



JED397: Physics and Chemistry of Materials Doctoral School Days

Degradation of organic pollutants by a new eco-compatible process

Molecular approach using FTIR-ATR at the surface-water interface

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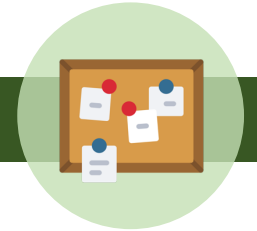
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2 & 3 November 2023

Our motivation

Increase of **organic pollutants** in nature

- Insecticides, herbicides
- Plasticizers, surfactants, chlorinate solvents
- **Antibiotics**, analgesics, hormones



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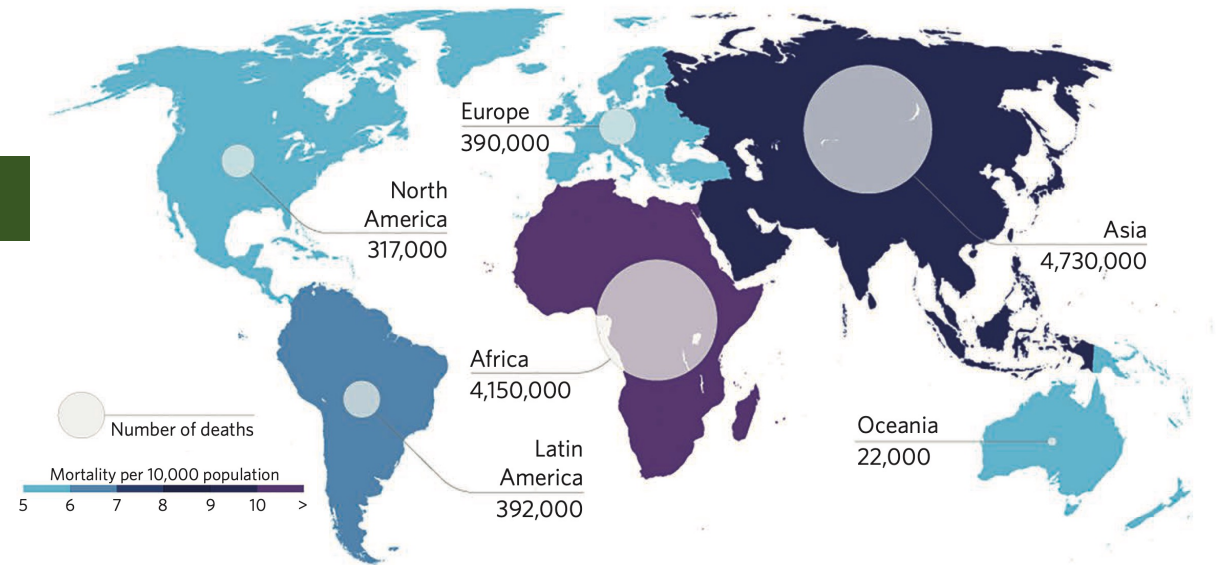


Fig 1. Deaths attributable to antimicrobial resistance every year by 2050.¹

The problematic

- **Poorly biodegradable** → **accumulate**
- **↗ input** → **↗ toxicological concerns**
- **Potential risks** to human health and aquatic life

¹ Sugden, R. *et al.* *Nature Microbiology* (2016).

