxides supported on Glass Fiber fabric (GF), washcoat of alumina realized before oxide deposition and oxide deposited by the incipient wetness method

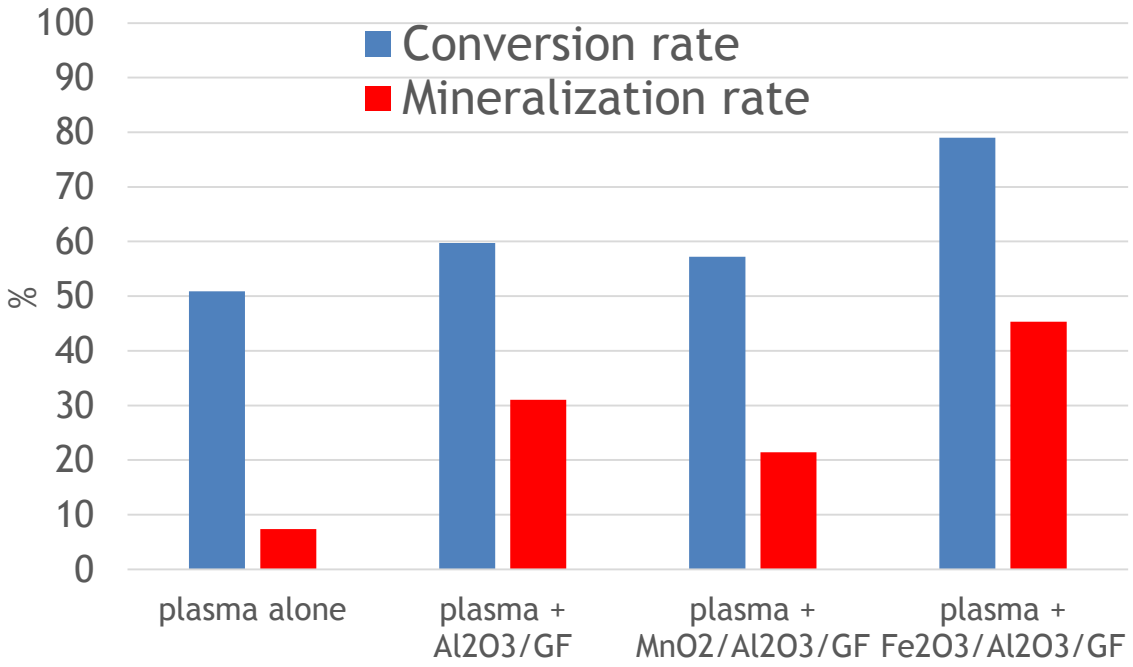
Al_2O_3/GF	MnO_2/Al_2O_3/GF	Fe_2O_3/Al_2O_3/GF
47 m^2/g	45 m^2/g	57 m^2/g





Effects of the plasma-catalysis coupling: conversion and mineralization

Operating conditions:
Plasma: 500 Hz, 11.2 kV
[para] = 25 mg.L^{-1}
$V_{treated}$ = 40 mL
Treatment duration : 30 min



