Advances on biomass-derived microporous carbons for efficient removal of pharmaceuticals from wastewater

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Image credits: José Manuel Pereira

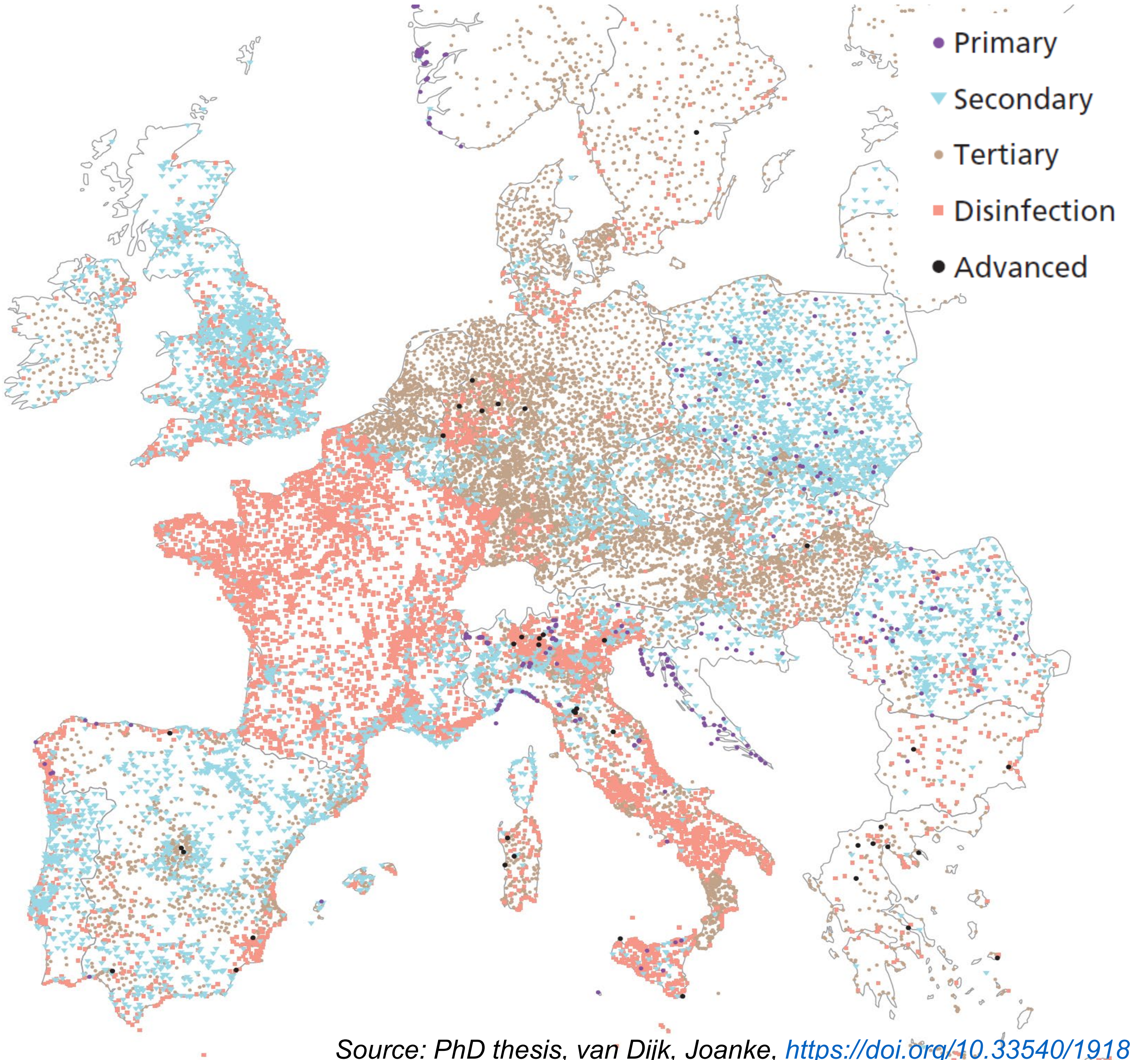
Contextualization

Chemicals released by Sewage Treatment Plants (STP) are identified as one of the **main pressures on surface water**, with **pharmaceuticals** being amongst the most representative.

Pharmaceutical emissions can be strongly reduced by STP, ranging from an average of **9 % for STP with primary treatment** to **84 % for STP with advanced treatment**!

