Degradation of amoxicillin in water treated with DBD plasma

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Outline

- Introduction to my STSM
- Motivation
- Experimental setup
- Diagnostic methods
- Results
- Summary
- Next step
COST TD1208

„Electrical Discharges with Liquids for Future Applications”

- 3 weeks of Short-Term Scientific Missions (STSM) at Departament of Chemistry University of Padova, Italy

- Purpose of STSM was to use Non thermal plasma DBD discharge to degrade amoxicillin solution

- Learn HPLC/MS analysis from experienced team of prof. C. Paradisi
Motivation

- Amoxicillin is one of the main antibiotics polluting the waters

- Can DBD discharge degrade amoxicillin?

- If yes, what is the mechanism/kinetics?
Experimental set up

- Glass reactor (95x75x60 mm)
- Power supply: AC (50 Hz; 16-18 kV)
- 2 parallel wires (0.15 mm diam., 73 mm length, 38 mm one to other)
- Distance wire - solution: 15 mm
- Volume of treated solution: 70 mL
Diagnostics: HPLC and FTiR

- Pump system P2000 Spectra System and diode detector UV6000LP
- Eulents:
  - 99:1 H$_2$O and acetonitrile plus phosphate buffer (20 mM) with pH of 2.2
- Column used:
  - Zorbax SB-Aq

- FTiR spectrometry using NICOLET 5700
  - CO$_2$ band at 2340 cm$^{-1}$
  - Humid air flow passing through the reactor at 30 mL/min
Mass Spectrometry

- Positive polarity
- N₂ dry gas temperature 350°C
- N₂ 10 L/min
- Capillary voltage 4000 V
- Eluents:
  - Acetonitril + 0.1% formic acid
  - H₂O + 0.1% formic acid
  - Gradient from 5% to 100% in 20 min
- Column used:
  - Gemini C18 150 x 4.6

Agilent Technologies mass spectrometer with ion trap MSD Trap SL model G2245D with ESI and HPLC series 1100 with binary pump model G1312A
RESULTS

**CO₂ measurement**

100 % of carbon mass emitted

5 % of carbon mass emitted
HPLC results

Init. concentration $3 \times 10^{-4}$ M

**A** – Amoxicillin
**P1** – Degradation product 1
**P2** – Degradation product 2
**N** – Nitric acid

**HPLC chromatogram of amoxicillin degradation**

**Degradation of amoxicillin and reaction constants**

<table>
<thead>
<tr>
<th>init. conc. (M)</th>
<th>$k$ (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3 \times 10^{-4}$</td>
<td>$k_1 = 0.0237$</td>
</tr>
<tr>
<td>$10^{-5}$</td>
<td>$k_0 = 0.07$</td>
</tr>
</tbody>
</table>
Amoxicillin MS

Amoxicillin and fragmentation spectra at retention time of 4.1 min
Degradation product P2 eluted with retention time of 2.2 min is a di-hydroxylated product of mass 398 m/z. A possible structural attribution is shown.
Degradation products P1 and P3 eluted with retention times of 1.7 and 2.5 min, respectively.

Oxidation of aliphatic acid in two different positions amoxicillin of mass 382 m/z
Summary

DBD discharge degradation of amoxicillin

- Degradation rate constant is higher when the initial concentration is lower
- Can achieve 100% degradation but degradation fragments still remain
- CO$_2$ is one of the products

<table>
<thead>
<tr>
<th>#</th>
<th>Retention time (min)</th>
<th>MS fragments (m/z)</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.7</td>
<td>148; 189; 247; 274; 337; 365; 382</td>
<td>Identified as P1</td>
</tr>
<tr>
<td>2</td>
<td>2.2</td>
<td>148; 176; 233; 291; 370; 381; 398</td>
<td>Identified as P2</td>
</tr>
<tr>
<td>3</td>
<td>2.5</td>
<td>148; 189; 247; 274; 337; 365; 382</td>
<td>Identified as P3</td>
</tr>
<tr>
<td>4</td>
<td>4.3</td>
<td>114; 160; 208; 366; 388</td>
<td>Amoxicillin (A)</td>
</tr>
</tbody>
</table>
Spark in water

**REACTOR PARAMETERS:**
- Cylindrical reactor made of PTFE
- Inner diameter: 25 mm
- High voltage electrode -> Stainless steel hypodermic needle, inner diameter: 1.6 mm
- Outer diameter: 2 mm
- Grounded electrode -> Stainless steel rod, diameter: 5 mm
- Gap between the electrodes: from 3 mm
- Water flow 30 ml/min
HPLCMS triple quadrupole

- Shimadzu LCMS-8040
- Eluents:
  - Acetonitril + 0.1% formic acid
  - H₂O + 0.1% formic acid
  - Gradient from 5% to 95% in 10 min
- Column used:
  - Kinetex C18

- Q3 SIM for 366 m/z
- At retention time 1.6 min