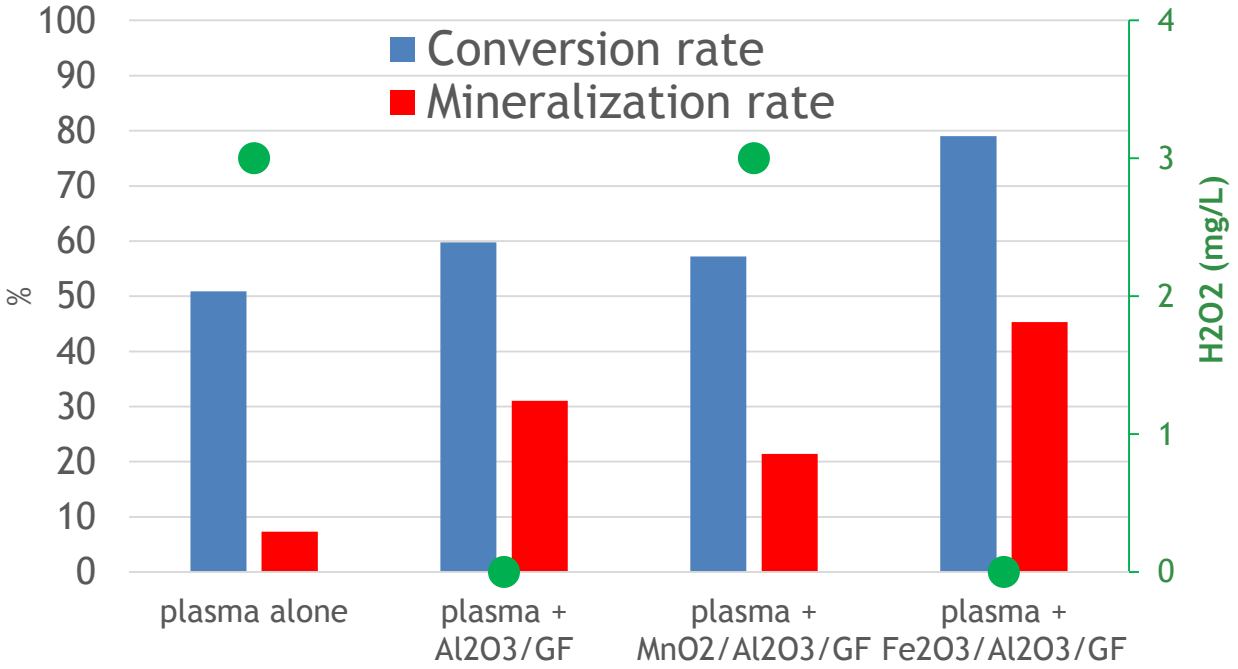
➔ Improvement of the conversion and mineralization rates with the plasma catalyst coupling

➔ No degradation of paracetamol with catalysts alone

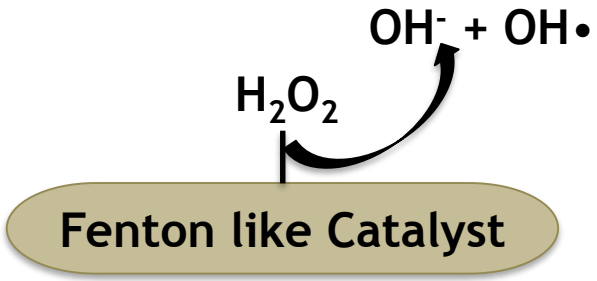
Best results obtained with $Fe_2O_3/Al_2O_3/GF$

Effects of the plasma-catalysis coupling: [H_2O_2]

Operating conditions:
Plasma: 500 Hz, 11.2 kV
[para] = 25 mg.L^{-1}
$V_{treated}$ = 40 mL
Treatment duration : 30 min



