Promising research results on a few potential applications of non-thermal plasma

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- **Plasma treatment of wastewater**
    - degradation of organic compounds in water – ANTIBIOTICS

- **Plasma agriculture**
    - treatment of seeds for productivity enhancement – SUNFLOWER

- **Plasma processing of materials**
    - functionalization for catalytic activity improvement – GRAPHENE OXIDE

- **Plasma synthesis of materials**
    - production of nanoparticles from liquid precursors – Au NANOPARTICLES

Degradation of antibiotic pollutants in water by non-thermal plasma

➢ Antibiotics – contaminants of emerging concern (CEC)

- High consumption, inefficient degradation → contamination
- Negative effects on aquatic and terrestrial species
- Antimicrobial resistance

➢ Antibiotics degradation by non-thermal plasma – literature results

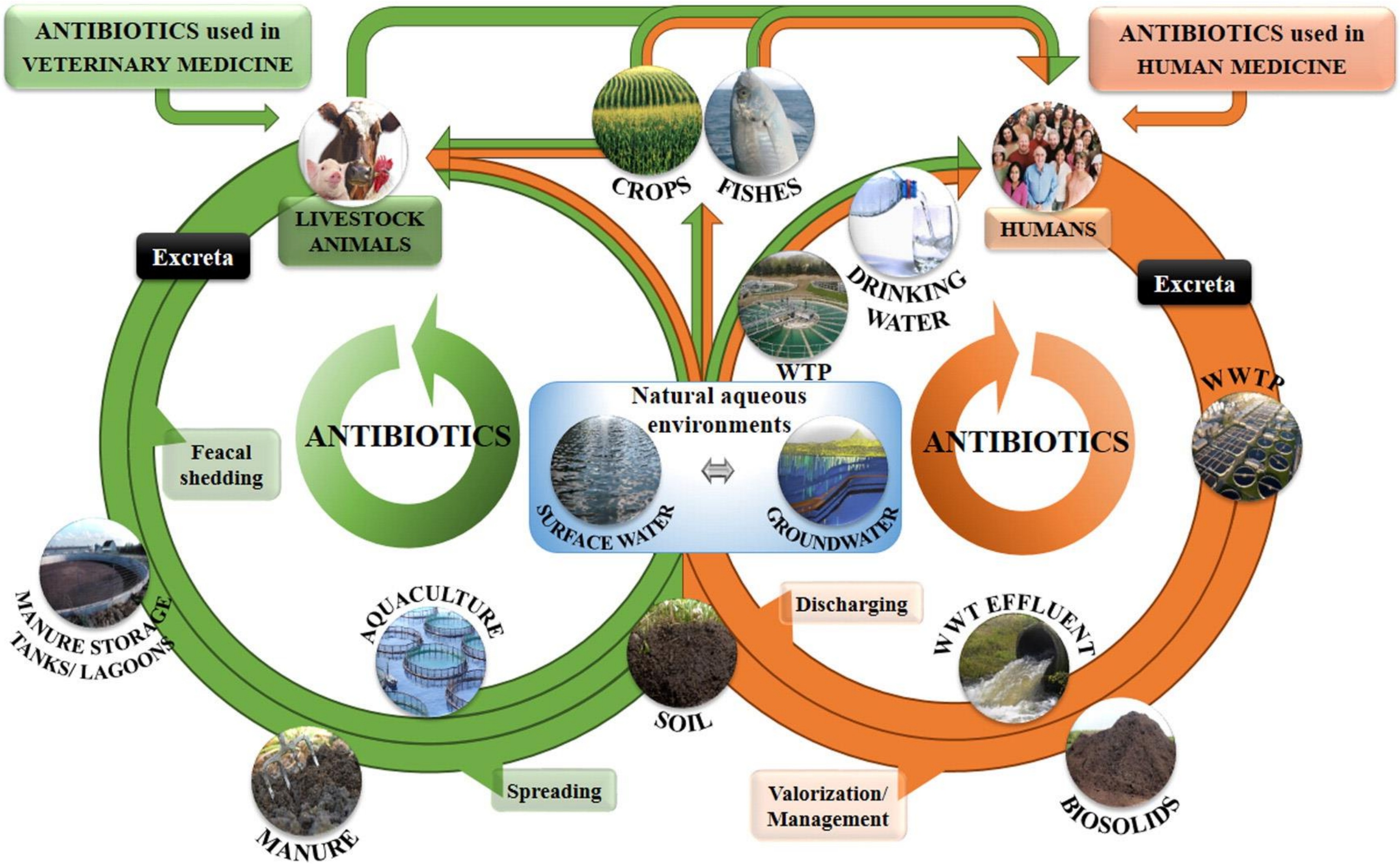
- Plasma reactor configurations and operating conditions
- Mechanisms of antibiotics degradation by non-thermal plasma

Sources of antibiotics

Main sources: Human and veterinary medicine

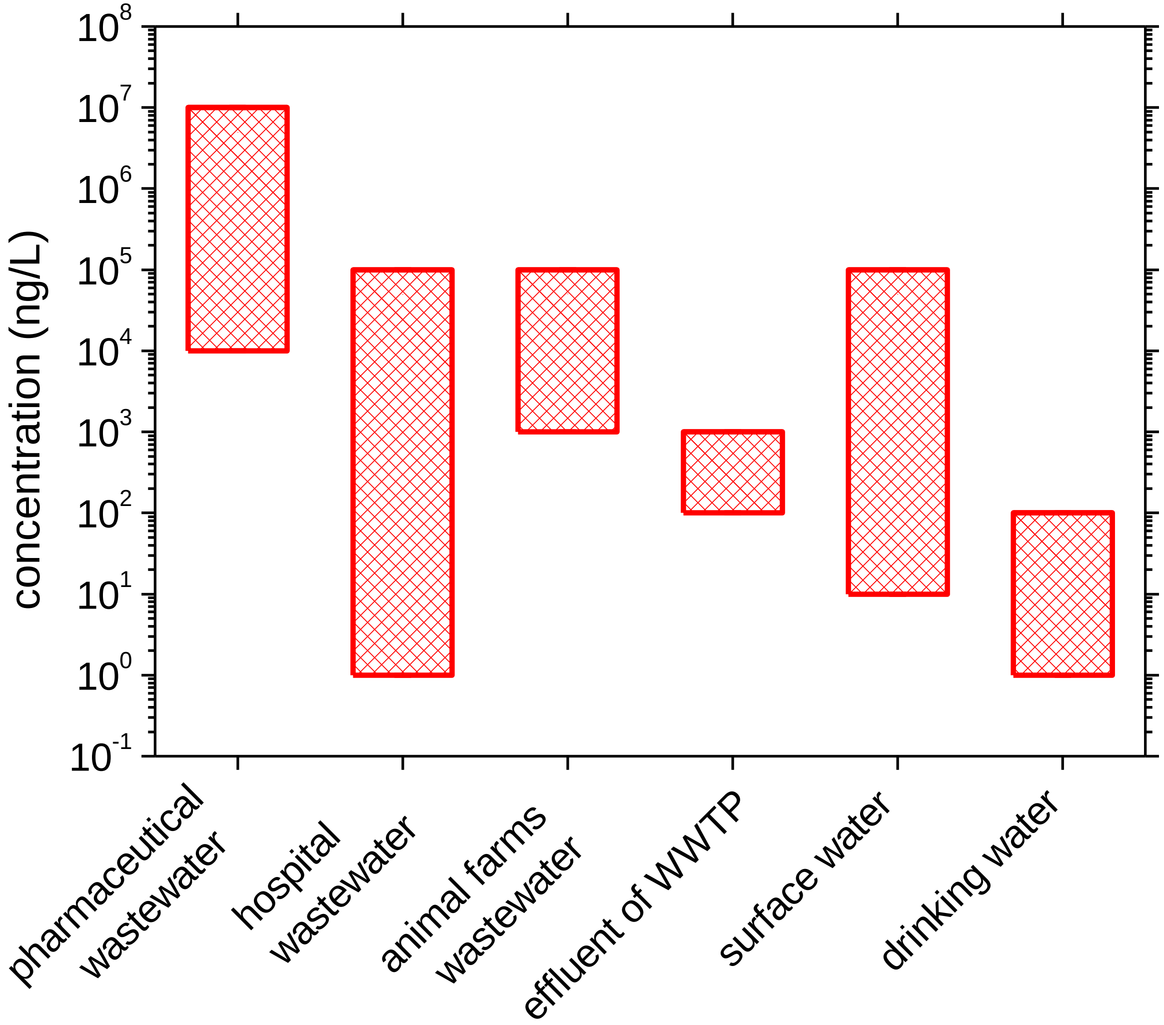
Other sources:

- Improper disposal of unused medicines
- Release of pharmaceutical waste from manufacturing facilities
- Accidental spills during manufacturing or distribution



Carvalho, I.T., Santos, L., Environ Int (2016), http://dx.doi.org/10.1016/j.envint.2016.06.025

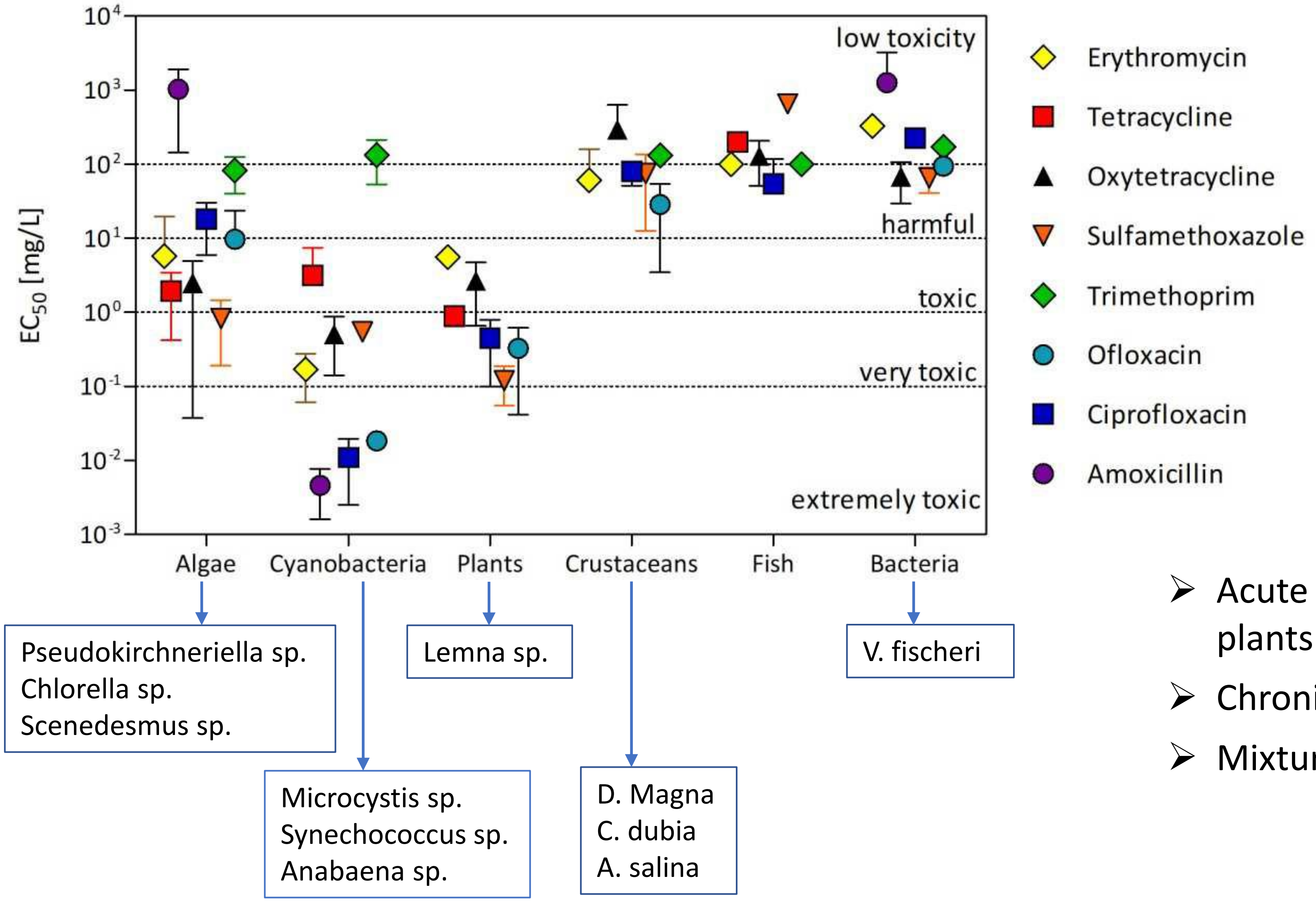
Concentrations of antibiotics in various wastewaters and water bodies



- pharmaceutical manufacturing wastewater: tens of μg/L – tens of mg/L
- hospital wastewater: ng/L – hundreds of μg/L
- animal farms wastewater: μg/L – hundreds of μg/L
- effluent of wastewater treatment plants: hundreds of ng/L – μg/L
- surface water: tens of ng/L – hundreds of μg/L
- drinking water: ng/L – hundreds of ng/L

M. Magureanu et al., J. Hazard. Mater. 417 (2021) 125481, https://doi.org/10.1016/j.jhazmat.2021.125481

Ecotoxicity of selected antibiotics towards different groups of organisms



- Acute toxicity bioassays: cyanobacteria, algae and plants sensitive organisms (EC_{50} μg/L – mg/L)
- Chronic effects (not considered)
- Mixtures – additive effects

