Preventing the Rising Tide of AMR: Utilising MOFs to Remove Antibiotics from Wastewater

Aoife Quinlivan
University of Nottingham, UK
aoife.quinlivan@nottingham.ac.uk
The challenges of global water pollution: antibiotics as emerging pollutants and drivers for antimicrobial resistance

Sorbents as potential solutions: introducing metal-organic frameworks for wastewater remediation

Application of metal-organic frameworks for antibiotic removal from water matrices: towards achieving a circular economy
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Emerging Pollutants and Antibiotics

COMMISSION IMPLEMENTING DECISION (EU) 2020/1161
of 4 August 2020

establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council

Watch list of substances for Union-wide monitoring as set out in Article 8b of Directive 2008/105/EC

<table>
<thead>
<tr>
<th>Name of substance/group of substances</th>
<th>CAS number (1)</th>
<th>EU number (1)</th>
<th>Indicative analytical method (1) (2)</th>
<th>Maximum acceptable method detection limit (ng/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amoxicillin</td>
<td>26787-78-0</td>
<td>248-003-8</td>
<td>SPE-LC-MS-MS</td>
<td>78</td>
</tr>
<tr>
<td>Ciprofloxacin</td>
<td>85721-33-1</td>
<td>617-751-0</td>
<td>SPE-LC-MS-MS</td>
<td>89</td>
</tr>
<tr>
<td>Sulfamethoxazole (1)</td>
<td>723-46-6</td>
<td>211-963-3</td>
<td>SPE-LC-MS-MS</td>
<td>100</td>
</tr>
<tr>
<td>Trimethoprim (1)</td>
<td>738-70-5</td>
<td>212-006-2</td>
<td>SPE-LC-MS-MS</td>
<td>100</td>
</tr>
</tbody>
</table>
Antibiotics: Environmental Sources & Consequences

Sources

Consequences

Accelerate antimicrobial resistance (AMR)

10 million deaths a year by 2050

24 million people in extreme poverty by 2030

Top 10 global health threat


aoife.quinlivan@nottingham.ac.uk  Challenge: antibiotics pollution in water  » Solution: MOFs as sorbents  » Application: removal of antibiotics using MOFs
To develop a process to **remove antibiotics** from municipal **wastewater** using **metal-organic frameworks**. The end goal of the project is to develop an **industrially viable** wastewater treatment technology.
The challenges of global water pollution: antibiotics as emerging pollutants and drivers for antimicrobial resistance

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The Challenge of Antibiotic Removal from Waters

Advanced Wastewater Treatment Technologies

- **Oxidation**
  - Expensive
  - Creates toxic byproducts

- **Biodegradation**
  - One microbe will not degrade all antibiotics
  - Produces contaminated sludge

- **Membranes**
  - Unsuitable pore sizes
  - Difficult to clean and maintain

Sorption – promising treatment technology

Sorbents used to remove antibiotics

- **Granular activated carbon**
  - Expensive
  - Large quantities needed
  - Larvae growth increases maintenance

- **Zeolites**
  - Limited functionality
  - Low sorption capacities

Other materials that can be used as sorbents...

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Metal-Organic Frameworks (MOFs) as Sorbents

• Permanent porosity – high sorption capacity
• Ability to functionalise the linkers – selective sorption
• Can be stable in water
• Tunable particle size

For MOFs to be industrially viable they must:

1. Be readily and cheaply available
2. Remove target contaminant from water
3. Function under application conditions
4. Be regenerated for reuse


challenge: antibiotics pollution in water » solution: MOFs as sorbents » application: removal of antibiotics using MOFs
Introducing the MOF: MIL-100(Fe)

Components

Fe$^{3+}$
Lewis Acid

OH

OH

+ 

COOH

HO

CO

HO

CO

Ligand

Properties

Pore openings
~ 6 & 9 Å

Surface area
1797 m$^2$/g

Good stability in water

Can remove ciprofloxacin from water

Synthesis

Microwave, 6 min, 300 W

130 °C

15 mL H$_2$O

FeCl$_3$

Product Recovery

Orange powder

1. J. Mater. Chem. A, 2018, 6, 11564-11581  

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Antibiotic Sorption from Water using MIL-100(Fe)

Must be able to remove target contaminant under *wastewater-relevant* conditions

- **Temperature** (10-25 °C)
- **pH** (6-8)
- **Concentration** (ng/L-µg/L)

**Amoxicillin antibiotic (AMX)**

β-lactam

WHO List of Essential Medicines¹

Recommended for EC's 3rd Watch List²

Present in water in high concentrations

**Incubator**

Changing **AMX concentration**

- 50, 100 & 300 µg/L
- 20 °C
- 24 h

Changing **water temperature**

- 5, 10 & 20 °C
- 100 µg/L
- 24 h


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As AMX antibiotic concentration increases, the sorption capacity increases

- Increased difference in concentration gradient between antibiotic solution and MOF sorbent
- Via the mass transfer process

Unrealistically high pollutant concentrations will result in higher sorption capacities

Unlikely that the sorbent will perform at lower concentrations

Sorption experiments must be done using real-world pollutant concentrations
AMX Sorption using MIL-100(Fe): varying concentration

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As the **temperature** of the water **increases**, the **sorption capacity** **decreases**

- Sorption of AMX onto MIL-100(Fe) is an **endothermic process**
- Equilibrium reached **faster** at **lower temperatures**

Temperature impacts the **sorption capacity** and the **rate of sorption**

Wastewater **temperature varies** with **location** and **time of year**

**Sorbents** need to be **tested** within a range of **realistic temperatures**
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AMX Sorption using MIL-100(Fe): real wastewater effluent

MIL-100(Fe) does remove amoxicillin antibiotic from real wastewater effluent

- Sorption capacity is decreased when using real wastewater effluent
- Due to the presence of other pollutants which may compete for sorption onto MIL-100(Fe)
- Sorption experiments must be carried out in real-world matrices
Summary

The challenge: antibiotics are emerging pollutants and need to be removed from wastewater

- Identified the need to develop technologies for antibiotic removal

Sorbents as potential solutions: exploring the feasibility of using metal-organic frameworks for antibiotic removal

- Suggested MOFs as sorbents and introduced MIL-100(Fe)

Application of metal-organic frameworks for antibiotic removal from water matrices: towards achieving a circular economy

- Presented results using MIL-100(Fe) to remove AMX from water and wastewater
Conclusions and Next Steps

**Conclusions**

- **Antibiotic concentration** and **water temperature** influence **removal capacity**
- Sorbents must be tested under **real-world conditions**
- MIL-100(Fe) is able to **remove** AMX from **real wastewater effluent**

**Next steps**

- Carry out further sorption experiments using **wastewater effluent**
- **Characterise** MIL100(Fe) **after** sorption experiments to investigate **sorbent-sorbate interactions**
- Sorption experiments using MIL100(Fe) and **other antibiotics**
Acknowledgements

• Rachel Louise Gomes
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Thank you for listening

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