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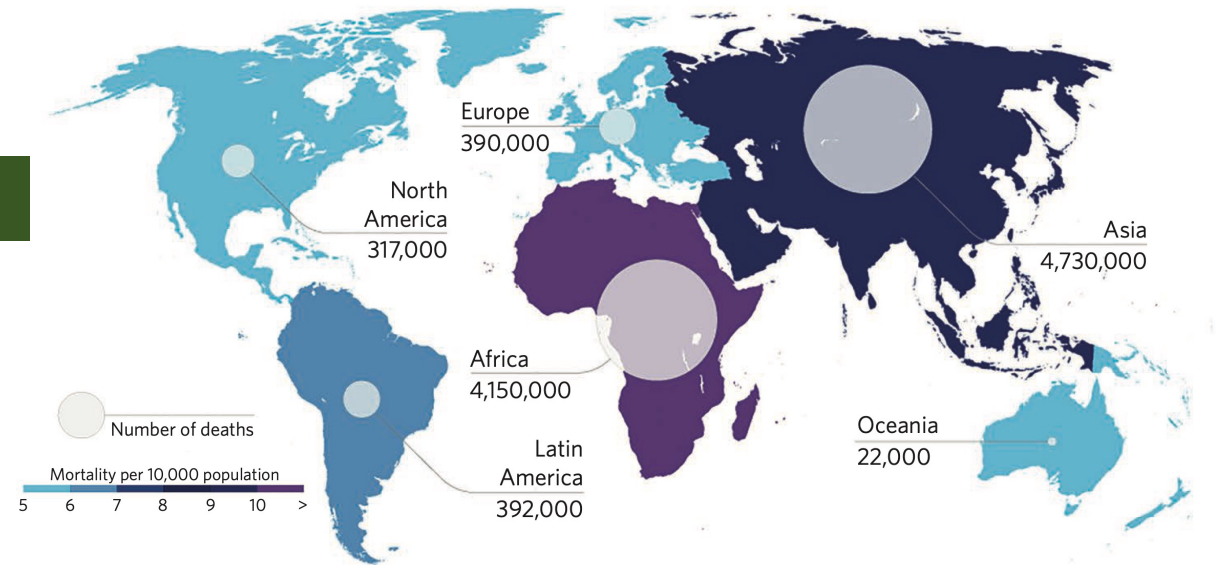


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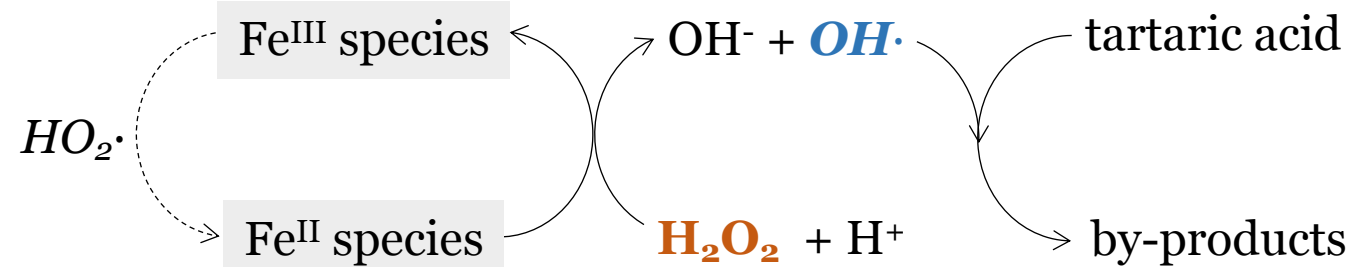
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Goal

- ❑ **Remediation processes**
 - Advanced Oxidation Processes (AOPs)
 - Exploring **Fenton-based reactions**

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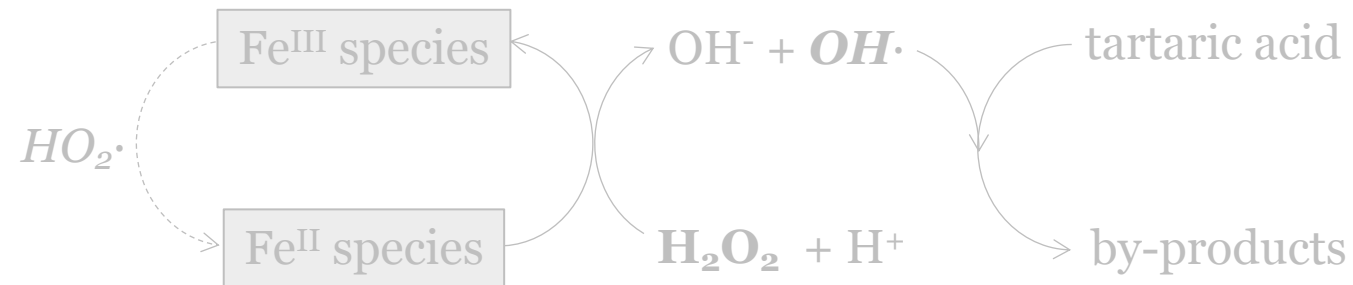
The classical reaction Fenton²