P. Kovalakova et al., Chemosphere (2020), doi: https://doi.org/10.1016/j.chemosphere.2020.126351

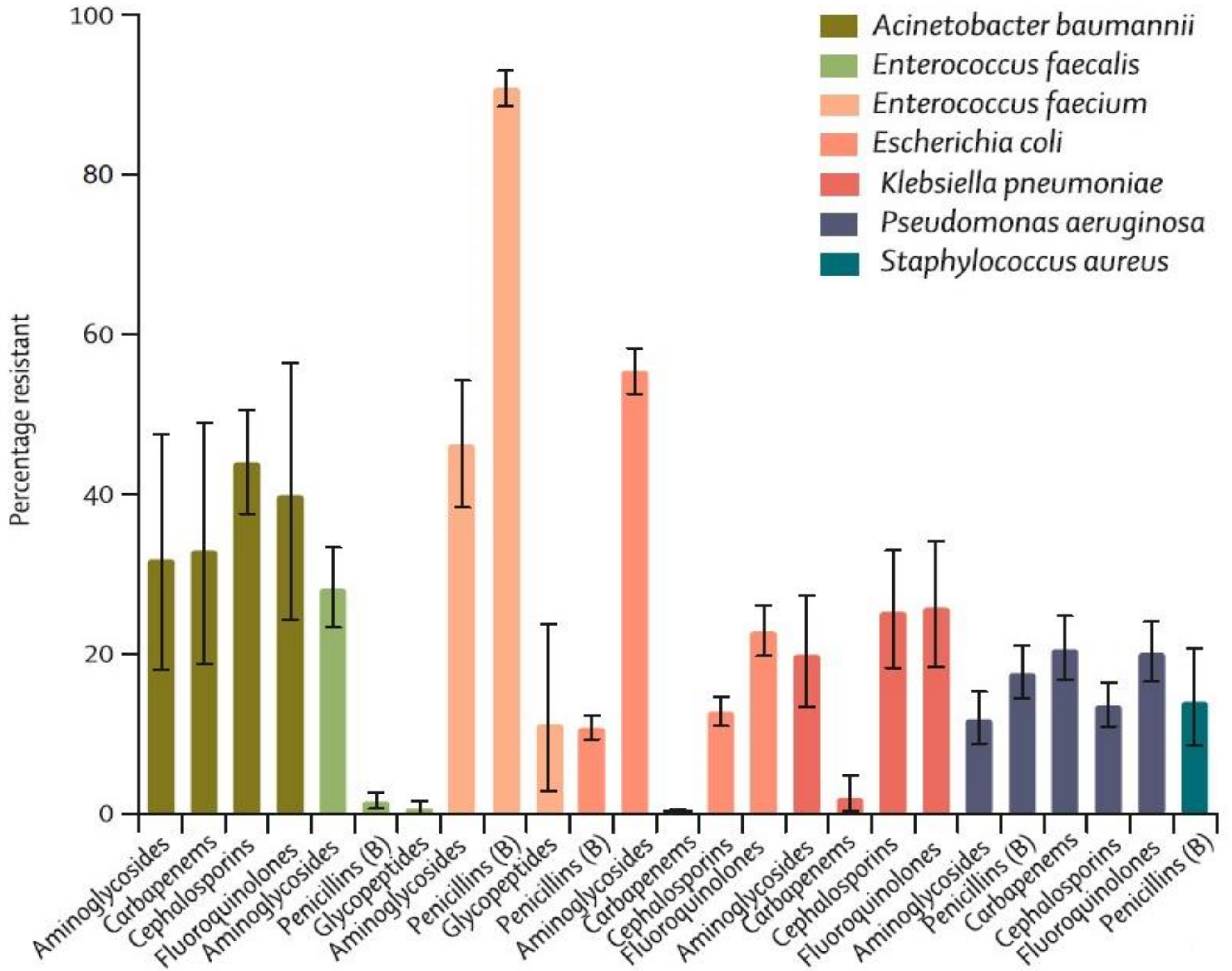
Plasma treatment of wastewater

Antimicrobial resistance

- Accelerated by the presence of antibiotics in the environment at sub-lethal levels:
  - spread of mutations that promote survival
  - shorten the time bacteria need to acquire resistance to new drugs
- Coded by antibiotic resistance genes (ARGs)
  - vertical transmission
  - horizontal transmission

- Increasing AMR + slow development of new antibiotics → one of the most stringent public health crisis

Average global resistance rate for the specified antibiotic-pathogen combination



Laxminarayan, R. et al. The Lancet Infectious Diseases Commission on antimicrobial resistance: 6 years later. The Lancet Infectious Diseases 20, e51–e60 (2020).

Degradation of antibiotics by non-thermal plasma – the key parameters

- Antibiotic Removal

$$R = \left(1 - \frac{c_t}{c_0}\right) \cdot 100$$

c_o – initial concentration of antibiotic
c_t – concentration of antibiotic after the treatment time *t*

- Mineralization (A → CO_2 + H_2O + Inorganic, Total Organic Carbon analysis)

$$M = \left(1 - \frac{TOC_t}{TOC_0}\right) \cdot 100$$

TOC_0 – initial content of organic carbon in solution
TOC_t – organic carbon content after the treatment time *t*

- Energy efficiency / yield (g/kWh, R 50% / 90%)

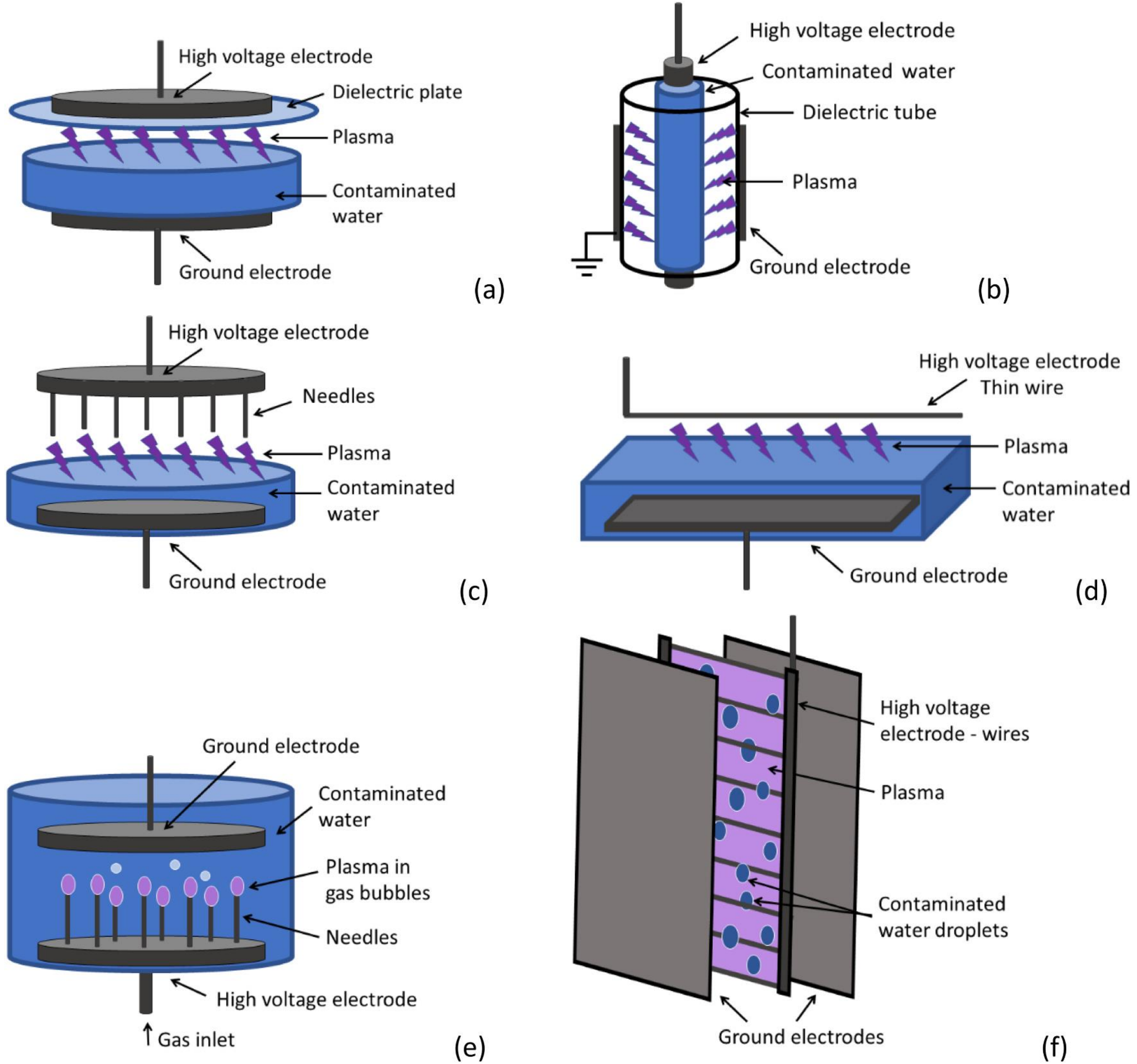
$$Y = \frac{c_0 \cdot V \cdot R}{P \cdot t} \cdot \frac{1}{100}$$

V – solution volume
P – discharge power

Plasma treatment of wastewater

Reactor design

- Most used – DBD, corona discharges in contact with liquid
- Enhanced mass transfer of the active species from the plasma to the liquid
- Large plasma-liquid contact surface (multiple needles / wires corona)
- High surface-to-volume ratio (thin solution films, discharge in gas bubbles, water droplets, ...)
- Plasma-catalysis
- Gas recycling



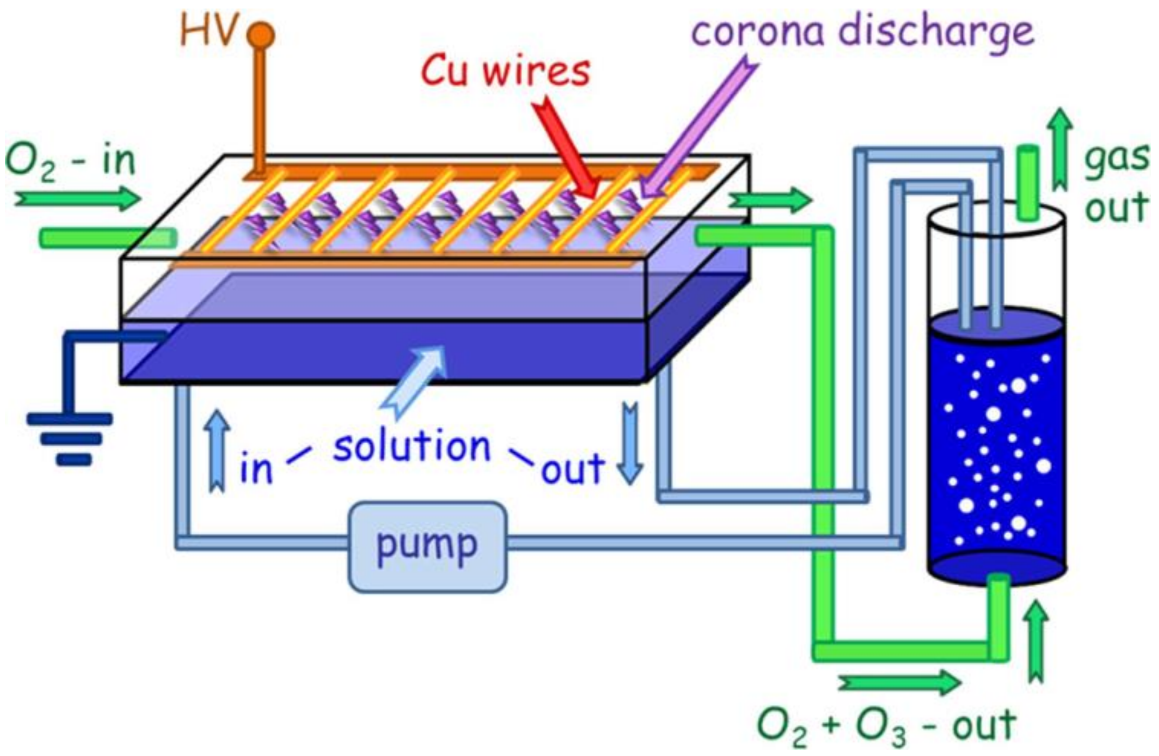
Plasma treatment of wastewater

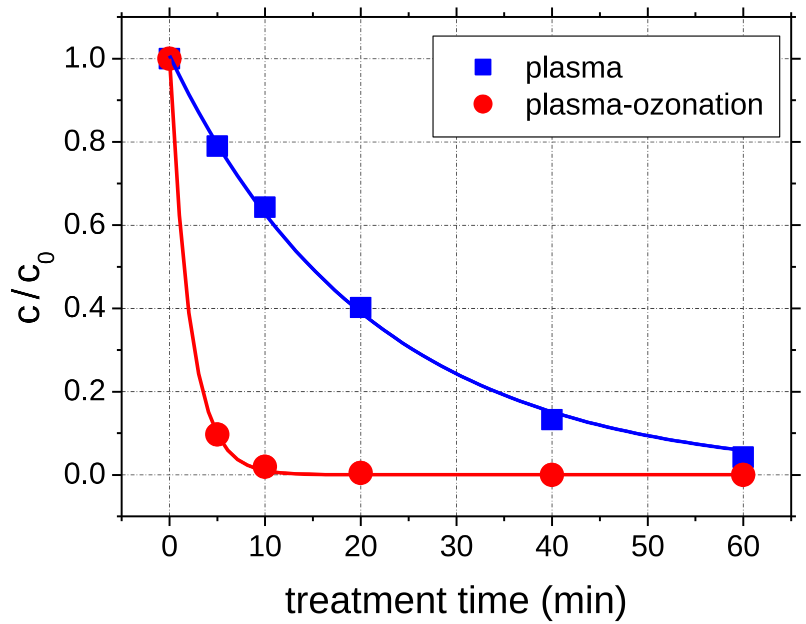
Plasma-catalysis – type and role of the catalyst

