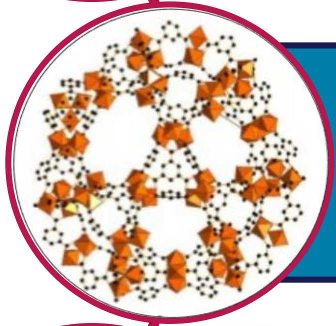
Preventing the Rising Tide of AMR: Utilising MOFs to Remove Antibiotics from Wastewater

Aoife Quinlivan

University of Nottingham, UK
aoife.quinlivan@nottingham.ac.uk

Presentation Outline

The challenges of global water pollution: antibiotics as emerging pollutants and drivers for antimicrobial resistance

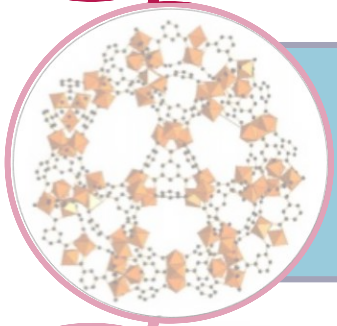


Sorbents as potential solutions: introducing metal-organic frameworks for wastewater remediation

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

Presentation Outline

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

Emerging Pollutants and Antibiotics

COMMISSION IMPLEMENTING DECISION (EU) 2020/1161

of 4 August 2020

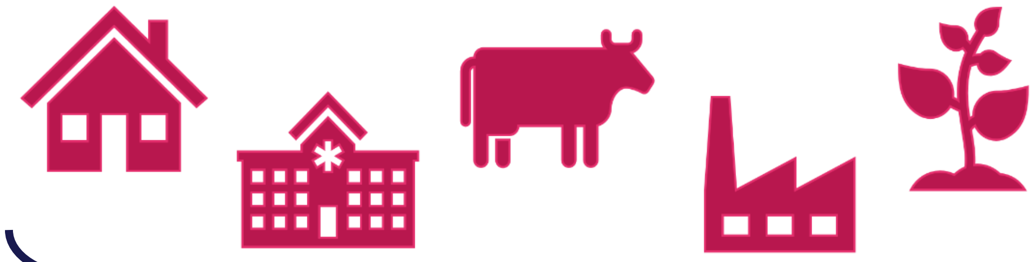
establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council

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

Name of substance/group of substances	CAS number (1)	EU number (2)	Indicative analytical method (3) (4)	Maximum acceptable method detection limit (ng/l)
Amoxicillin	26787-78-0	248-003-8	SPE-LC-MS-MS	78
Ciprofloxacin	85721-33-1	617-751-0	SPE-LC-MS-MS	89
Sulfamethoxazole (5)	723-46-6	211-963-3	SPE-LC-MS-MS	100
Trimethoprim (5)	738-70-5	212-006-2	SPE-LC-MS-MS	100

Antibiotics: Environmental Sources & Consequences

Sources



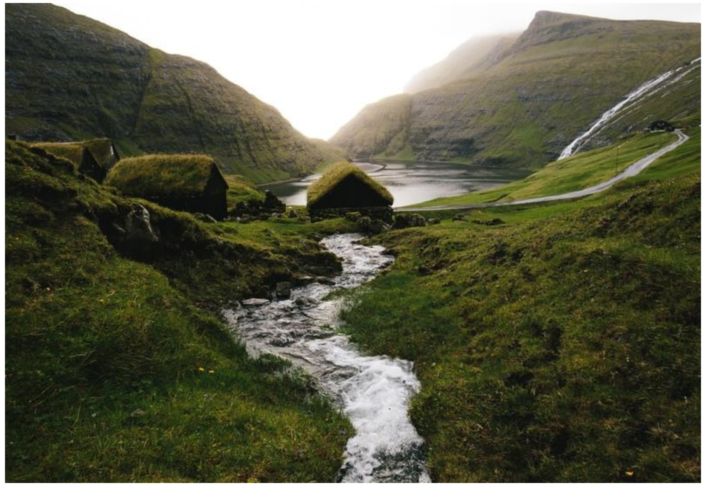
Consequences

Accelerate **antimicrobial resistance** (AMR)