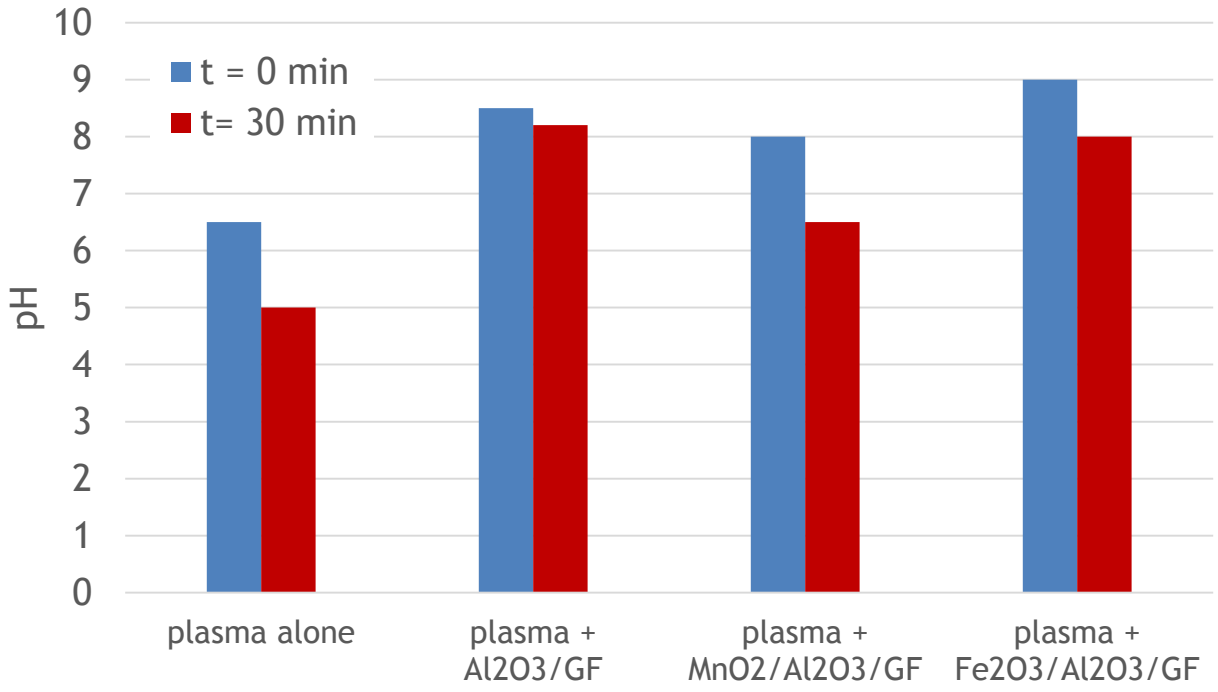
H_2O_2 limit detection: 1mg.L^{-1}



A better use of H_2O_2 with Al_2O_3/GF and Fe_2O_3/Al_2O_3/GF

Effects of the plasma-catalysis coupling: pH

Operating conditions:
Plasma: 500 Hz, 11.2 kV
[para] = 25 mg.L^{-1}
$V_{treated}$ = 40 mL
Treatment duration : 30 min



Final conductivity (µS.cm^{-1})
Plasma alone: 37
Plasma + Al2O3/GF: 227
Plasma + MnO2/Al2O3/GF: 192
Plasma + Fe2O3/Al2O3/GF: 196

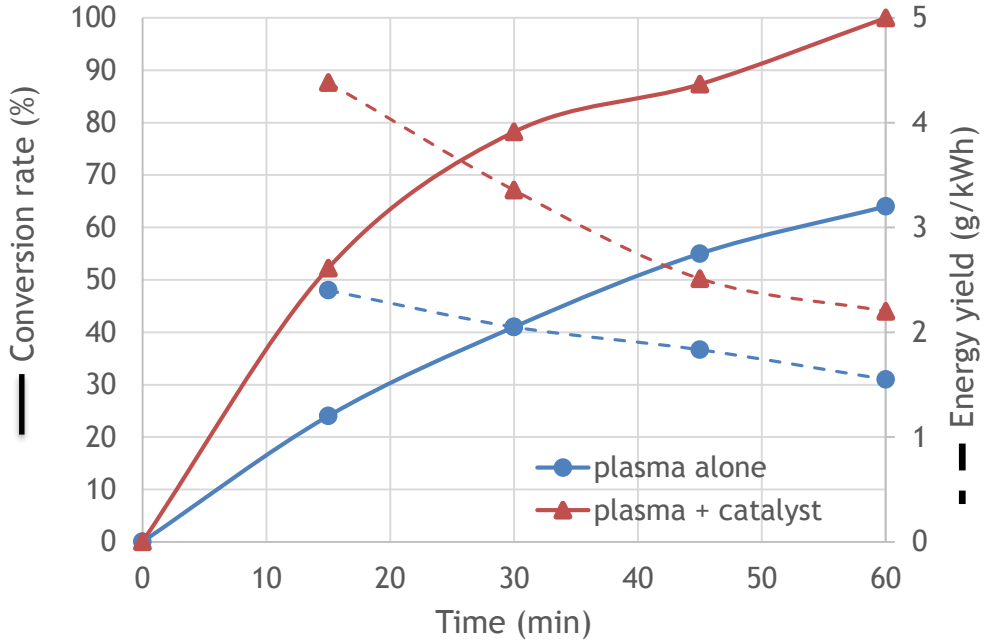
formation of nitrates and carboxilic acids (observed by HRMS analysis) ➔ decrease of the pH