- Use of **strong oxidants** for *hydroxyl generation*

Fenton-based reactions

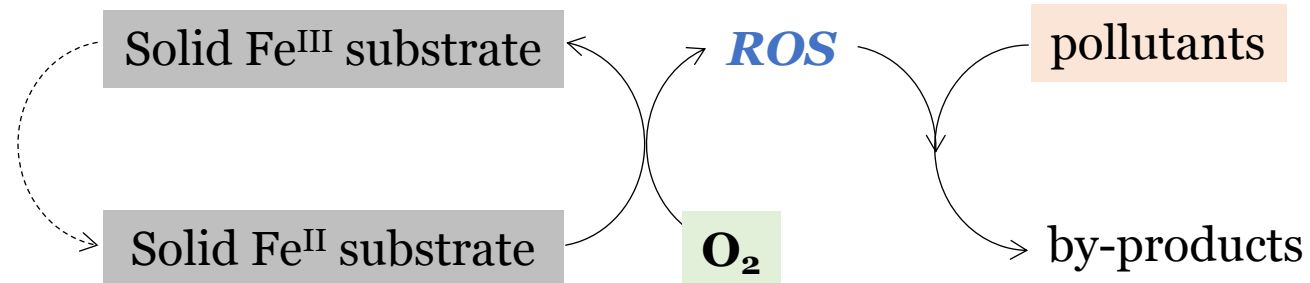
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The classical reaction Fenton²



- Use of strong oxidants for *hydroxyl generation*

Target: a new eco-compatible process³



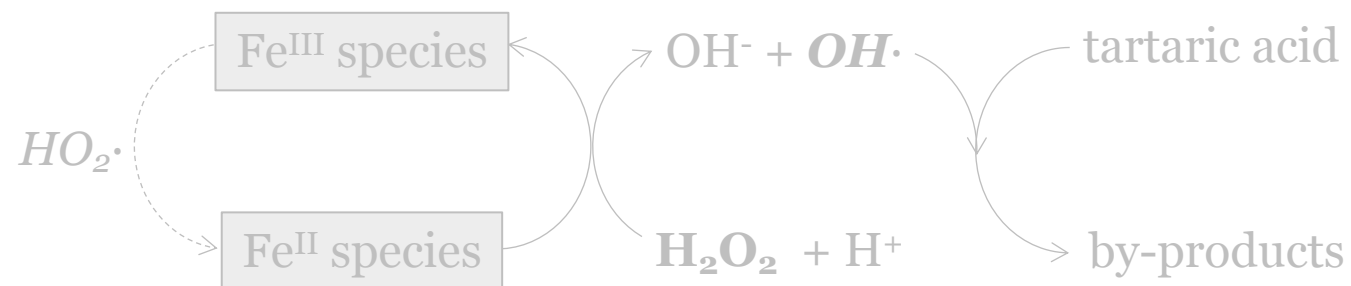
- Use of **less aggressive oxidants** for *Reactive Oxygen Species* generation

Fenton-based reactions

² Fenton, H. *Journal of the Chemical Society* (1894).

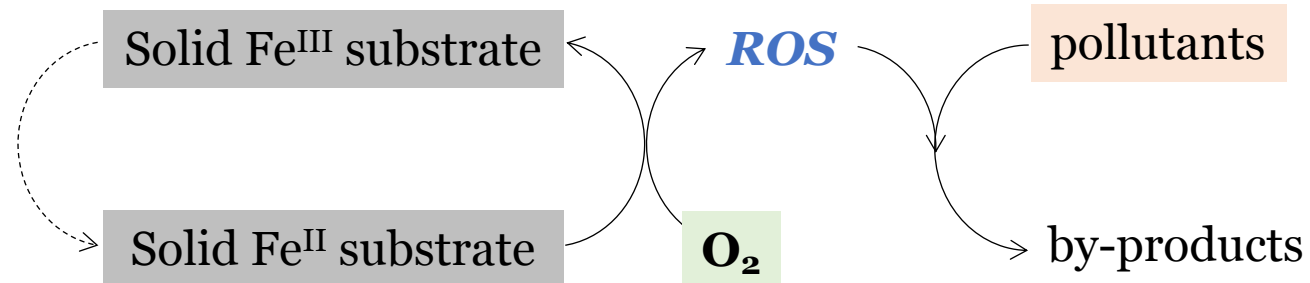
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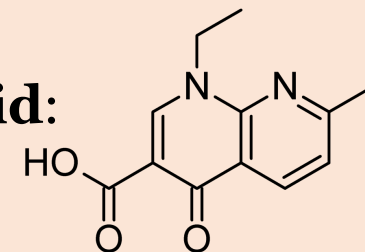
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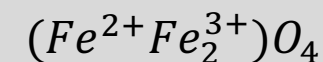
Oxygen:
oxidant agent