10 million deaths a year by 2050

24 million people in extreme poverty by 2030

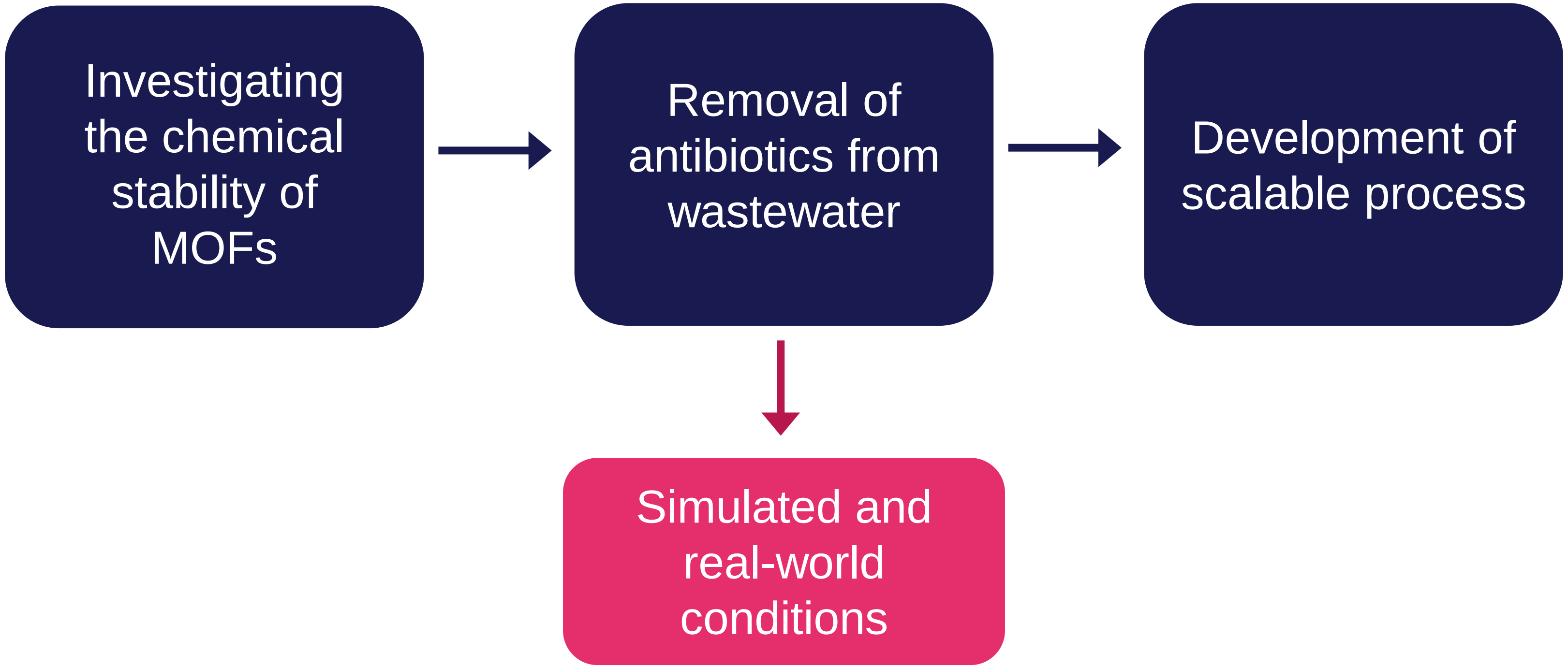
Top 10 global health threat



Chemosphere, 2009, **75**, 417-434. 2. UK Government, *Tackling Antimicrobial Resistance 2019-2024*, London, 2019.

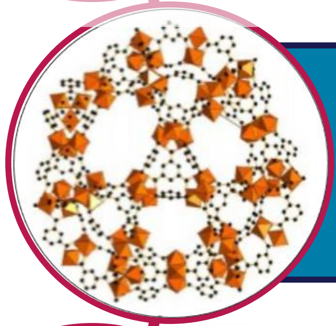
Research Overview

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.



Presentation Outline

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

The Challenge of Antibiotic Removal from Waters

Advanced Wastewater Treatment Technologies

- **Oxidation**
  - x Expensive
  - x Creates toxic biproducts
- **Biodegradation**
  - x One microbe will not degrade all antibiotics
  - x Produces contaminated sludge
- **Membranes**
  - x Unsuitable pore sizes
  - x Difficult to clean and maintain

Sorption – promising treatment technology

Sorbents used to remove antibiotics

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

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

Other materials that can be used as **sorbents…**

Chem. Rev., 2019, **119**, 3510-3673.

The Challenge of Antibiotic Removal from Waters

Advanced Wastewater Treatment Technologies

- **Oxidation**
  - x Expensive
  - x Creates toxic biproducts
- **Biodegradation**
  - x One microbe will not degrade all antibiotics
  - x Produces contaminated sludge
- **Membranes**
  - x Unsuitable pore sizes
  - x Difficult to clean and maintain