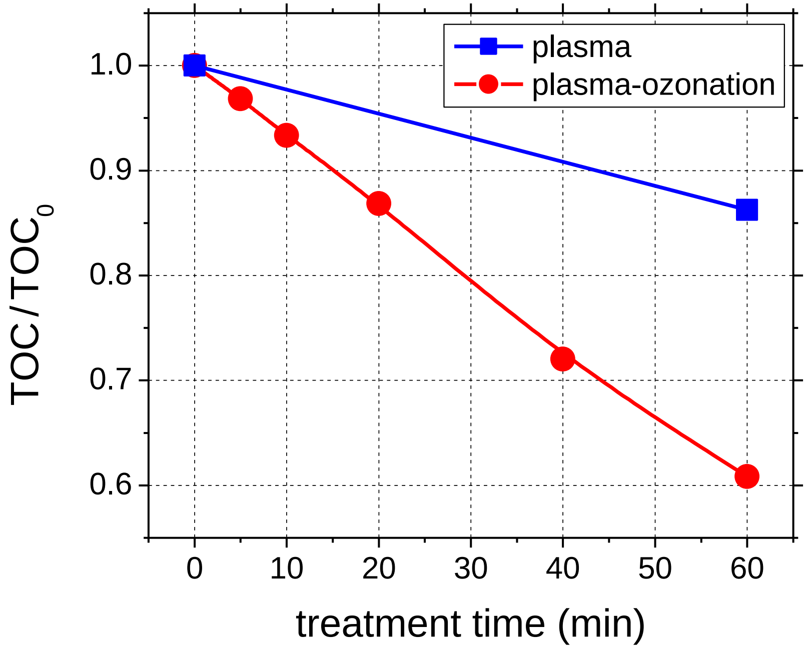
Catalyst	Preparation method	Antibiotic	Improvement by plasma-catalysis vs. plasma alone: Degradation rate / treatment time	Energy yield gain	Mineralization rate / treatment time	Proposed role of the catalyst	Reference
$FeSO_4$		Sulfadiazine	99% (73%) / 9 min	136%	34% (25%) / 30 min	Fenton reaction (Fe^{2+}/H_2O_2)	Rong and Sun, 2013
			98% (35%) / 3 min	280%	33% (25%) / 30 min		Rong et al., 2014
		Norfloxacin	89.7% (42%) /0.5 min	213%	72.5% (49.7%) / 15 min		Xu et al., 2020
TiO_2	Sol-gel method	Tetracycline	85.2% (62%) / 24 min	137%	53% (25%)	Photocatalysis - ROS (•OH, •O, $•O_2^-$, O_3) production by photogenerated electron–hole pairs	He et al., 2014a
Bi_2MoO_6	Solvent thermal method		96% (62%) / 24 min	155%	63% (25%)		He et al., 2014b
$rGO-TiO_2$ nanocomposites	Modified Hummers method for GO; Impregnation for rGO/TiO_2 or rGO/WO_3	Flumequine	99.4% (64%) / 60 min	155%	35.8% (27.2%)		Guo et al., 2019a
			99.4% (64.8%) / 60 min	153%	35.8% (27.2%)		Guo et al., 2019d
$rGO - WO_3$ nanocomposites		Enrofloxacin	99.1% (76%) / 60 min	130%	39.9% (31.6%)		Guo et al., 2019b
TiO_2/WO_3	Impregnation	Chloramphenicol	88.1% (51.3%) / 60 min	172%	42.5% (33.7%)		Guo et al., 2019c
$rGO-WO_3-Fe_3O_4$ nanocomposites	Impregnation	Thiamphenicol	99.3% (59%) / 60 min	168%	45.3% (27.5%)	ROS production by photocatalysis and Fenton-like reaction	Guo et al., 2021
Ag_3PO_4/ACFs		Levofloxacin	93.2% (63%) / 18 min	148%	46% (11.6%)	ROS production by photocatalysis (UV and visible radiation)	Gong et al. 2020
Mn/γ-Al_2O_3 (10 wt%)	Incipient wetness impregnation method	Tetracycline Hydrochloride	99.3% (69.7%) / 5 min (with O_2)	142%	COD removal with air: 57% (20%)	Decomposition of O_3 with •OH generation	Wang et al., 2019
Fe-Mn GAC	Impregnation – desiccation method	Oxytetracycline	93.5% (82%) / 20 min	114%	42.3% (36.7%)		Tang et al., 2019

Plasma treatment of wastewater

Plasma-ozonation / Gas recycling







Plasma – Y_{50} = 5.3 g/kWh

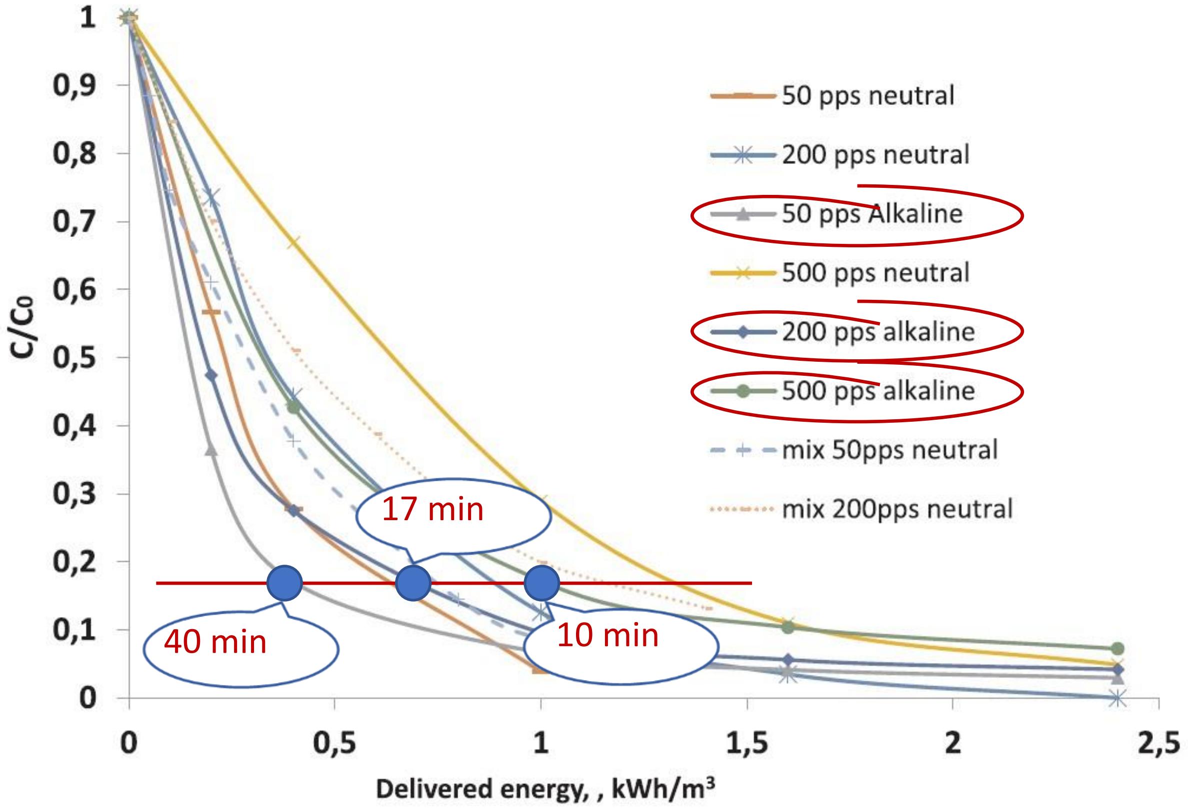
Plasma-ozonation – Y_{50} = 35.6 g/kWh

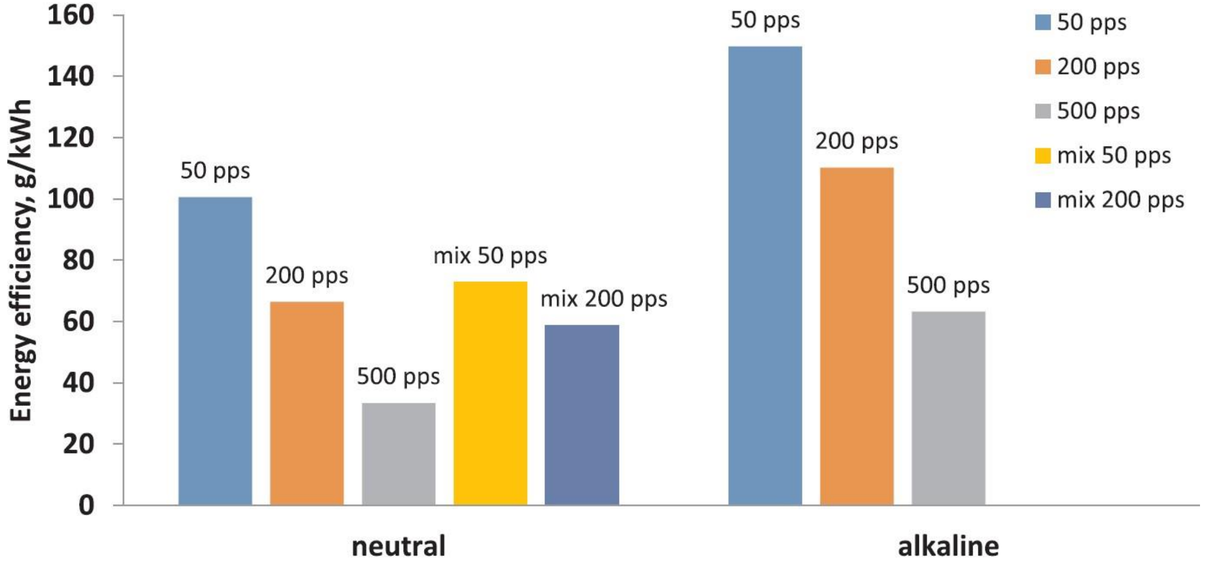
Large efficiency improvement due to ozone recycling

Effect of input energy

Higher power input → larger concentrations of active species → faster degradation of the target compounds

Degradation of amoxicillin in water by gas-phase pulsed corona discharge with liquid shower





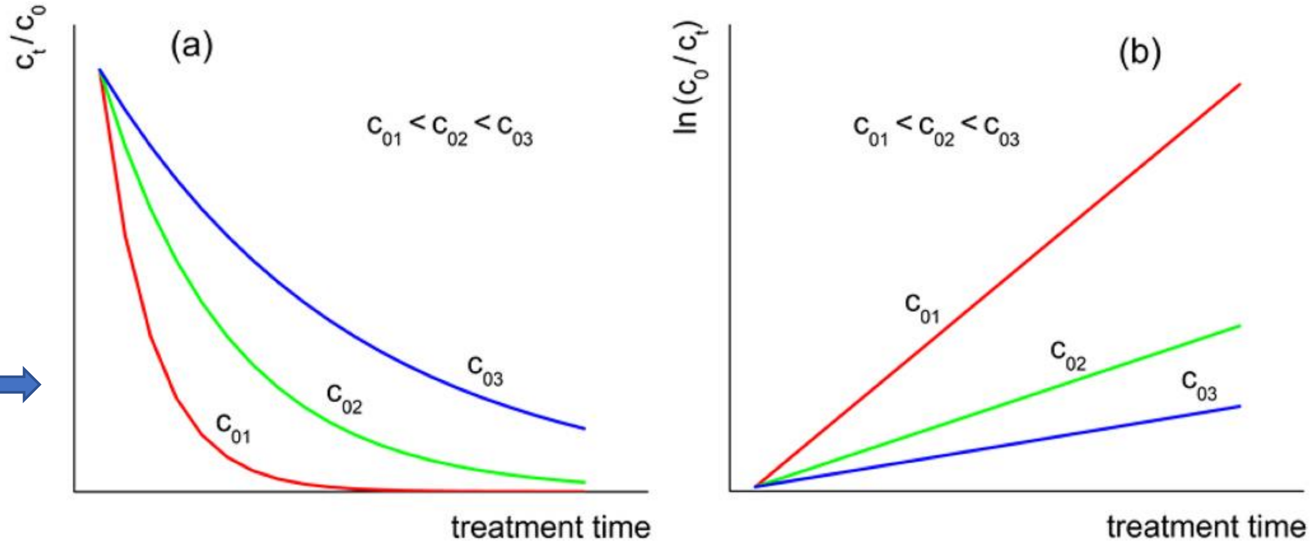
Sokolov et al., Chem. Eng. J. 334 (2018) 673–681, http://dx.doi.org/10.1016/j.cej.2017.10.071

Faster degradation for higher input energy, BUT generally lower energy efficiency

Plasma treatment of wastewater

Effect of initial concentration of antibiotic

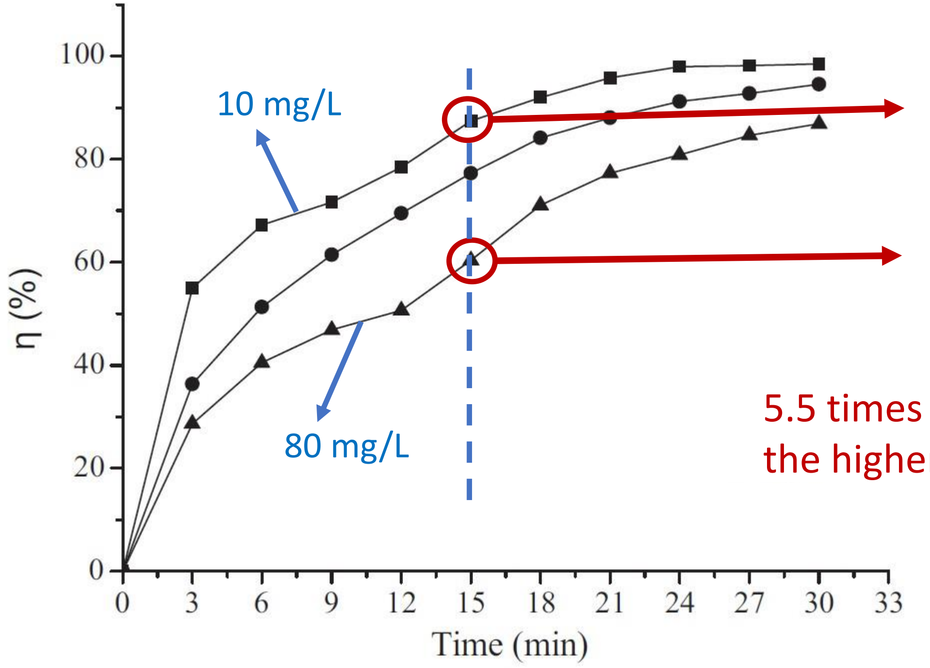
- Initial concentrations: mg/L – hundreds of mg/L
- Generally – first order kinetics $-\frac{dc_t}{dt} = k \cdot c_t$



- Higher initial concentration → slower removal
  - Competition for the reactive species between the parent compound and its degradation products
- Higher initial concentration →
  - → Higher amount of antibiotic removed
  - → Higher energy efficiency
  - Increase of the reaction probability with rising reactant concentration

Treatment of contaminated wastewater at the source of pollution

Degradation of sulfadiazine in water by falling liquid film DBD



S.-P. Rong et al. / Chinese Chem. Lett. 25 (2014) 187–192, http://dx.doi.org/10.1016/j.cclet.2013.11.003