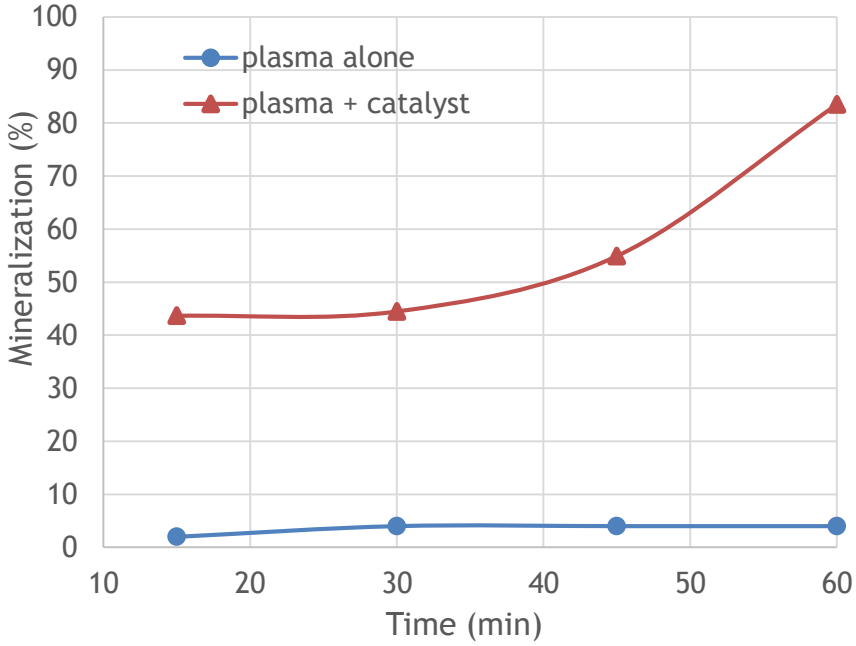
With catalysts, $pH_{plasma+catalysts} > pH_{plasma\ alone}$: high mineralization and less produced acids

Plasma alone *vs.* Plasma-catalysis coupling

Operating conditions:
Plasma: 500 Hz, 11.2 kV
[para] = 25 mg.L^{-1}
$V_{treated}$ = 40 mL

Catalyst : Fe_2O_3/Al_2O_3/GF





With plasma+catalyst: Improvement of the efficiency of the treatment

total conversion and mineralization rate of 84 % (after 1h of treatment)

Increase of the Energy yield higher

From 45 min, organic by-products degradation (observed by HRMS analysis)

Conclusion

- The **presence of the heterogeneous catalyst coupled to the plasma** significantly improves the paracetamol degradation compared to plasma alone

- The **influence of the nature oxide of the catalyst** was studied

  better results obtained with $Fe_2O_3/Al_2O_3/GF$ in terms of **conversion and mineralization rates and energy yields**

  after 1h of treatment with $Fe_2O_3/Al_2O_3/GF$, total conversion and mineralization rate of 84 %

Perspectives

To develop and characterize the home-made catalysts

To develop a plasma/catalyst reactor to treat liquids with flowing

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for catalysts characterization

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Thanks for your attention