Sorption – promising treatment technology

Sorbents used to remove antibiotics

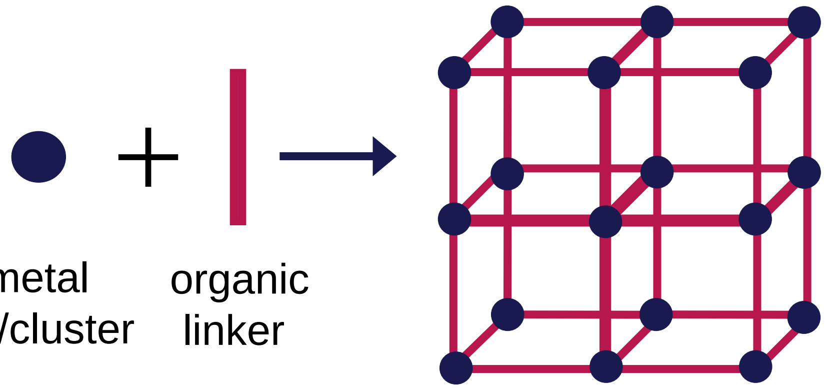
- **Granular activated carbon**
  - x Expensive
  - x Large quantities needed
  - x Larvae growth increases maintenance

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

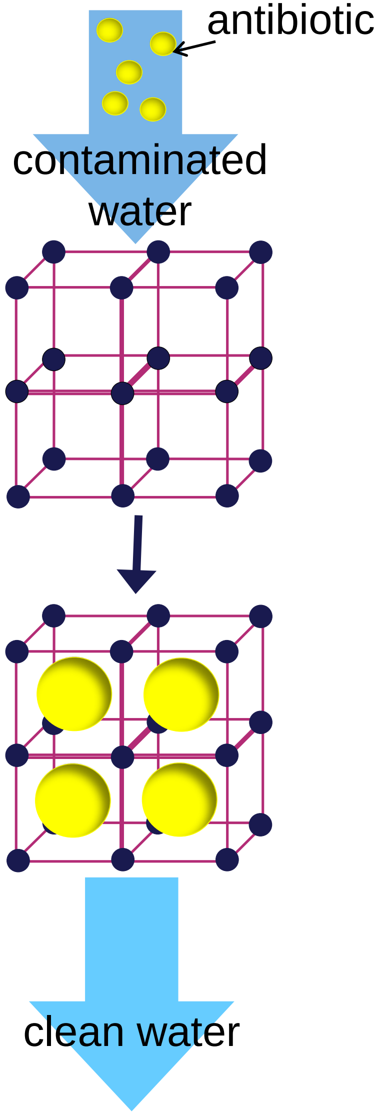
Other materials that can be used as **sorbents…**

Chem. Rev., 2019, **119**, 3510-3673.

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

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

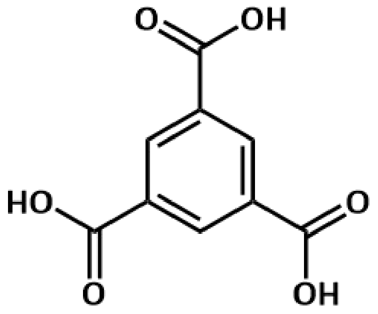
Introducing the MOF: MIL-100(Fe)

Components

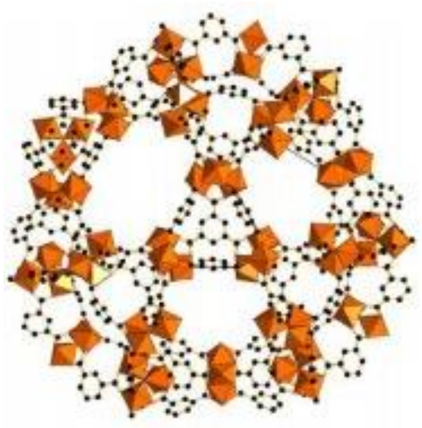
Fe^{3+}

Lewis Acid

+



Ligand



Properties

Pore openings
~ 6 & 9 Å[1]

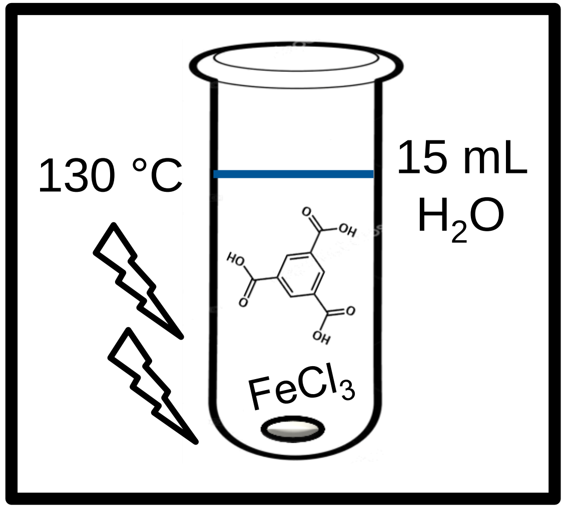
Surface area
1797 m^2/g

Good **stability** in water

Can **remove ciprofloxacin** from water[2]

Synthesis

Microwave, 6 min, 300 W



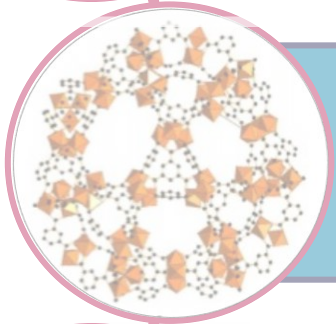
Product Recovery

Orange powder

1. *J. Mater. Chem. A*, 2018, **6**, 11564-11581 2. *J. Iran. Chem. Soc.*, 2016, **13**, 1617–1627.