Plasma treatment of wastewater

Degradation mechanism

Example: β-lactam antibiotics
amoxicillin and ampicillin

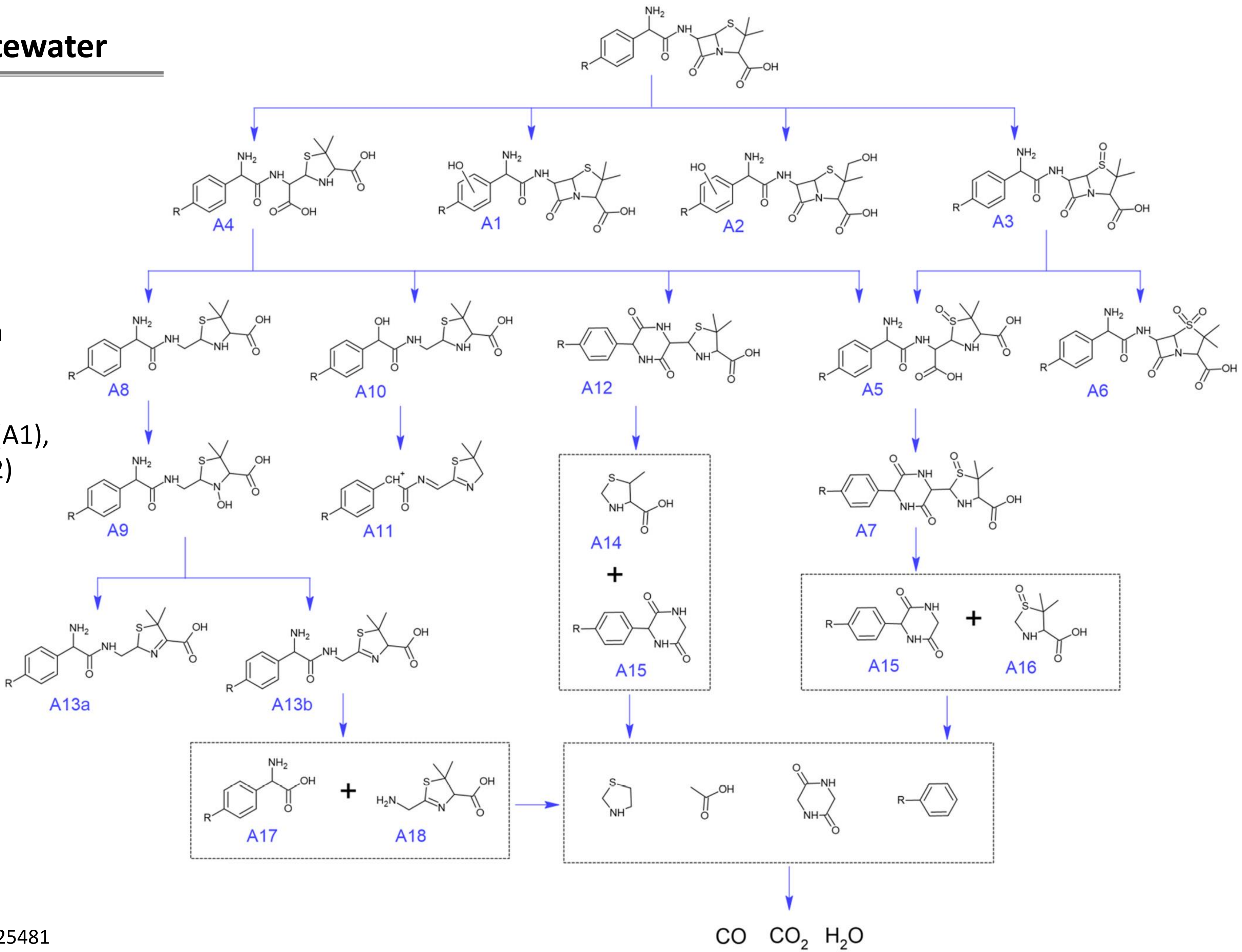
- ➢ Hydrolysis of the β-lactam ring (A4)
- ➢ Hydroxylation: of the benzene ring (A1), of benzene ring and a methyl group (A2)
- ➢ Oxidation of the S atom (A3)

…………….

- ➢ Fragmentation of the molecule

…………….

- ➢ Mineralization



Evaluation of the safety of plasma treated effluent

M. Magureanu et al., J. Hazard. Mater. 417 (2021) 125481

SUMMARY – Plasma treatment of antibiotic-containing water

- Non-thermal plasma CAN degrade antibiotics
- Challenge 1: Enhancing efficiency

  Y = mg/kWh – hundreds g/kWh
  - Reactor design optimization (maximizing production of active species + plasma-liquid species transfer)
- Challenge 2: Understanding of the degradation mechanism
  - Degradation pathways – intermediate products
- Challenge 3: Safety of the treated effluent
  - Toxicity (parent compound / intermediate degradation products / residual oxidants)
  - Residual biological activity (adaptation → resistance)
- Challenge 4: Up-scaling

ACKNOWLEDGMENTS:

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CNCS - UEFISCDI, project PN-III-P4-ID-PCE-2020-0335 (PCE 143 / 2021)

CNCS - UEFISCDI, contract no. 18 BM / 2019 – GREMI, University of Orleans

References

M. Magureanu et al., J. Hazard. Mater. 417 (2021) 125481

M. Magureanu et al., Water Research 81 (2015) 124-136

M. Magureanu et al., Water Research 45, 3407-3416.

Aim of plasma agriculture: higher productivity & reduced environmental footprint

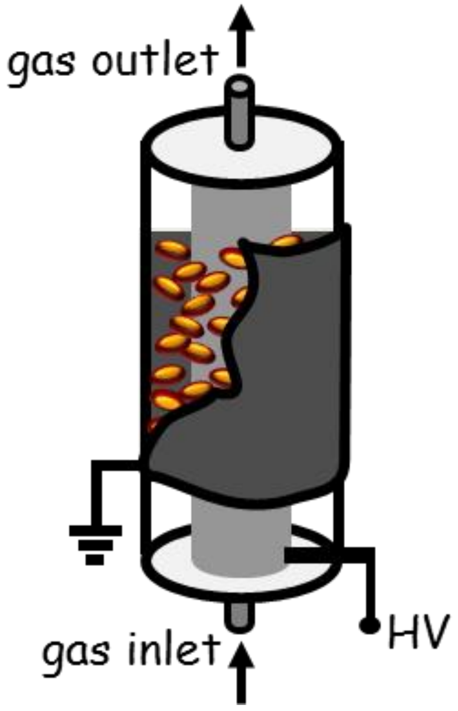
- Plasma treatment of seeds – direct, indirect
- Positive effect of plasma treatment: increased germination, enhanced plant growth and plant vigor, seed decontamination, improved stress tolerance
- Surface changes → increased hydrophilicity, water uptake
- Metabolic changes, phytohormone balance, gene regulation
- Challenges: cost of treatment, scalability, variability of the results, lack of field trials

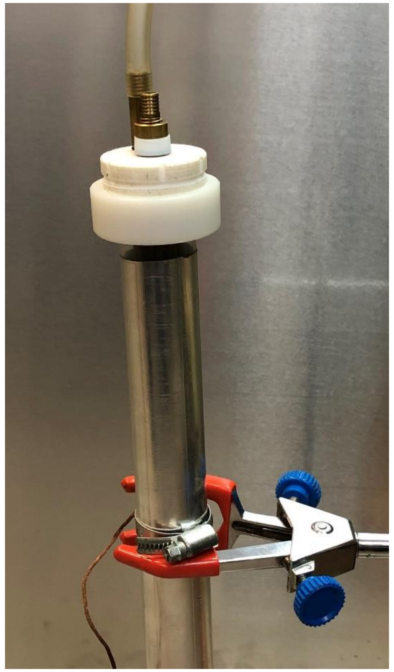
Plasma agriculture

Direct plasma treatment of sunflower seeds

- Laboratory tests: germination & early growth under controlled conditions
- Field tests: plants monitoring throughout the entire life span

packed-bed coaxial DBD



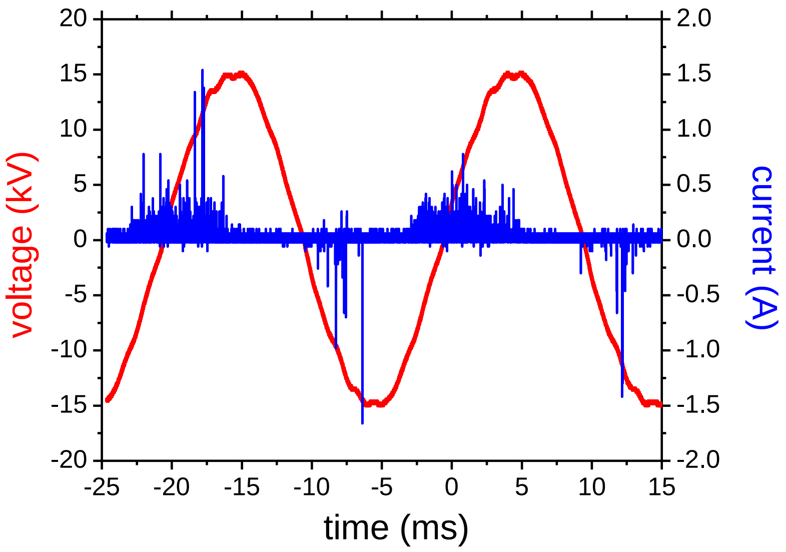


$\Phi_{inner\ electrode}$ = 21.7 mm

$\Phi_{outer\ electrode}$ = 34 mm

d_{gap} = 4.5 mm, L = 230 mm

a.c. excitation, ν = 50 Hz, V = 16 kV



Current waveforms - typical filamentary discharge

Average power (Lissajous method) = 5 W

Amount of seeds introduced in the plasma = 30 g

Treatment time = 10 min

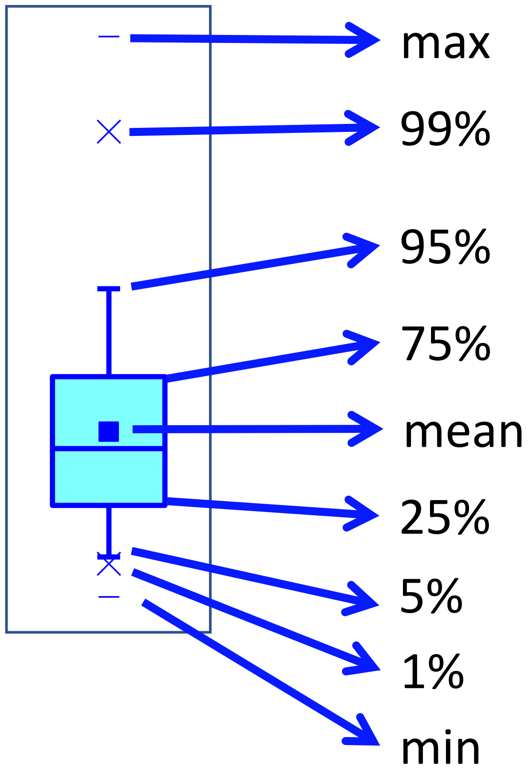
Laboratory tests: germination – between-paper method in Petri dishes

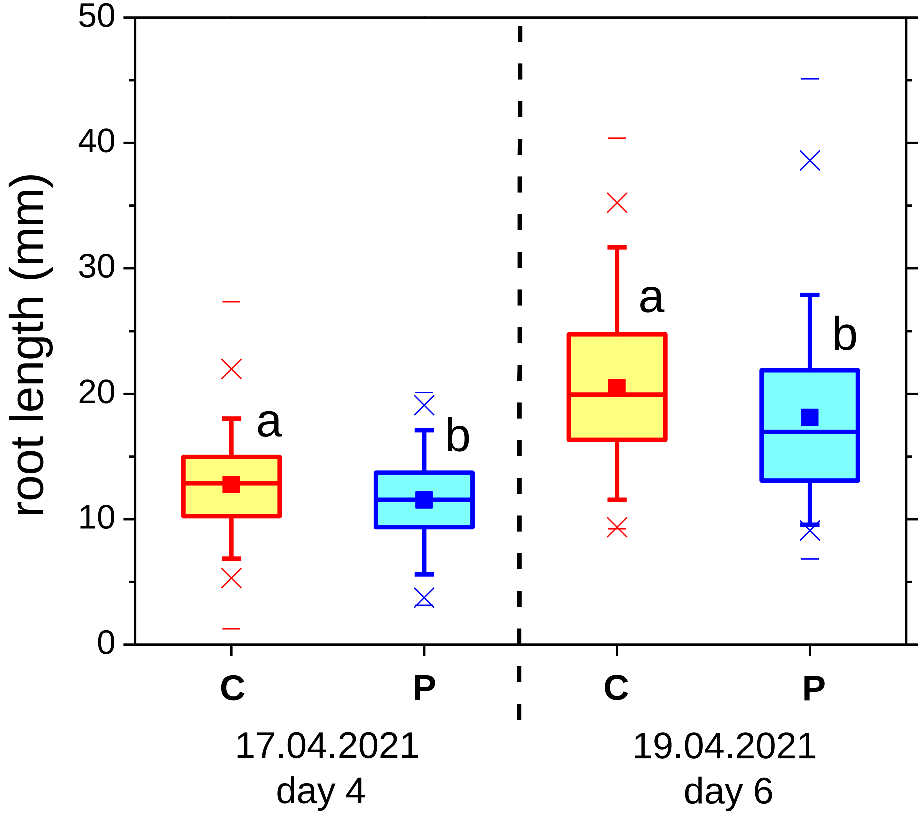
Six replicates of 16 seeds each + 1 replicate of 10 seeds

Conditions: Temperature 22 ^{o}C, 60% UR, light/darkness program 16/8 h – 7 days

Measurements: germination (2rd, 3th and 4th day), radicles length (4th and 6th day)

statistics





Germination %			
	day 2	day 3	day 4
control	81	98	98
plasma	74	98	98

Mean radicle length (mm)		
	day 4	day 6
control	12.8	20.5
plasma	11.5	18.1

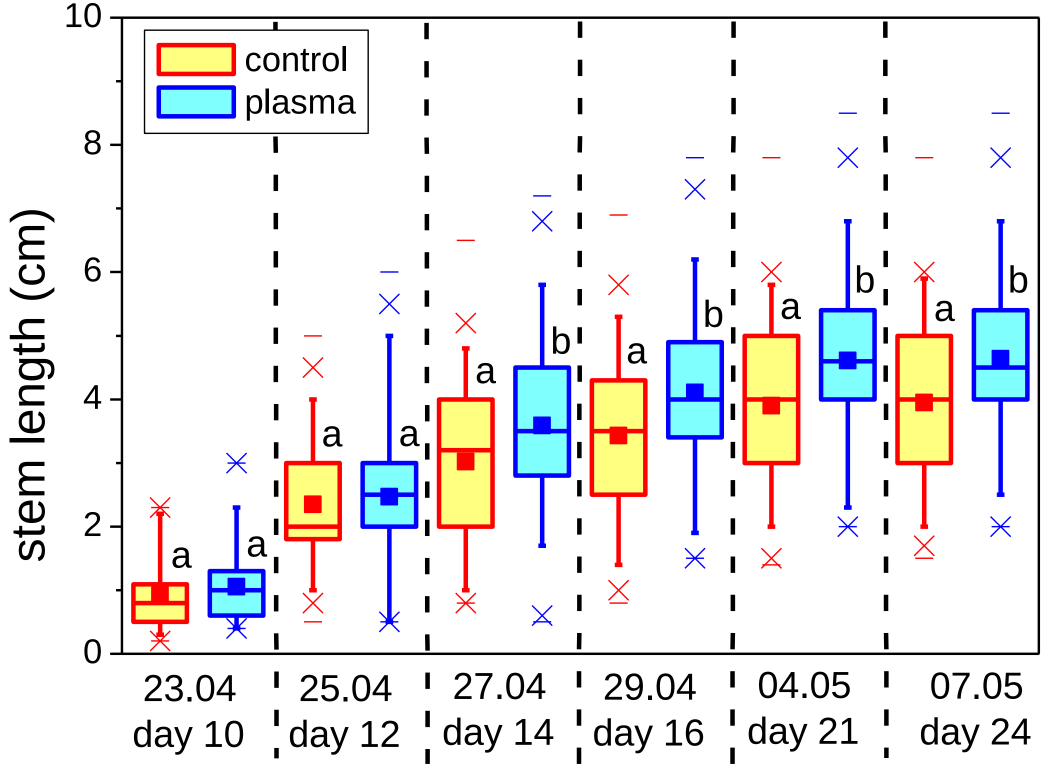
Laboratory tests – early growth – plant length