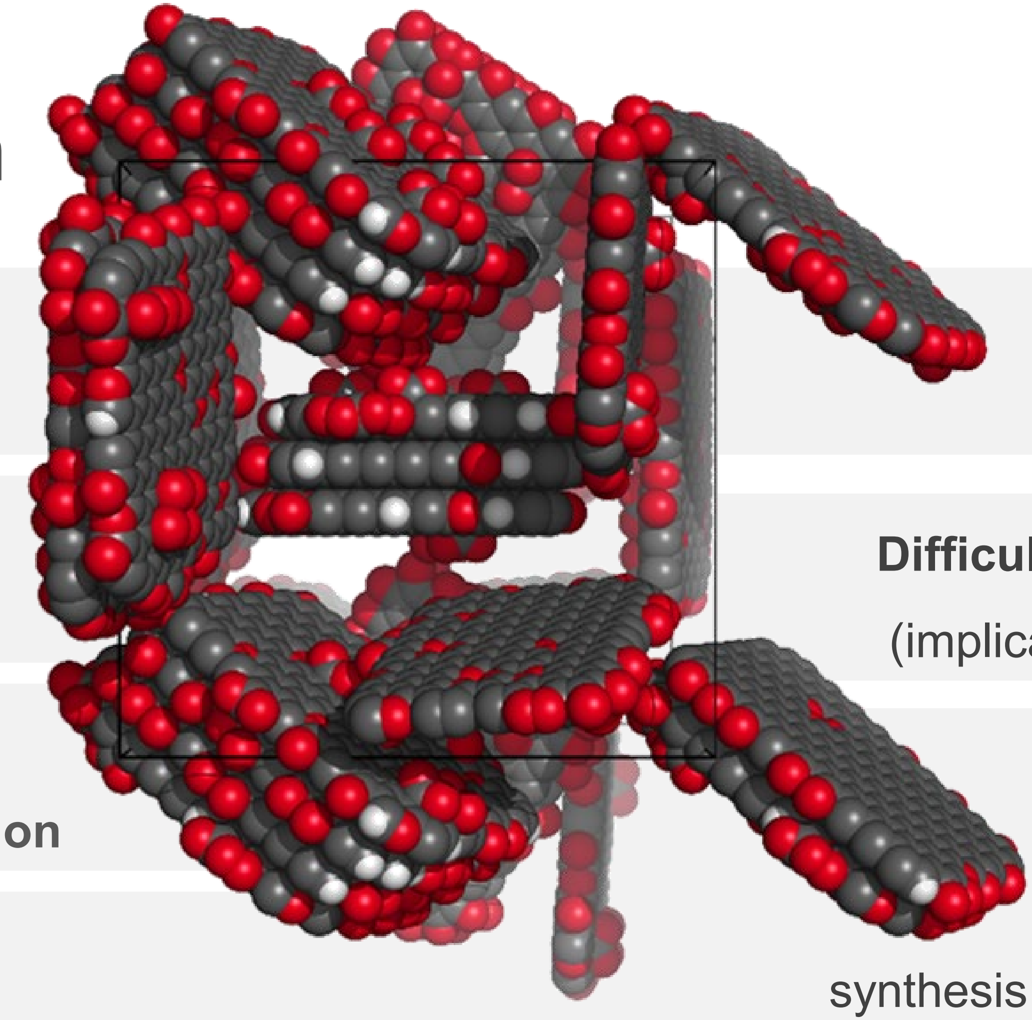
Activated carbon (AC) is one of the best performing advanced options… **why?**

Present Treatment Levels of STP



Source: PhD thesis, van Dijk, Joanke, https://doi.org/10.33540/1918

Activated Carbon



High specific surface area (S_{BET})

Microporous amorphous carbonaceous structure

Surface functional groups
Possible **surface functionalization**

Excellent features for **advanced wastewater treatment**

Lower performance for **trace** contaminants

Difficult separation from treated water (implications on costs and reutilization)

Limited sustainability due to fossil-based nature or heavy synthesis routes and difficult regeneration

Our Motivation

Efficient and **cost-effective wastewater treatments** are a must-have tool for ensuring

TREATMENTS SUSTAINABILITY

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WATER SAFETY AND CIRCULARITY

Our Main Goal

Developing **biomass-based (functionalized) activated carbons** to be applied as advanced wastewater treatments, for the removal of pharmaceuticals from wastewater, using:

Paper mill sludge

Spent brewery grains

Experimental approach

Biochar
- Pyrolysis
- Acid + water washing
- → **Biochar** (RemPharm)

J. Env. Man. 188 (**2017**) 203
J. Env. Man. 192 (**2017**) 15

Powdered AC
- Chemical activation
- Pyrolysis
- Acid + water washing
- **Conventional** *vs* **microwave** pyrolysis
- → **Powdered AC**

J. Haz. Mat. 370 (**2019**) 212
Sci.Total Env. 752 (**2021**) 141662
J. Haz. Mat. 431 (**2022**) 128556
Env. Tech. & Innov. 30 **(2023)** 103074

Functionalized AC
- Chemical activation
- Pyrolysis
- Acid + water washing
- **Grafting surface functionalization** (N,S or O)
- → **Functionalized AC**

J. Mol. Liq. 299 (**2020**) 112098
J. Mol. Liq. 323 **(2021)** 115003
New work
submitted Sci.Total Env.

Magnetic AC (WASTE MAC)
- Chemical activation
- Pyrolysis
- Acid + water washing
- ***In-situ* or *ex-situ* synthesis of magnetic oxides**
- Water washing
- → **Magnetic AC**

ES&PR 28 (**2021**) 18314
Nanomaterials 11 **(2021)** 287
CEJ 426 **(2021)** 129974
J. Haz. Mat. 443 **(2023)** 130258

Biochar-MIP
- Pyrolysis
- Acid + water washing
- ***In-situ* synthesis of Molecular Imprinting Polymers**
- → **Biochar-MIP**

On-going!

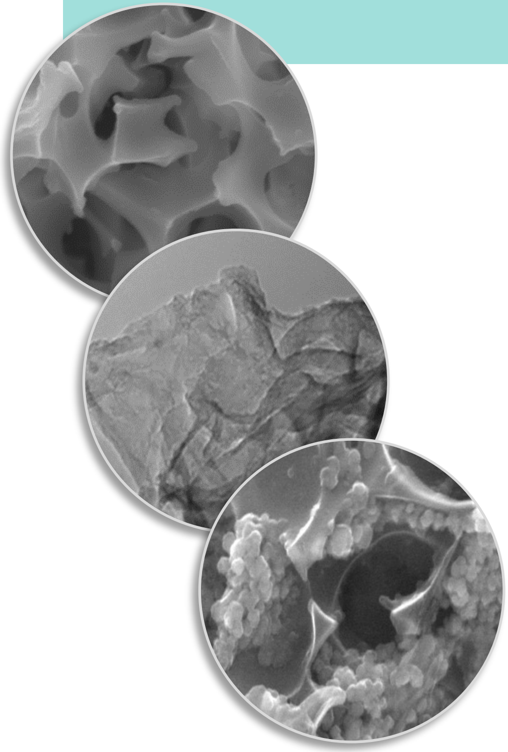
AC-enzyme composites
- Chemical activation
- Pyrolysis
- Acid + water washing
- **Enzyme functionalization** for synergistic adsorption/ degradation
- → **AC-enzyme composites**

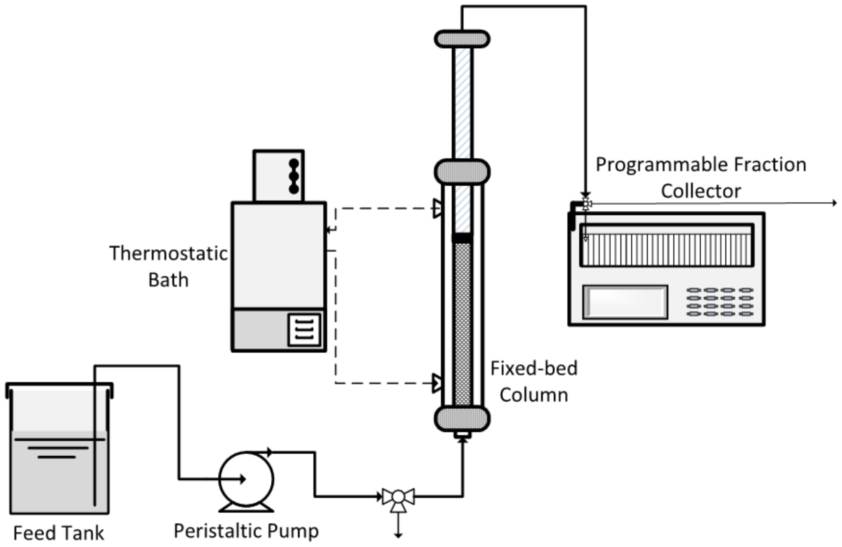
SYNERGY Project
Recently started!!