Presentation Outline

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

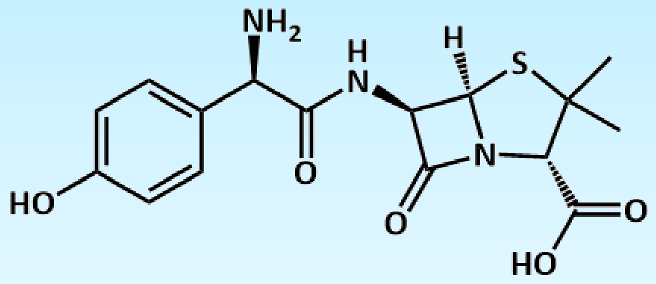
Application of metal-organic frameworks for antibiotic removal from water matrices: towards achieving a circular economy

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)

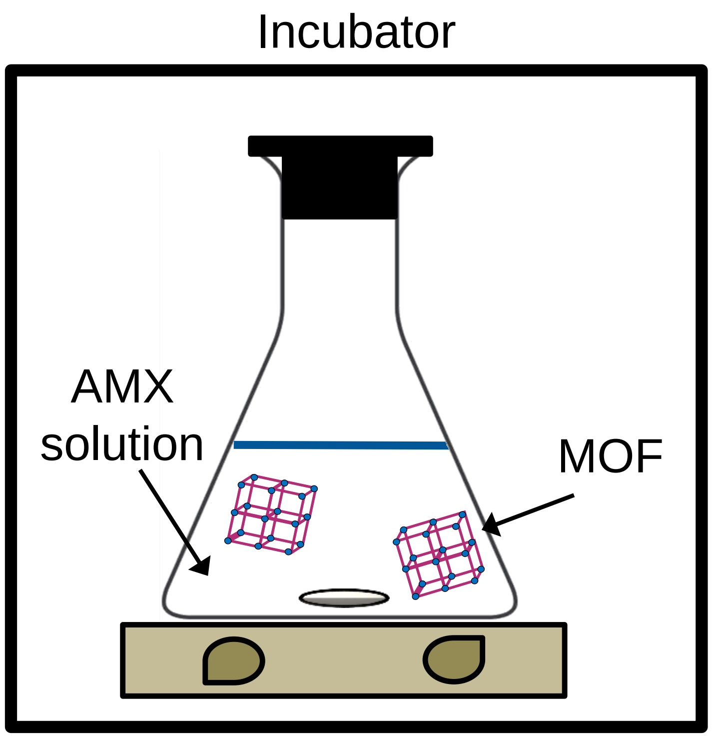
Amoxicillin antibiotic (AMX)
β-lactam



WHO List of Essential Medicines[1]

Recommended for EC's 3rd Watch List[2]