Nalidixic acid:
antibiotic



Magnetite:
iron oxide



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Oxidative Degradation of Nalidixic Acid by Nano-magnetite via Fe^{2+}/O_2 -Mediated Reactions

Sandy G. Ardo,[†] Sylvie Nélieu,[‡] Georges Ona-Nguema,[†] Ghislaine Delarue,[‡] Jessica Brest,[†] Elsa Pironin,[†] and Guillaume Morin^{*†}

² Fenton, H. *Journal of the Chemical Society* (1894).

³ Ardo, S. et al. *Environmental Science & Technology* (2015).

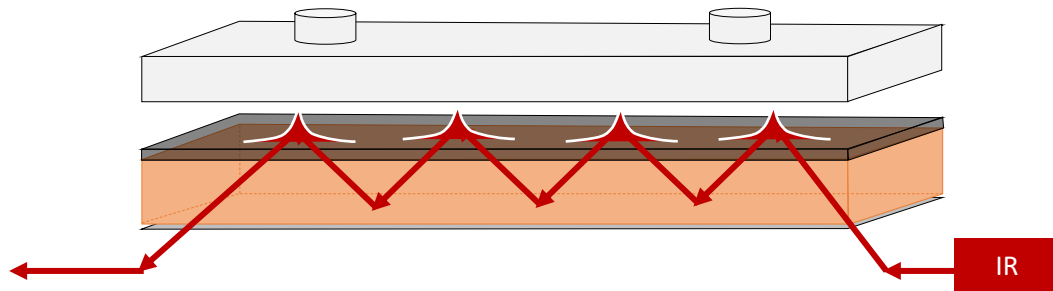
Objective → Obtain **kinetics information** and propose **mechanism**

Experimental: → Rapid Scan Infrared Spectroscopy in **Attenuated Total Reflectance** mode (ATR-FTIR)



ATR advantages:

- ✓ **Surface selective**
- ✓ Attenuates **strong signals** from liquid phase



Objective → Obtain **kinetics information** and propose **mechanism**

→ Rapid Scan Infrared Spectroscopy in **Attenuated Total Reflectance** mode (ATR-FTIR)