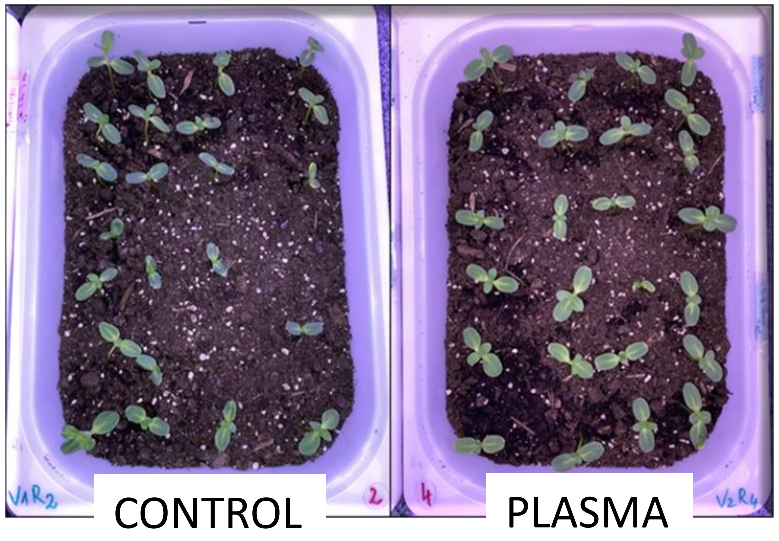
(seeds transferred in organic substrate)

Four replicates of 24 seeds each

Conditions: 25 °C, 60% UR, light/darkness program 16/8 h – 3 weeks

Measurements: stem length (10th to 24th day), cotyledons (10th day), plant length and weight – fresh and dry (30th day)





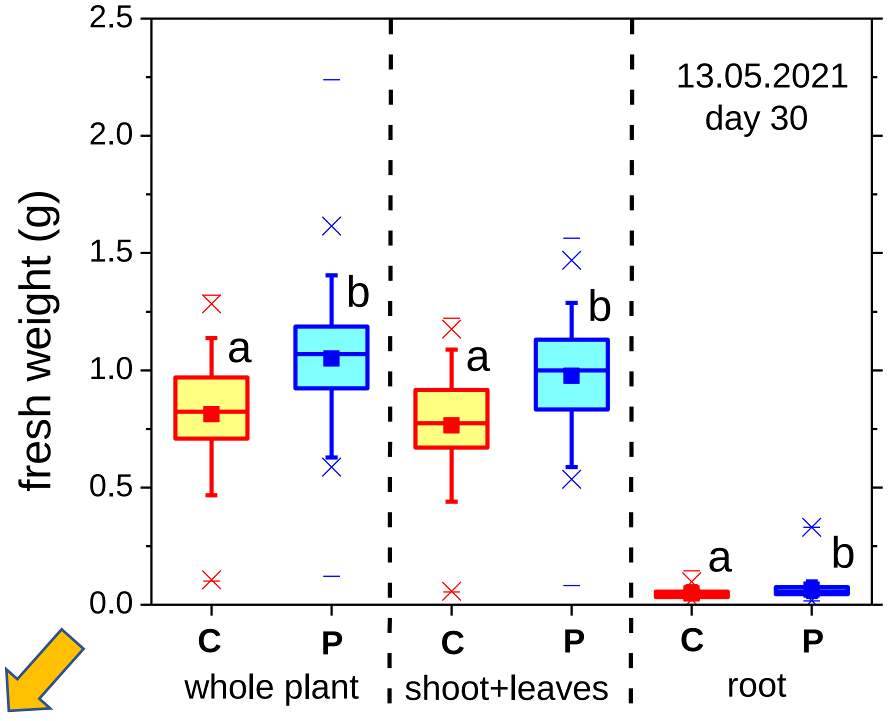
Faster plant growth for plasma treated seeds

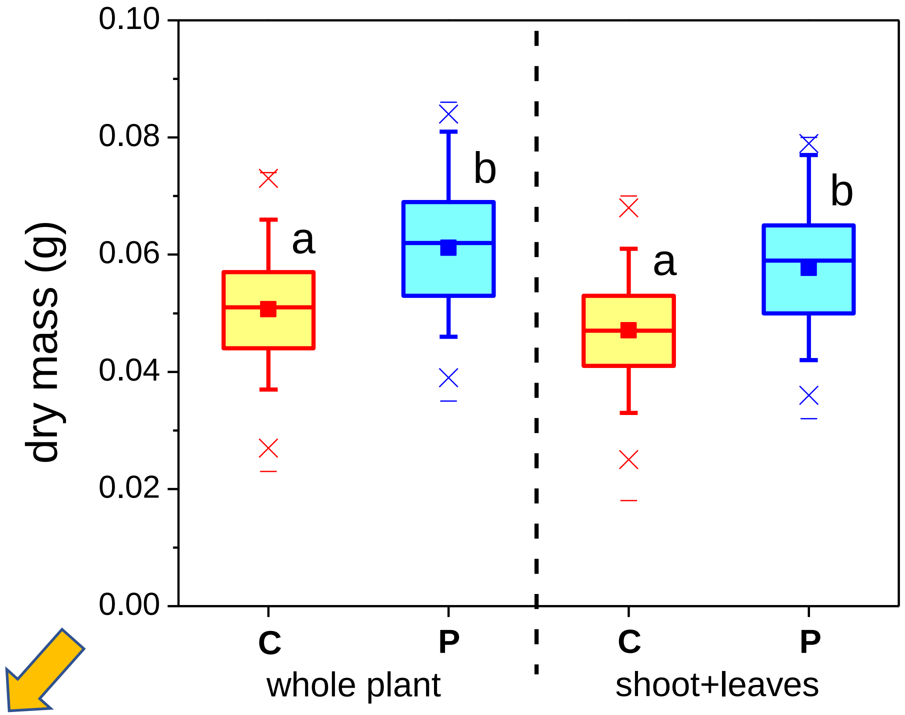
Improved growth uniformity for plasma treated seeds

Mean stem length (cm)			
	day 10	day 16	day 24
control	0.9	3.4	3.9
plasma	1.1	4.1	4.6

} ~ 20%

Laboratory tests – early growth – plant weight





Whole plant (mg)		Shoot + leaves (mg)		Root (mg)	
control	Plasma	control	plasma	control	plasma
812	1049	765	976	47	64

~ 29% ~ 28% ~ 36%

Whole plant (mg)		Shoot + leaves (mg)		Root (mg)	
control	plasma	control	plasma	control	plasma
50.7	61.2	47.1	57.7	3.6	3.5

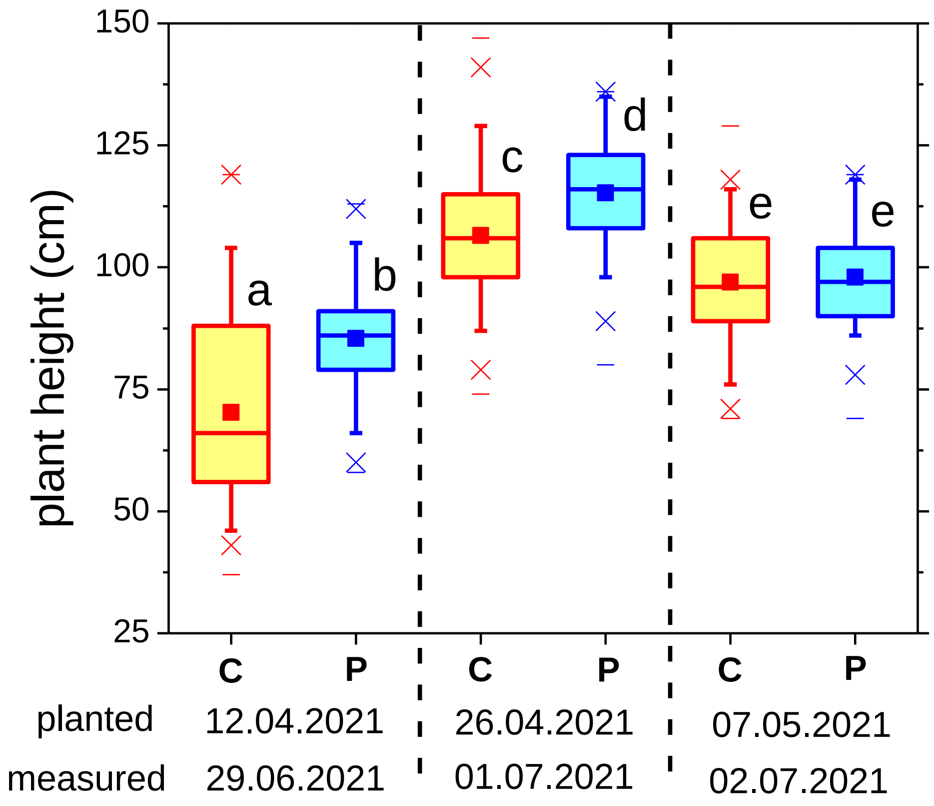
~ 21% ~ 23%

Field tests – plant height, number of leaves, capitulum diameter

Seed treatment: 07.04.2021 and 21.04.2021, ~ 100 g

Sowing: 12.04.2021 (E1), 26.04.2021 (E2), 07.05.2021 (E3)

Measurements: plant height, number of leaves, capitulum size (29.06-02.07.2021)



- The largest effect of plasma treatment occurs for the earliest sowing period: taller plants, with more leaves and larger capitulum diameter
- Improved growth uniformity for plasma treated seeds
- For late sowing, plasma treatment has a detrimental effect on capitulum diameter

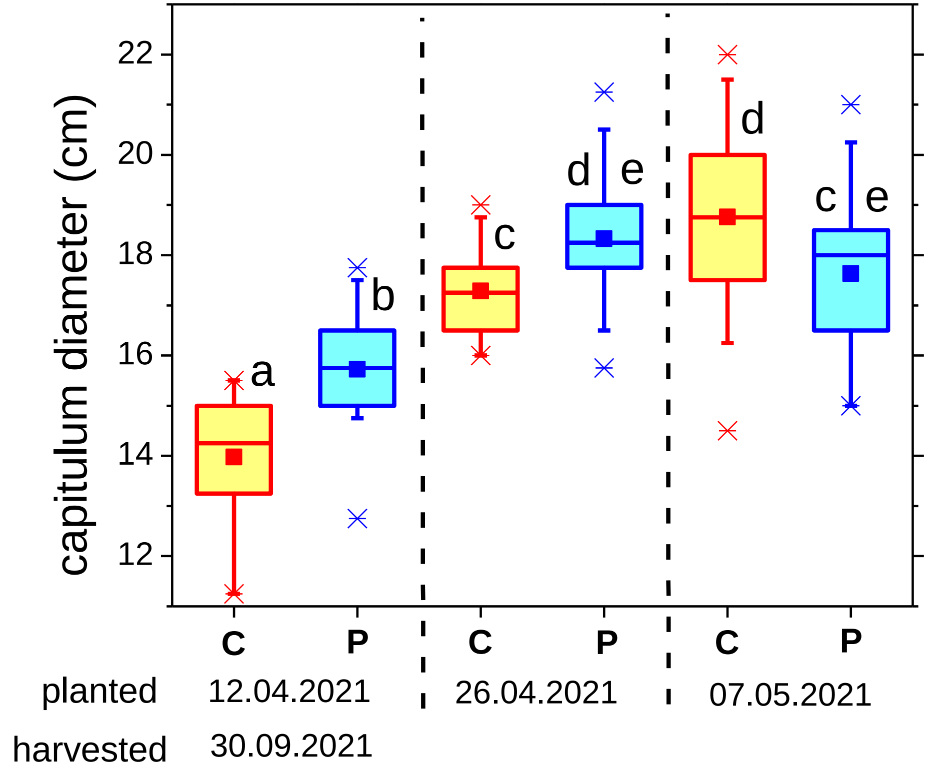
Mean plant height (cm)					
E1		E2		E3	
control	plasma	control	plasma	control	plasma
70.3	85.4	106.5	115.2	97	98

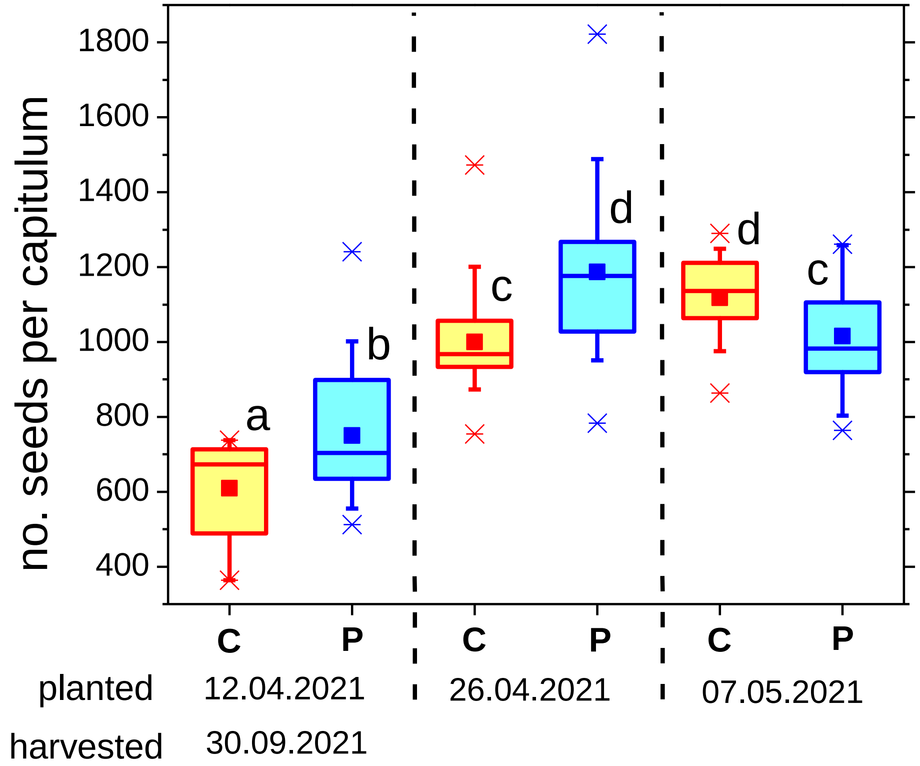
E1: ~ 21%

E2: ~ 8%

Field tests – Harvest

30.09.2021 – measurements: capitulum size and weight, number and mass of seeds per plant → calculation of yield