Present in water in high concentrations



Changing **AMX concentration**

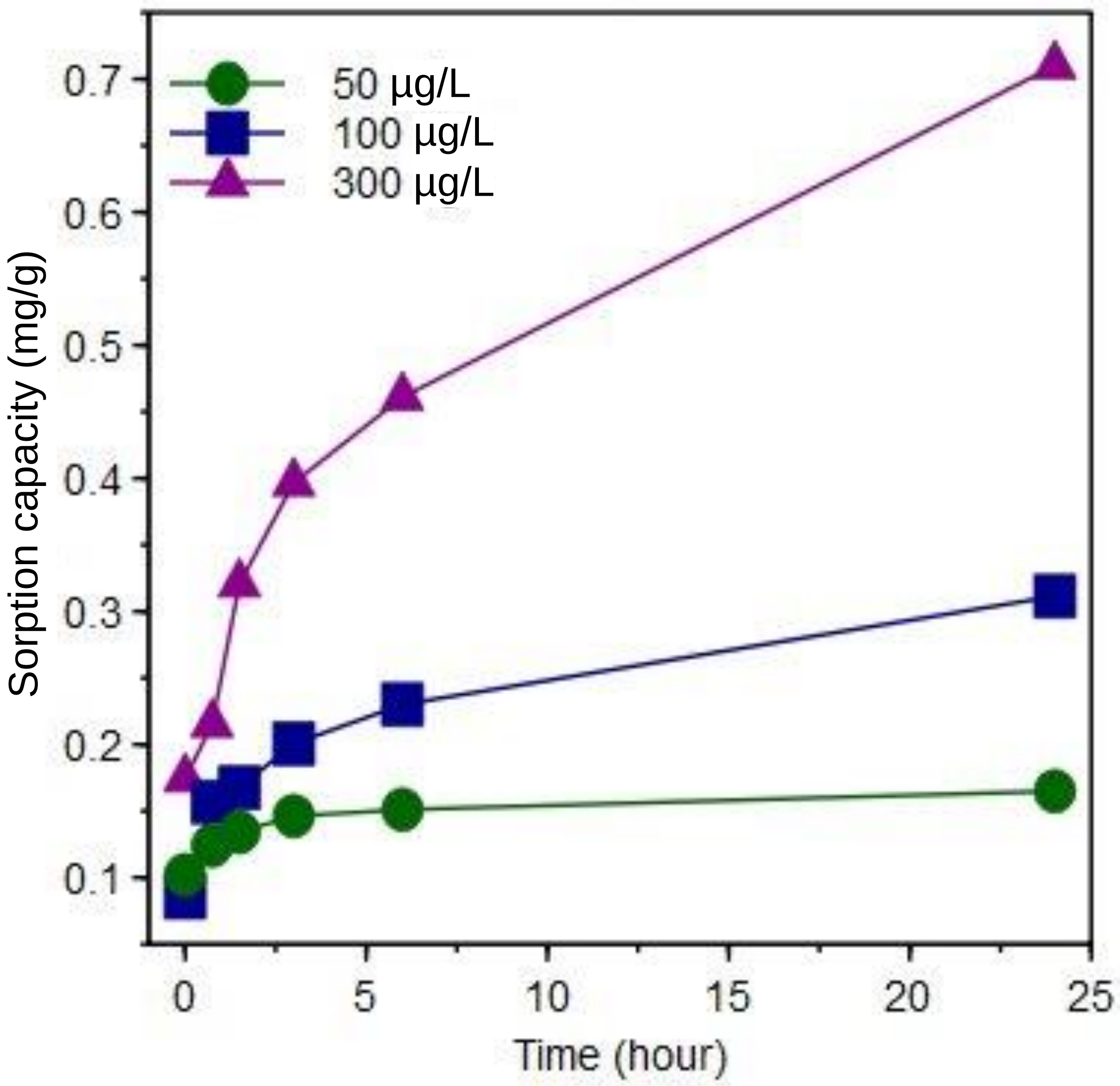
- 50, 100 & 300 µg/L
- 20 °C
- 24 h

Changing **water temperature**

- 5, 10 & 20 °C
- 100 µg/L
- 24 h

1. *WHO Model List of Essential Medicines*, 2017. 2. *Review of the 1st Watch List under the Water Framework Directive and recommendations for the 2nd Watch List,* Luxembourg, 2018.