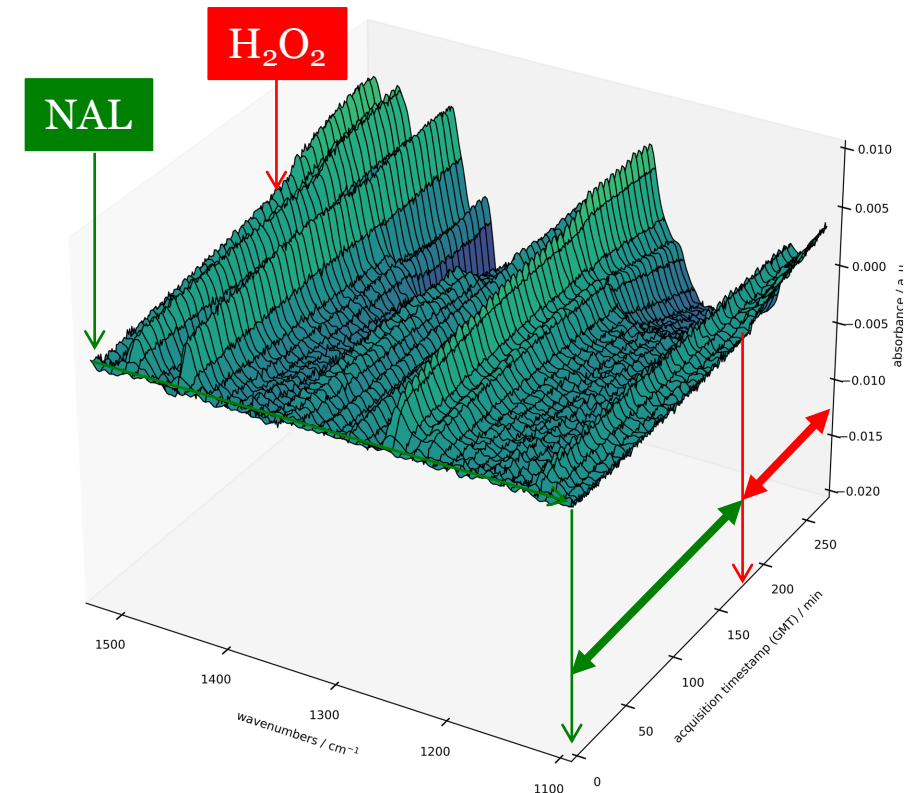
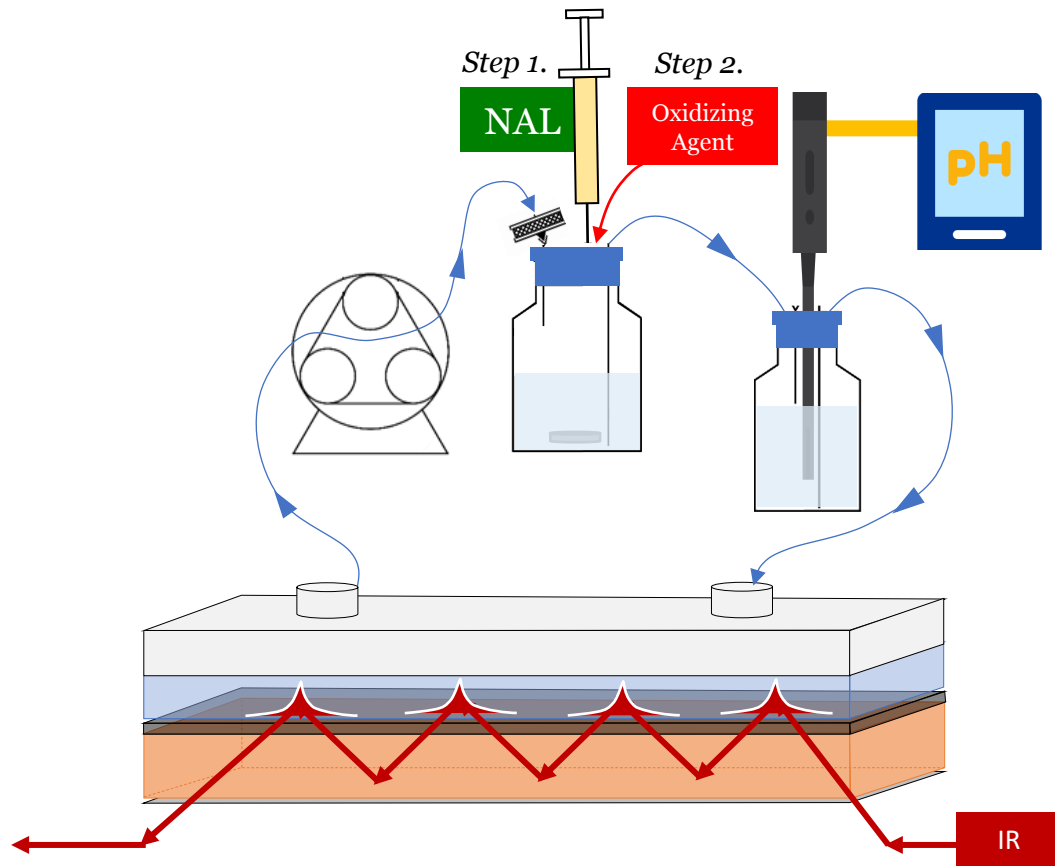


Fig. 4: Pollutants **adsorption** and **reduction** triggered by H_2O_2 (3h+1.5h)