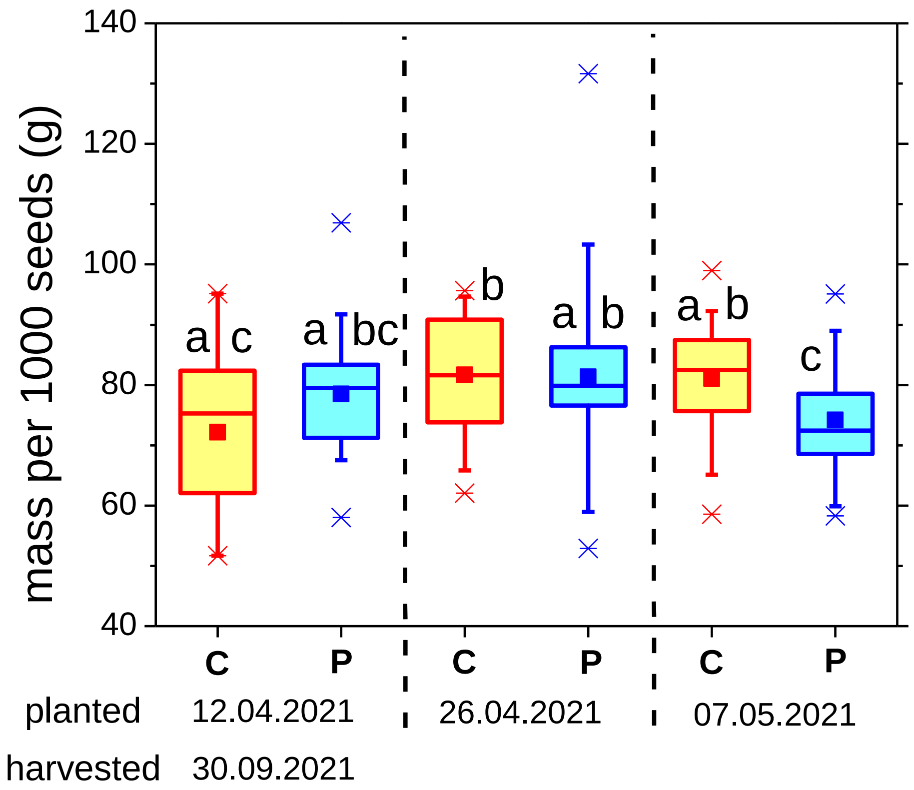


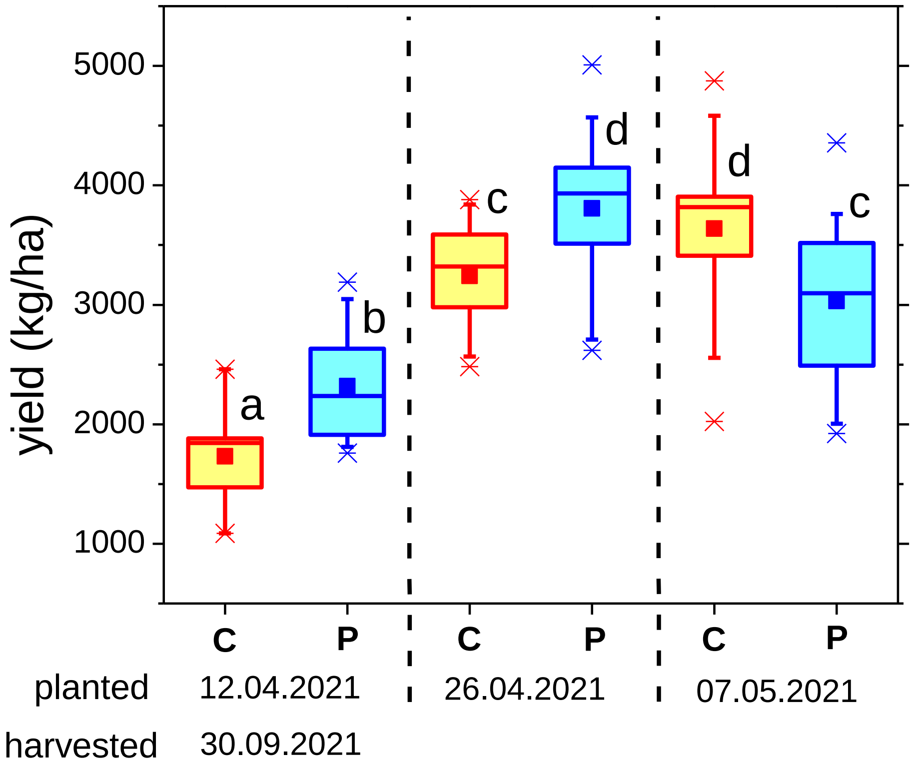


Capitulum diameter (cm)					
E1		E2		E3	
control	plasma	control	plasma	control	plasma
14.0	15.7	17.3	18.3	18.8	17.6

Number of seeds per capitulum					
E1		E2		E3	
control	plasma	control	plasma	control	plasma
609	750	1000	1187	1117	1015

Field tests – Harvest – calculation of yield





Yield (kg/ha)					
E1		E2		E3	
control	plasma	control	plasma	control	plasma
1731	2319	3243	3807	3639	3031

~ 34% (E1) ~ 17% (E2)

The mass per thousand seeds is not significantly influenced by plasma treatment for the seeds sown during the optimal period

For late sowing, plasma treatment has a detrimental effect

The largest effect of plasma treatment occurs for the earliest sowing period → earlier sowing should be further investigated

SUMMARY – Plasma treatment of sunflower seeds

- Germination tests and early growth measurements under controlled conditions are not sufficient to predict later plants evolution
- The sowing period is important
  - Positive effect of plasma treatment for seeds sown during the optimal period (plant height, number of leaves, capitulum size, number of seeds per plant, yield)
  - Detrimental effect of plasma for late sown seeds
- Plasma treatment increased the yield with more than 30% for the earliest sowing period → earlier sowing should be further investigated

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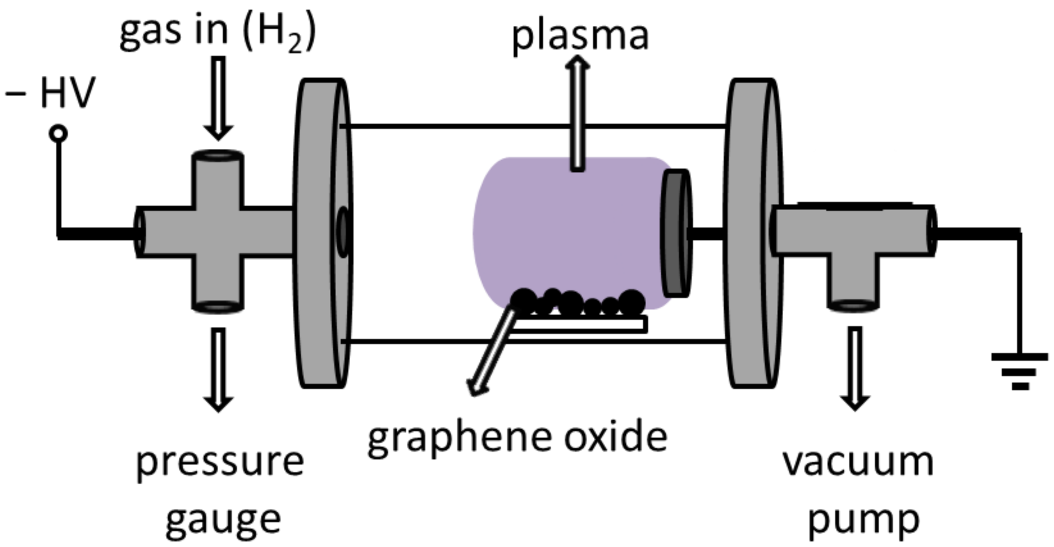
COST Action CA19110 “Plasma Applications for Smart and Sustainable Agriculture”

Improvement of catalytic activity of graphene oxide by H_2 plasma treatment

Interest – replacing noble metal catalysts with carbon-based materials – graphene

- treatment of graphene oxide in a d.c. glow discharge in H_2 (negative glow / positive column)
- test reaction – hydroisomerisation of 1-octene



Φ_{tube} = 65 mm, L_{tube} =

$\Phi_{cathode}$ = 25 mm, Φ_{anode} = 40 mm

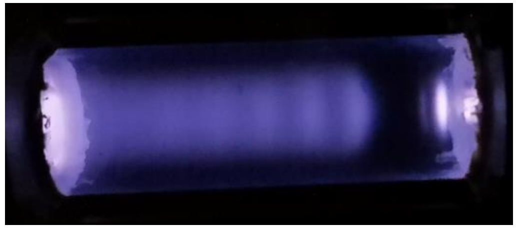
$p_0 = 3 \times 10^{-3}$ mbar, H_2 flow = 5 − 55 mL/min, p = 0.1 − 1.5 mbar

negative glow (NG):

p = 0.1 mbar

V_a = 3 kV, V_d = 600 V, I_d = 1.25 mA

striated positive column



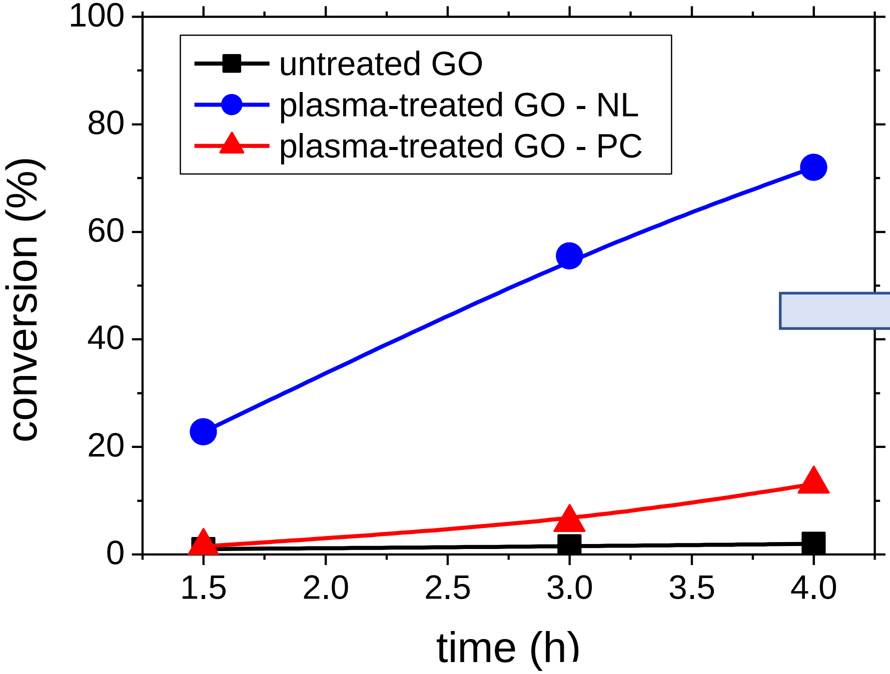
positive column (PC)

p = 1.5 mbar

V_a = 3 kV, V_d = 520 V , I_d = 1.27 mA

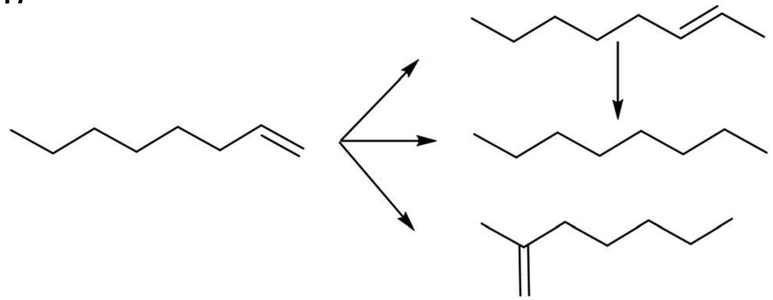
Catalytic test – hydroisomerisation of 1-octene