Experimental approach

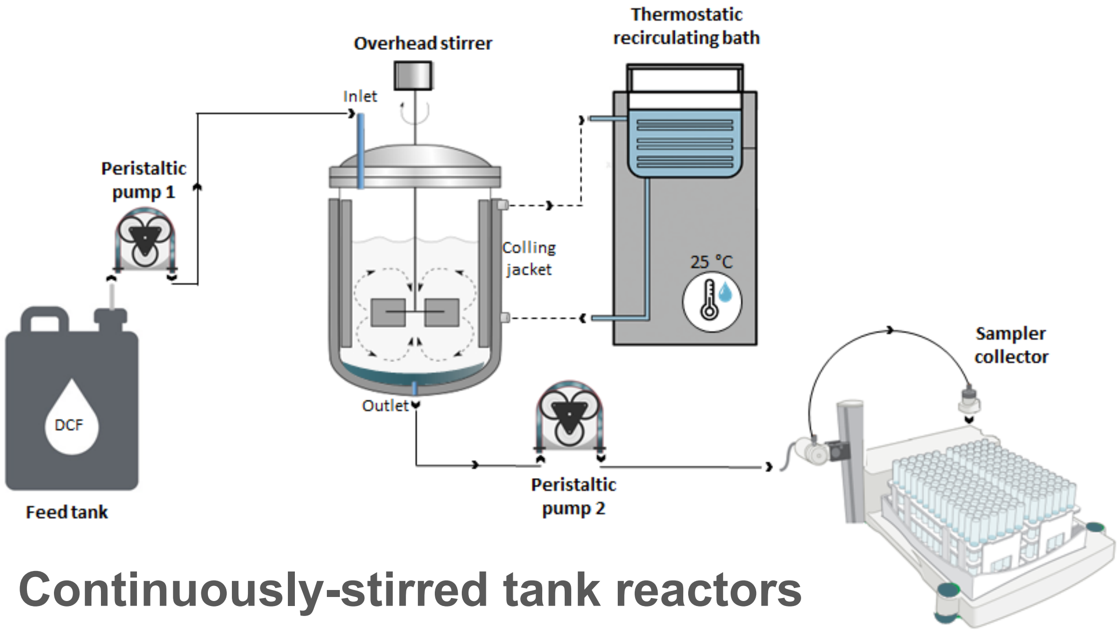
Biochar | Powdered AC | Functionalized AC (S, O, N) | Magnetic AC | Biochar-MIP | AC-enzyme composites

Batch adsorptive systems | Fixed bed-columns | Continuously-stirred tank reactors





Fixed-bed systems



Continuously-stirred tank reactors

Adsorption studies

Kinetic, isothermal and thermodynamic

Single and competitive conditions

Controlled lab conditions and **real wastewaters**

Case Study 1 - Multivariable optimization of brewery-waste AC

Main goal: Obtain an AC from spent brewery grains using a **quick microwave pyrolysis** process with **minimal use of activating chemicals** comparing to literature studies and high adsorptive performance towards antibiotics

Fractional Factorial Design

3 factors at 3 levels

+ Activating agent: precursor ratio (*w/w*)
+ Pyrolysis residence time
+ Temperature