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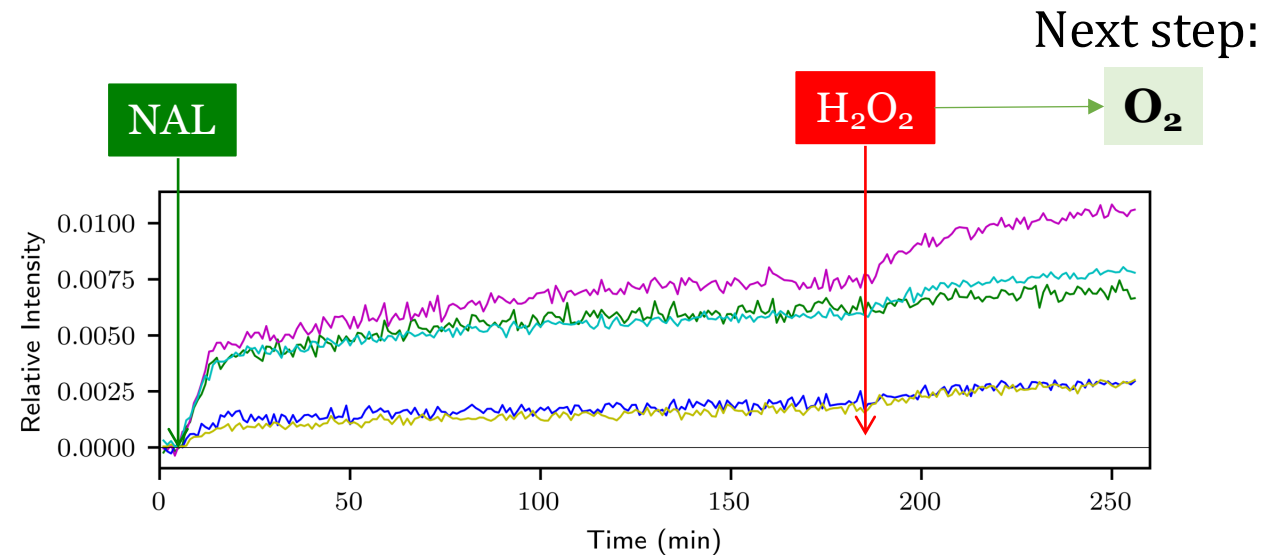
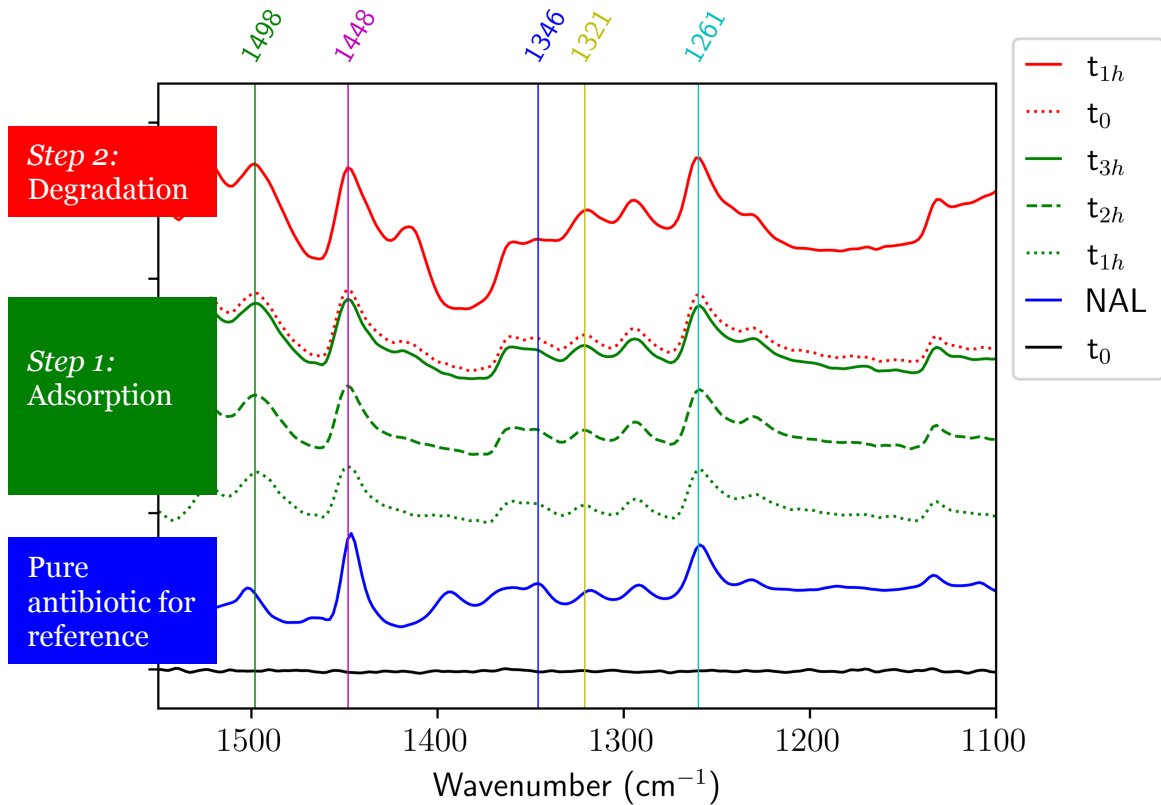