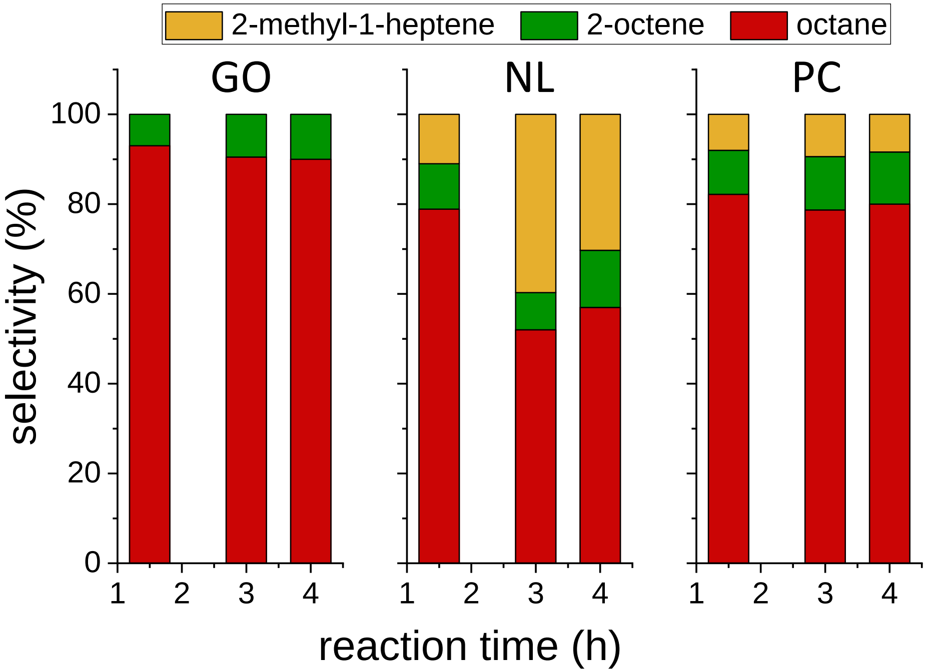
p_{H2} = 30 bar, T = 80 ^{o}C,
m_{GO} = 10 mg GO catalyst
1.5 mL 1-octene, 1.5 mL of n-heptane as solvent



considerable increase in the catalytic activity of GO as a result of H_2 plasma treatment

especially for GO treated in NG



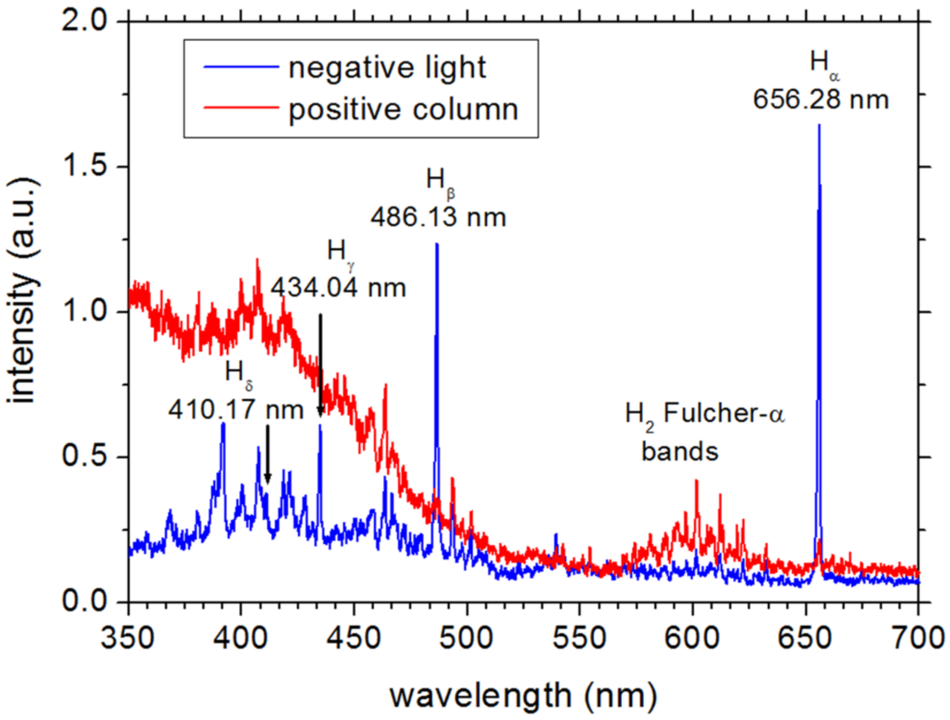


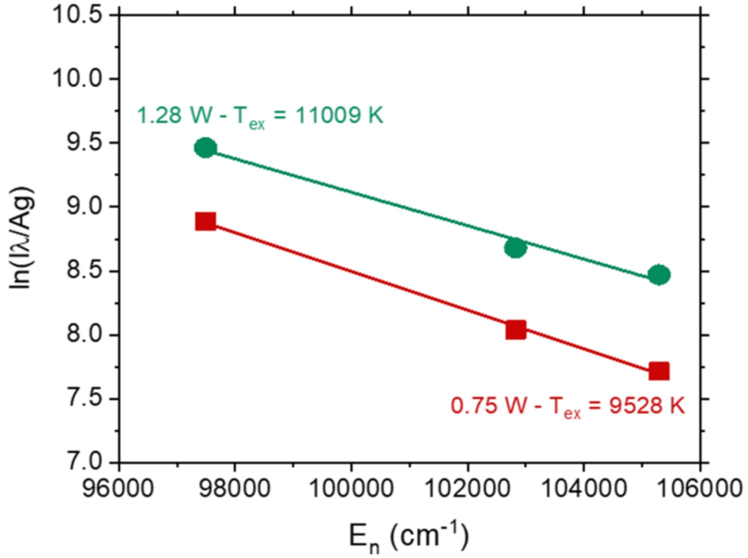
skeletal isomerization suggests the presence of acidic groups

plasma treatment - bifunctional acidic and hydrogenating catalyst

Plasma processing of materials

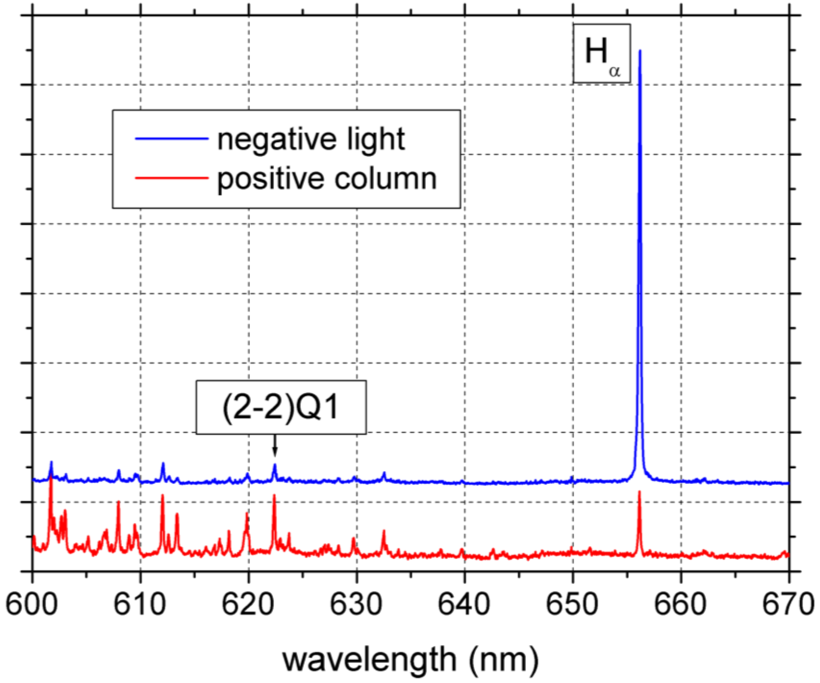
OES H_2 plasma





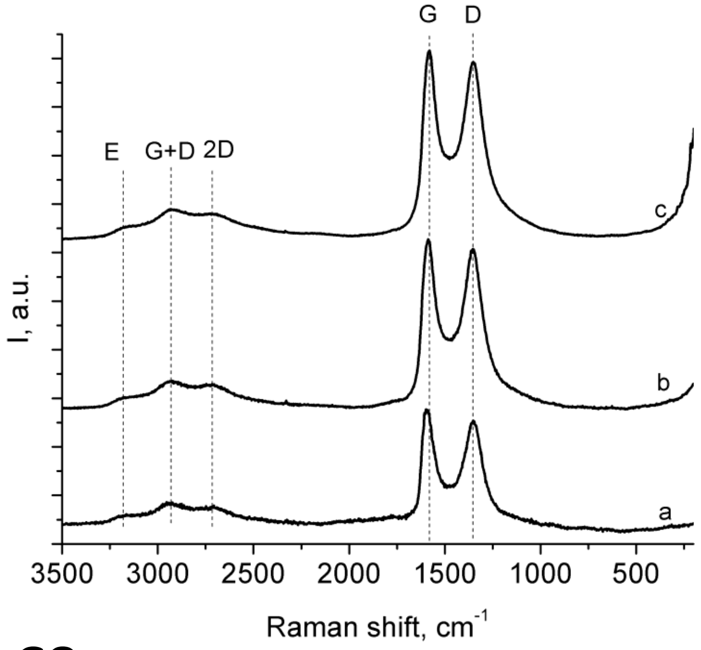
In the NL, the excitation temperature (T_{ex}) is below 1 eV and slightly increases with applied voltage

In the PC, T_{ex} could not be determined by the Boltzmann plot

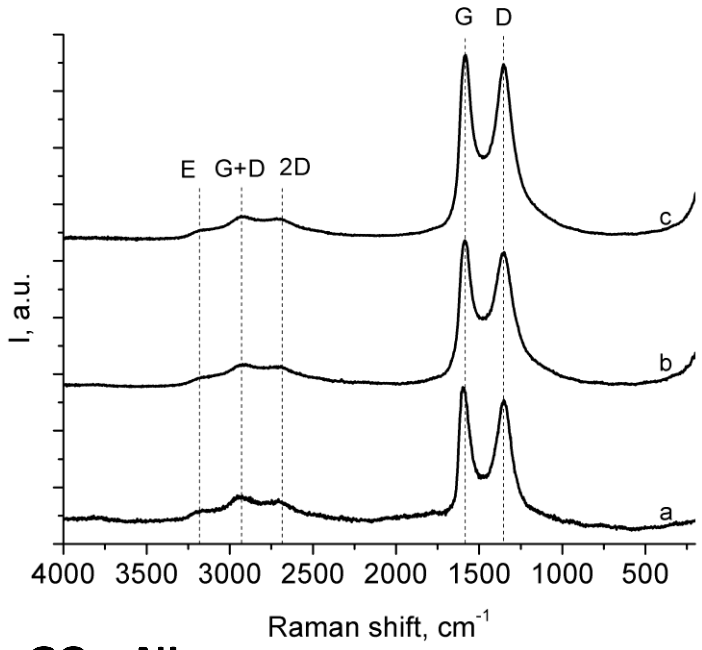


Significantly higher dissociation of H_2 to H in the NL than in the PC

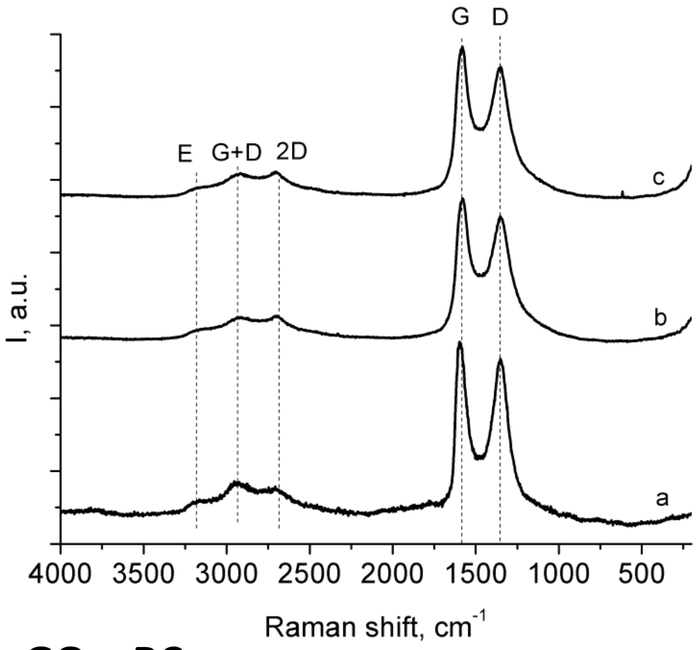
Raman measurements



GO:
a – fresh; b – spent 1st cycle; c – 2nd cycle



GO – NL:
a – GO precursor; b – NL fresh; NL – spent



GO – PC:
a – GO precursor; b – PC fresh; c – PC spent

Sample	GO Precursor	H_2 plasma-activated GO	
		NL series	PC series
D/G ratio – fresh catalyst	1.46	1.86	1.71
D/G ratio – tested catalyst	1.55 – 1st cycle 1.58 – 2nd cycle	1.88	1.73

Increase of the D/G ratio
↓
higher concentration of defects
↓
more active sites

SUMMARY – Plasma treatment of graphene oxide

- remarkable enhancement of the catalytic activity of graphene oxide, especially when treated in the NL
- higher population of defects produced by the plasma – active sites → increased conversion
- surface functionalization – acidic species → change in products distribution (skeletal isomerization)
- NL vs. PC – higher electron temperature and higher dissociation of H_2 in NL

References

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Prof. Hermenegildo Garcia et al., Universitat Politècnica de València – graphene synthesis and characterization