AMX Sorption using MIL-100(Fe): varying concentration



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**

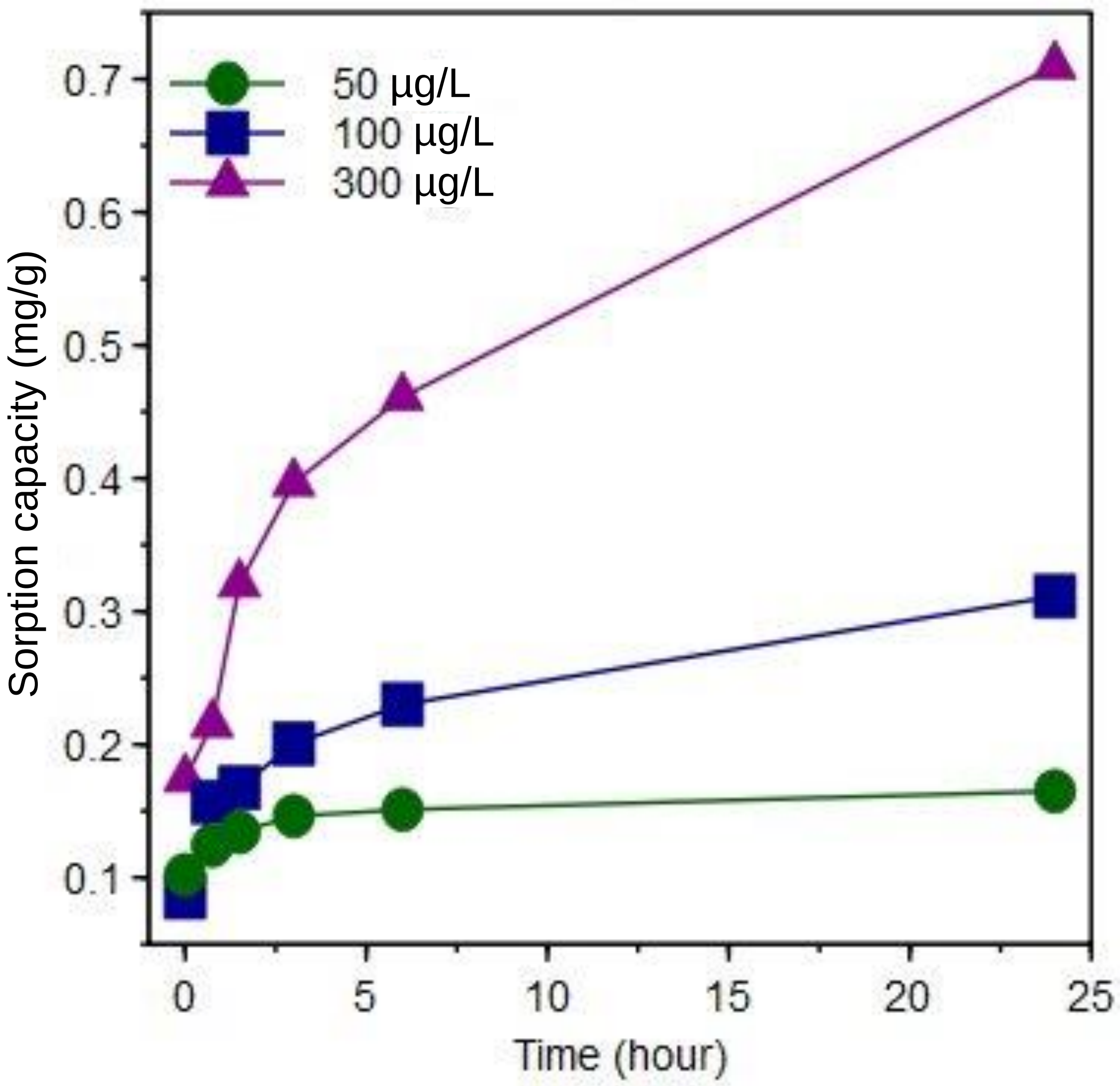
↓

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



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**

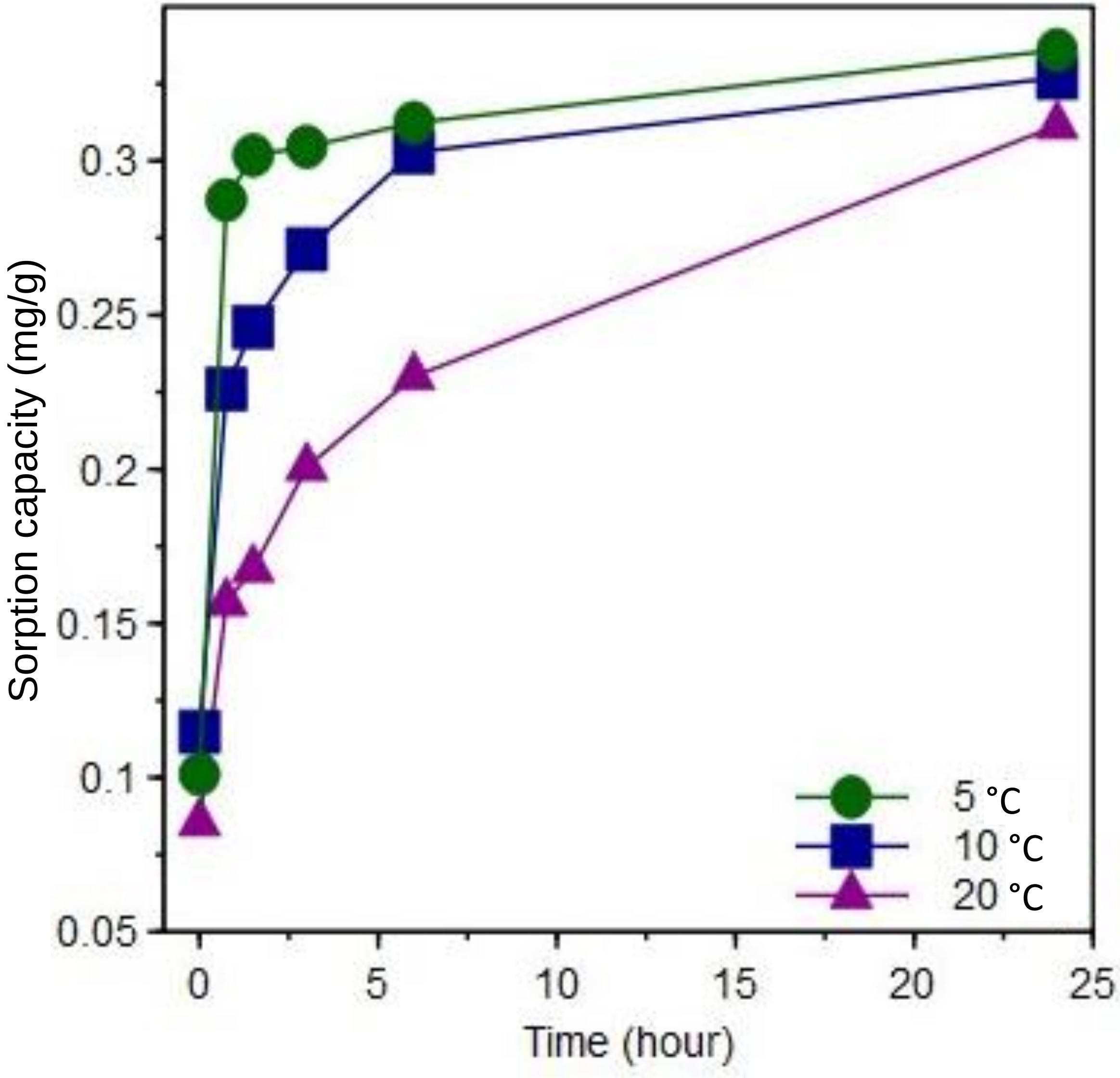
↓

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 temperature



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**

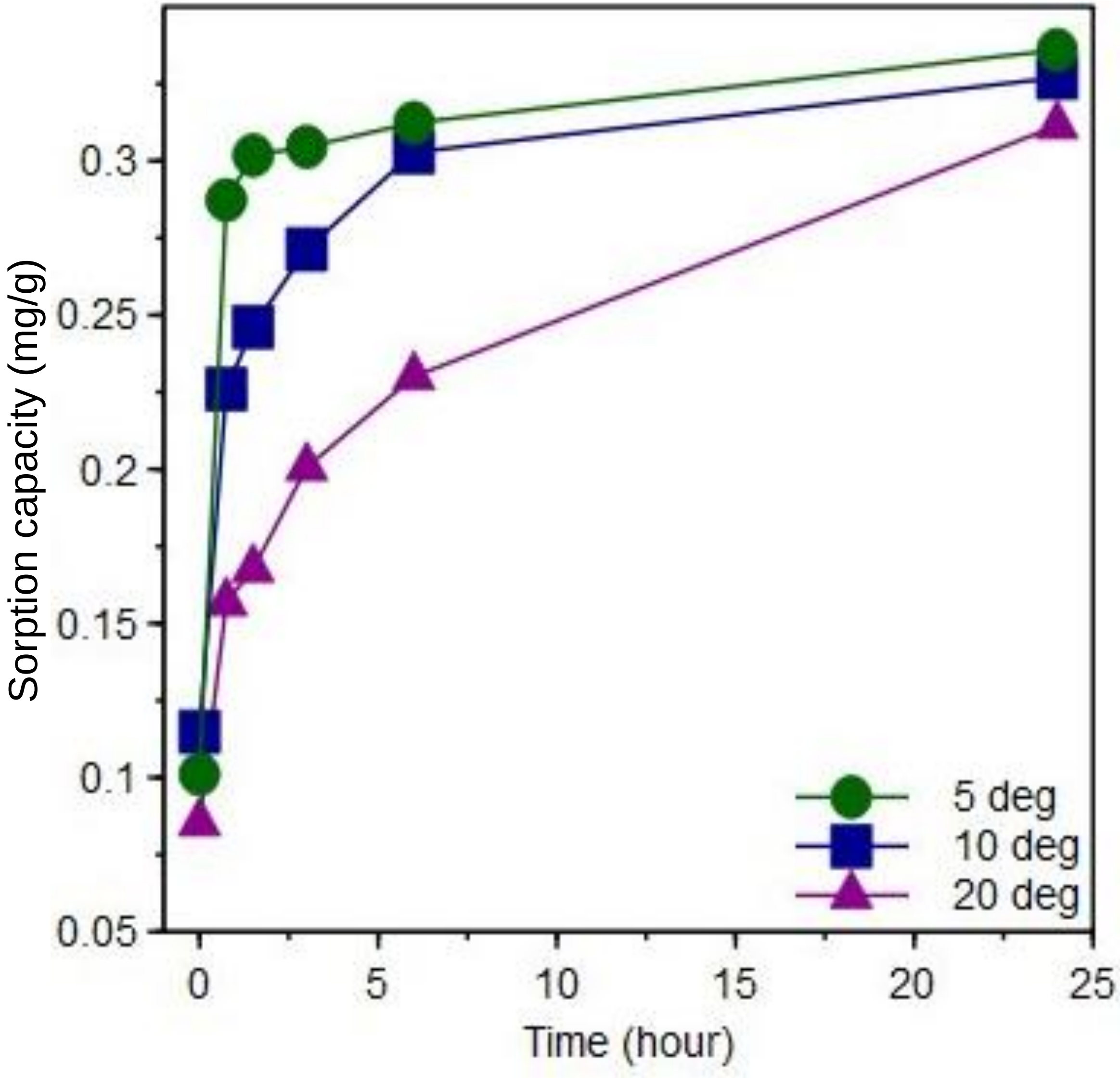