Fig. 5: Followed degradation kinetics after adsorption step.



Conclusions:

- ✓ Characterization protocol established;
- ✓ Full molecular assignment for adsorption;
- ✓ On-going experiments using O₂ as oxidizing agent;

Perspective:

- Propose reaction mechanism;
- Explore substrates/pollutants.

*Thank you
for your attention!*

Let's chat!

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Degradation of organic pollutants by a new eco-compatible process: Kinetic approaches using FTIR-ATR at the surface-water interface

Ana.C.S Frantz^{1,2}, Alberto Mezzetti¹, Guillaume Morin², Xavier Carrier¹

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²Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie (IMPMC), UMR 7596, CNRS - Sorbonne Université, Paris, France

- The problematic**
 - of organic pollutants in nature
 - Poorly biodegradable → accumulation
 - Toxic in low concentrations → potential risks to human health and aquatic life.
 - Presence of antibiotics reverberates in antimicrobial resistance (AMR)
 - Need for remediation processes
- Remediation via Fenton-based techniques**
 - The Fenton reaction mechanism in aqueous phase⁽¹⁾
 $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH \cdot + OH^-$
 - Explores the iron redox cycle for OH[•] generation
 - Optimal in acid conditions (pH ~3)
 - Requires strong oxidants, H₂O₂
- Objectives**
 - Heterogeneous Fenton-based remediation with O₂ as oxidant⁽²⁾
 - Explores iron redox cycle for Reactive Oxygen Species (ROS) generation at neutral pH
 - Less aggressive oxidants, O₂
 - How are pollutants degraded by only using O₂ as oxidant at neutral pH with geo-inspired Fe(II)-rich substrates?
- Infrared spectroscopy in Attenuated Total Reflectance mode, FTIR-ATR**
 - Obtain kinetics information and propose degradation mechanism
 - Allows solid-liquid interface characterization
 - ZnSe crystal with multi-reflections
 - Evanescent wave, $d_p = \frac{2\lambda}{2n_1 \sin^2 \theta - n_2^2}$
 - IR beam
 - ATR advantages:
 - Attenuates strong signals coming from the liquid phase
 - Surface selective
 - Operational flow system: Prepared in glovebox (O₂ < 6 ppm), FTIR-ATR following happens in 2 steps:
 - Antibiotics adsorption onto Fe(II)-rich substrate
 - Adsorbed species degradation via ROS generation due to substrate oxidation
 - IR spectra of NAL adsorbing onto magnetite (1 molecule/nm²) compared to deprotonated NAL in solution (10 mM, pH 4) → Adsorption kinetics evaluation via peak evolution⁽³⁾
 - Reproducible nalidixic acid adsorption over magnetite under flow and anoxic conditions.
 - Deprotonated NAL molecule binds to magnetite surface via bidentate mode⁽⁴⁾.

References

⁽¹⁾ H. Fenton, *Ann. Chim. Phys.* (1836), 24, 336-354.
⁽²⁾ H. Fenton, *Ann. Chim. Phys.* (1836), 24, 336-354.
⁽³⁾ L. Li, et al. *ACS Applied Materials* (2016).
⁽⁴⁾ D. G. Evans, & C. Ferrel, *Chem. Commun.* (2007).
⁽⁵⁾ X. Li, et al. *Environmental Science & Technology* (2007).