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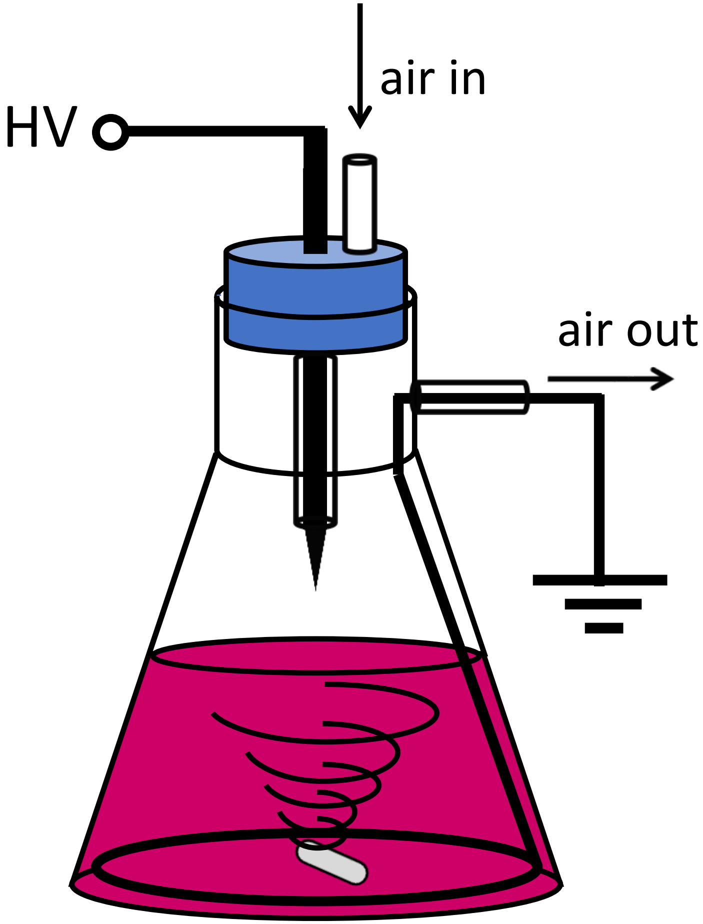
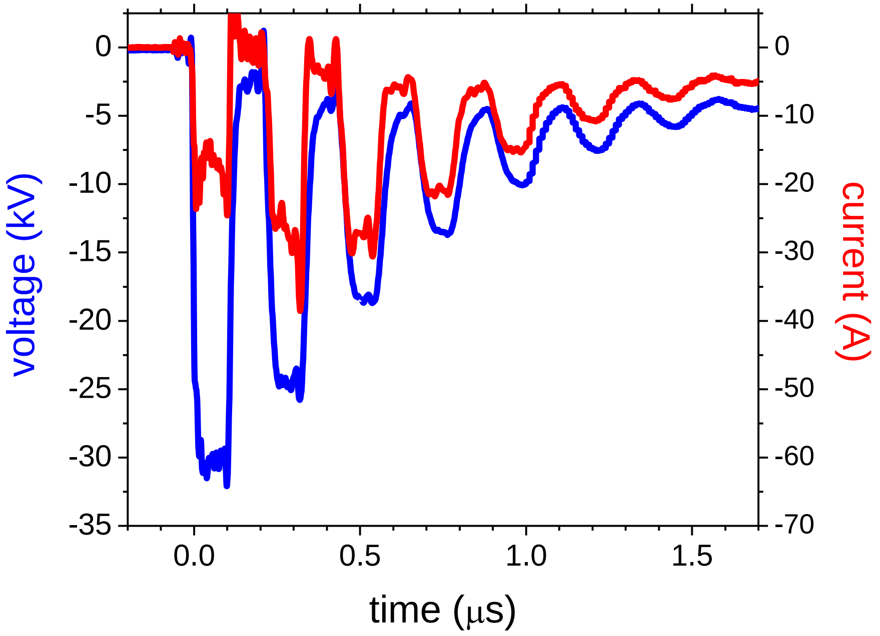
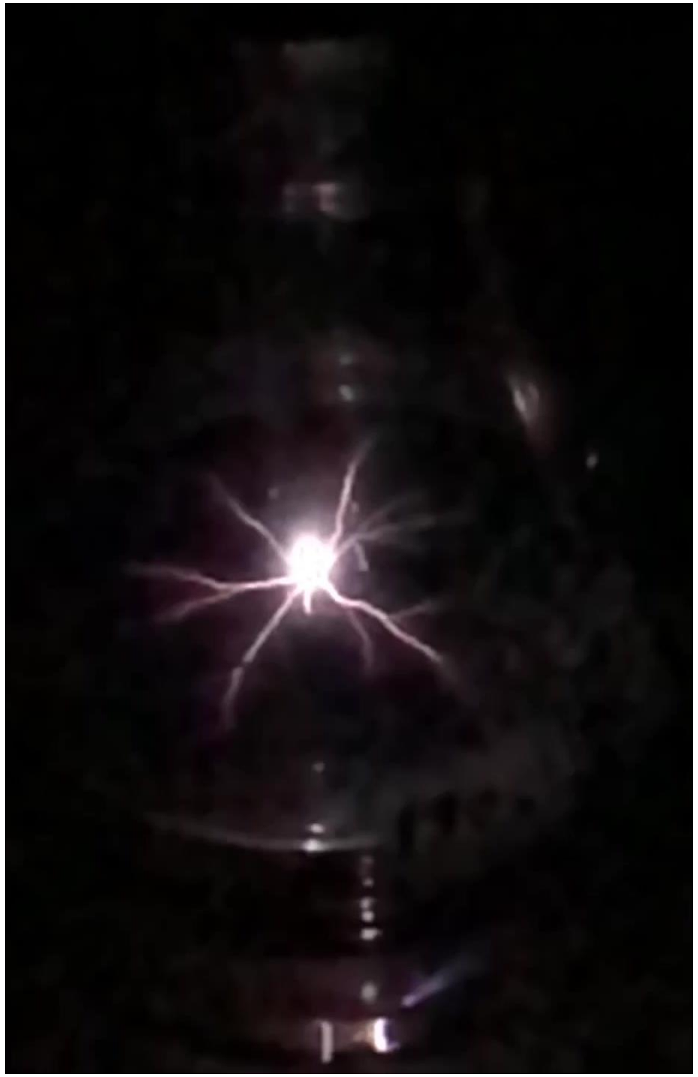
Au nanoparticles from liquid precursors ($HAuCl_4$) in a point-to-plate pulsed corona



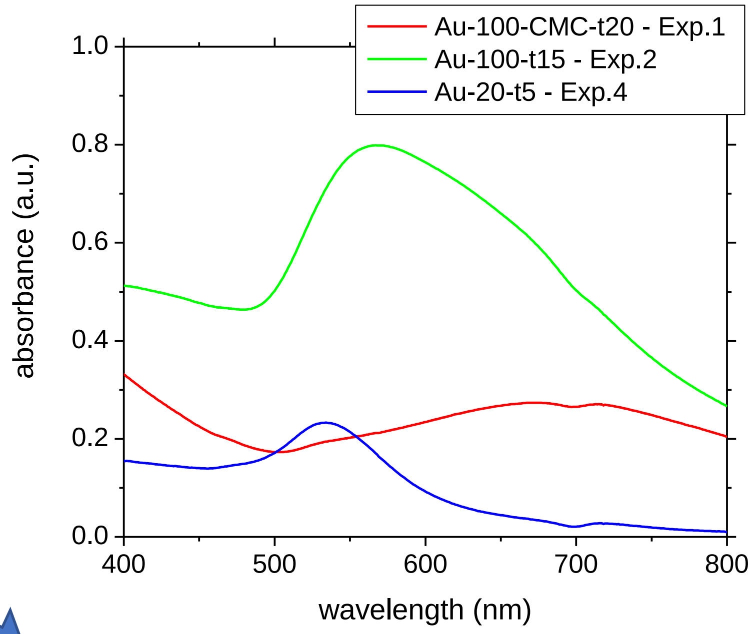


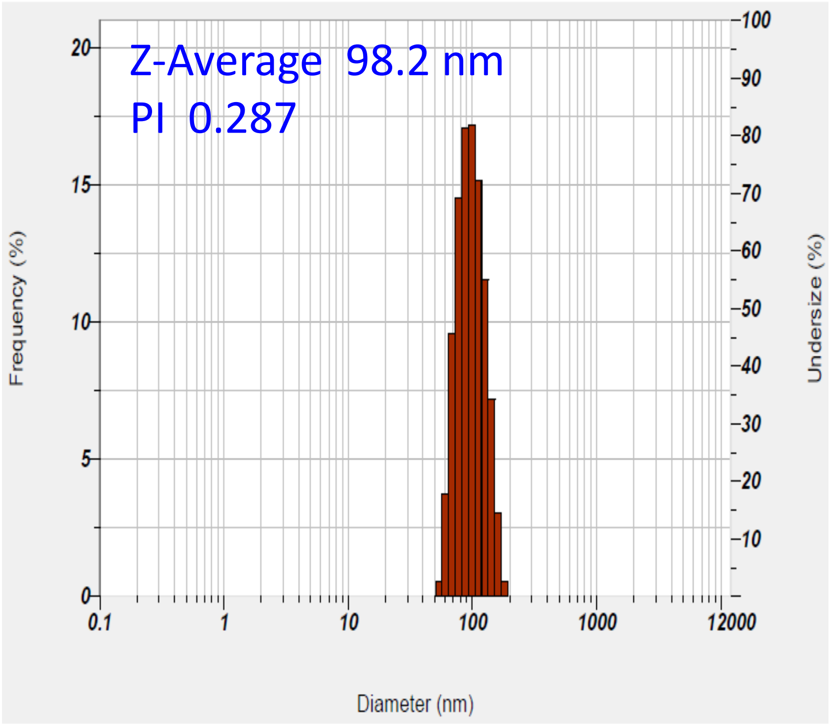


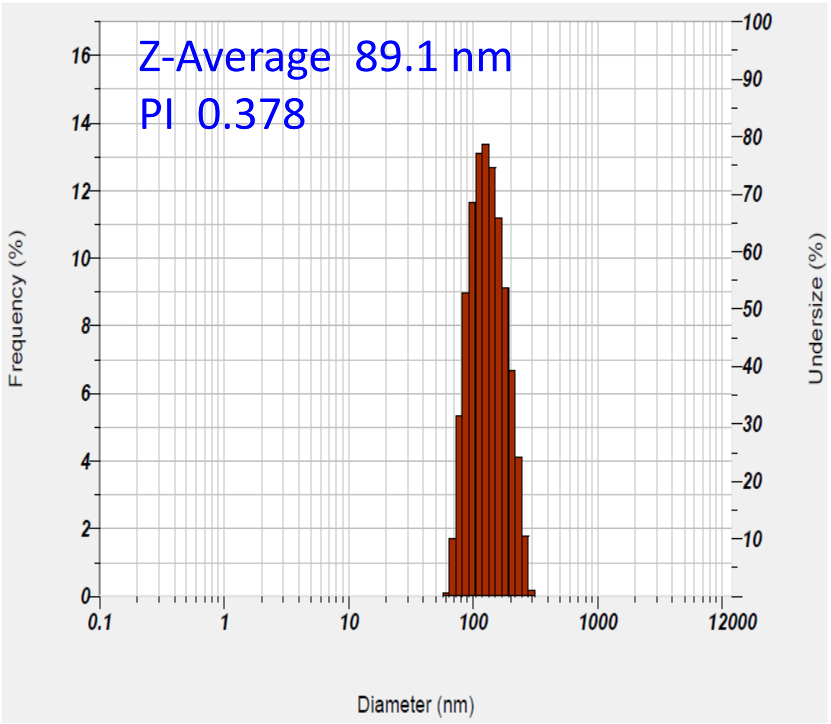
Plasma synthesis of materials

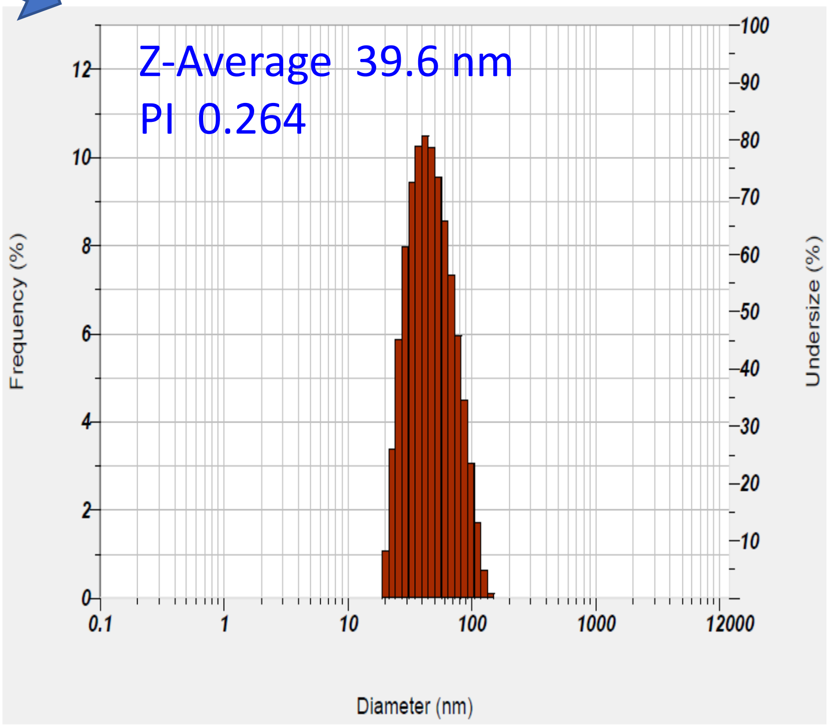
Sample ID	Exp. 1	Exp. 2	Exp. 3
$HAuCl_4$ concentration	100 mg/L	100 mg/L	20 mg/L
Stabilizer	CMCNa 1 mg/L	none	none
Plasma exposure time	20 min	15 min	5 min
Pulse frequency	41 Hz	41 Hz	64 Hz

* CMCNa – sodium carboxymethyl cellulose



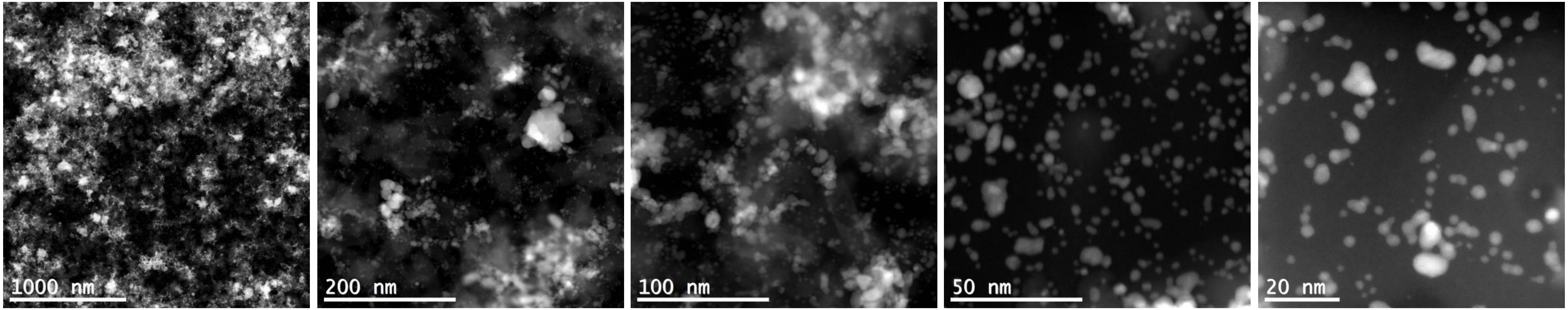




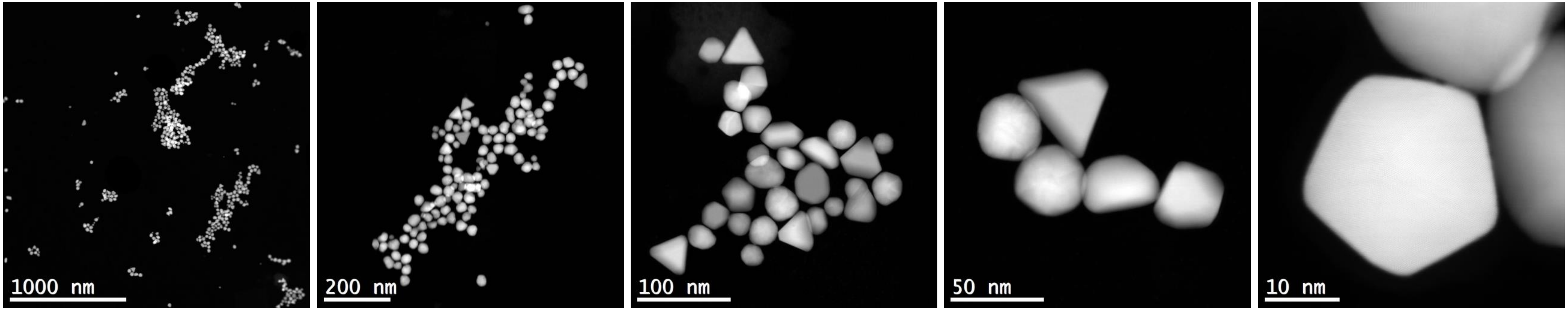


Plasma synthesis of materials

Exp.1: $HAuCl_4$ 100 mg/L + CMC-Na 1 mg/L



Exp.3: $HAuCl_4$ 20 mg/L



SUMMARY – Plasma synthesis of gold nanoparticles

- Stabilizer-free nanoparticle synthesis
- The size depends on the concentration of precursor

Work in progress …

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THANK YOU !

Questions ?