↓

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

↓

Sorbents need to be **tested** within a range of **realistic temperatures**

AMX Sorption using MIL-100(Fe): varying temperature



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**

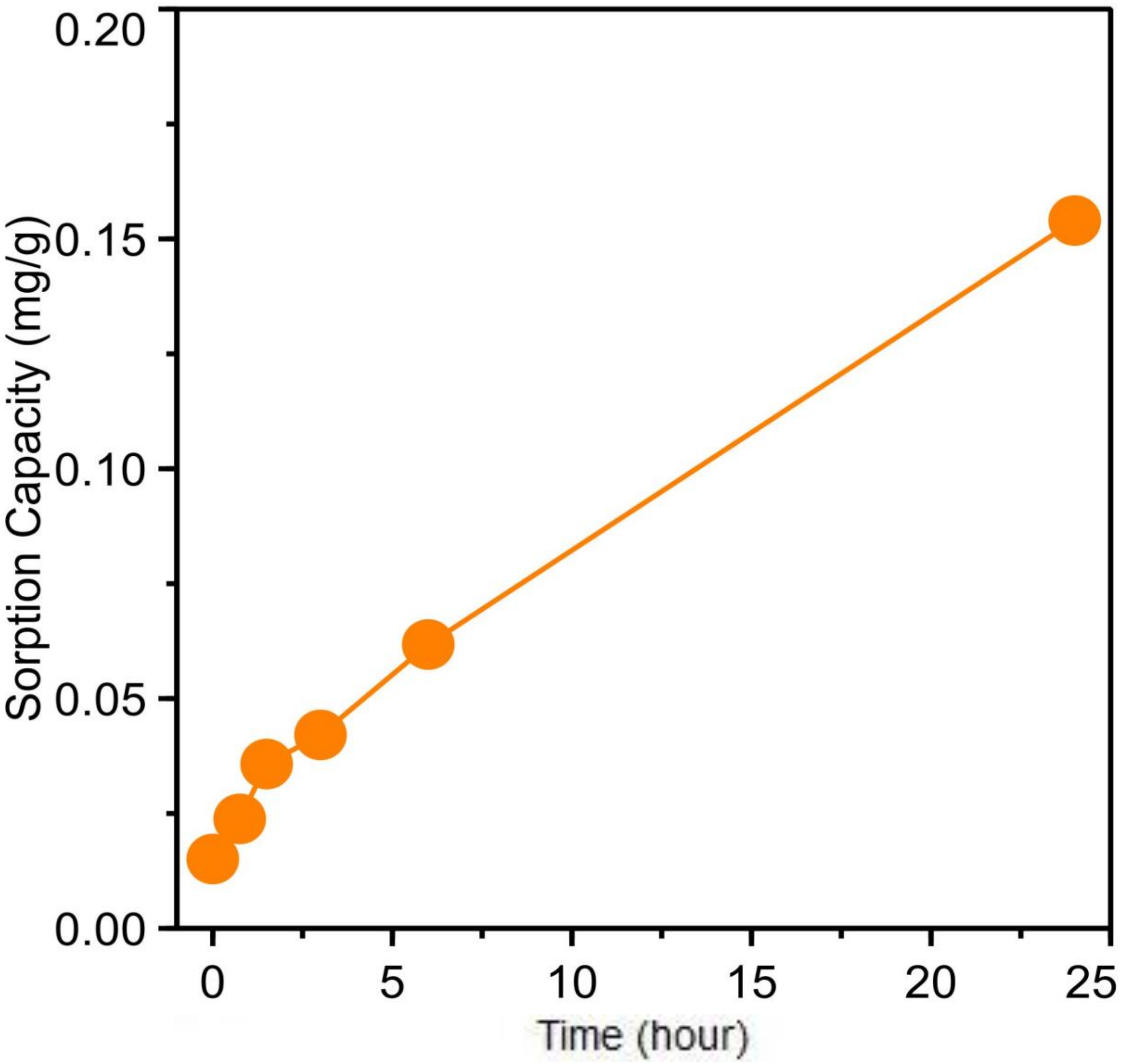
↓

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

↓

Sorbents need to be **tested** within a range of **realistic temperatures**

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)

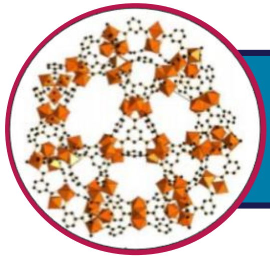
↓

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
- Andrea Laybourn
- Centre for Doctoral Training in Sustainable Chemistry
- Severn Trent Water Ltd

SEVERN TRENT

UKRI Engineering and Physical Sciences Research Council

University of Nottingham UK | CHINA | MALAYSIA

University of Nottingham

UK | CHINA | MALAYSIA

Thank you for listening

aoife.quinlivan@nottingham.ac.uk