AND

a 4th factor at 2 levels

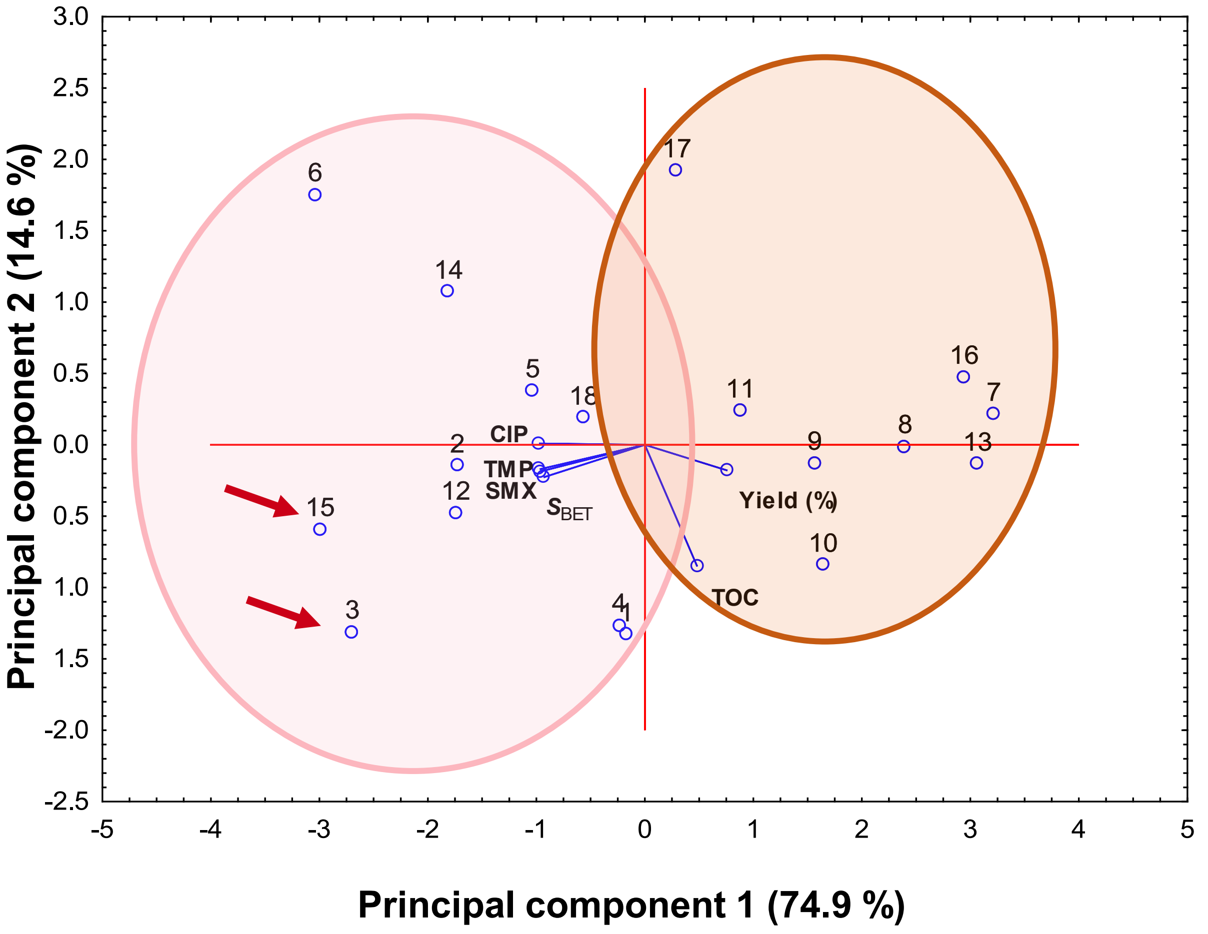
+ Nature of activating agent

N = 3^{3-1} x 2 = 18 materials

Responses for statistical analysis

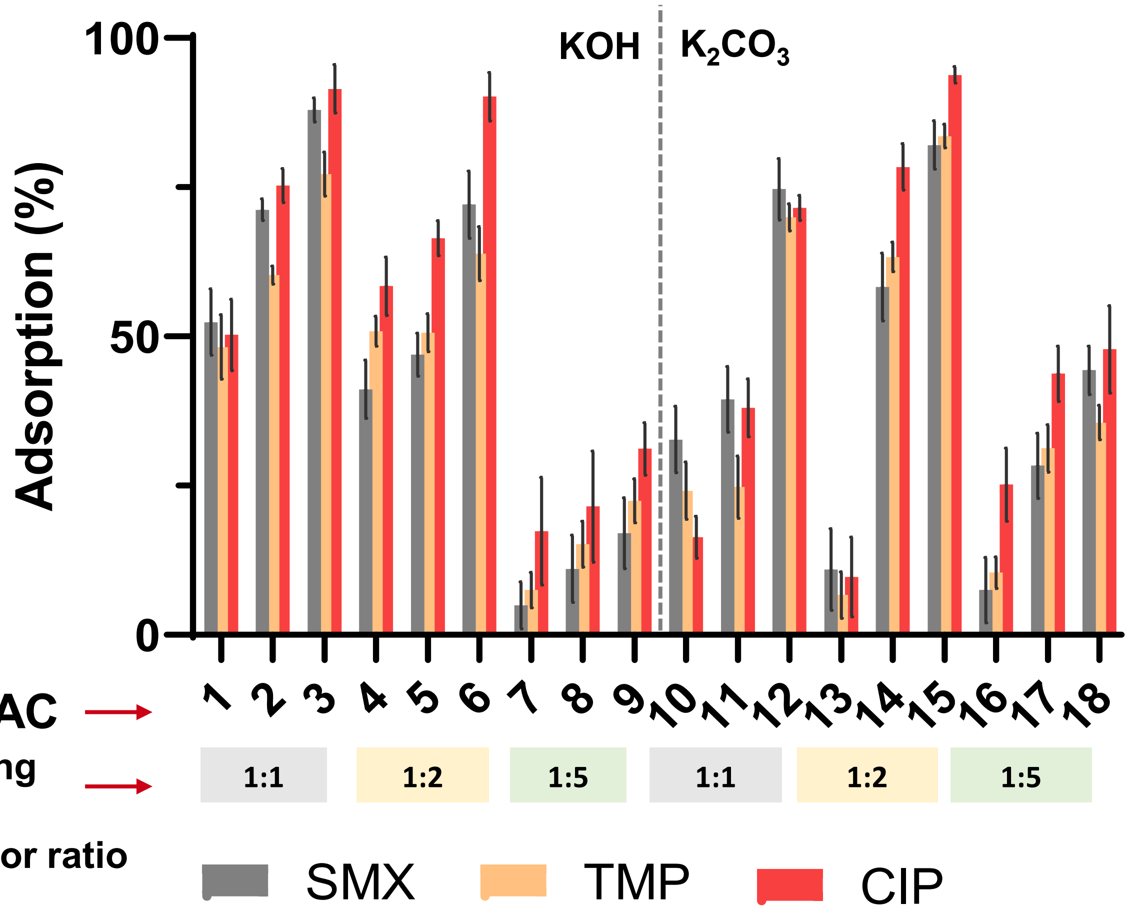
+ Specific surface area (S_{BET})
+ Product yield (%)
+ Total organic carbon (%)
+ Removal of antibiotics (%):

- Sulfamethoxazole (SMX)
- Trimethoprim (TMP)
- Ciprofloxacin (CIP)



Case Study 1 - Multivariable optimization of brewery-waste AC

Adsorption of antibiotics

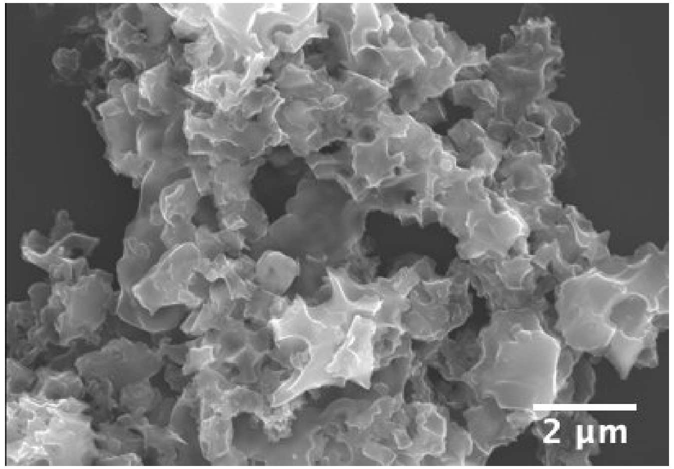


Sulfamethoxazole (SMX) | Trimethoprim (TMP) | Ciprofloxacin (CIP)

Batch adsorption studies conditions

+ Material dose: 25 mg L^{-1}
+ $[\text{Antibiotic}]_i$ = 20 μmol L^{-1}
+ 24 h, 80 rpm, 25 ºC

AC15



10000x

Highly microporous AC were obtained with S_{BET} up to 1400 m^2 g^{-1}, with excellent removal of antibiotics from water using very low AC doses – **5 x less activating agent and 8 x faster than conventional pyrolysis**

Case Study 2 – Multivariable optimization of magnetic AC

Main goal: Obtain a magnetic AC (**MAC**) with **minimal losses in performance** comparing to the non-magnetic material and **easily retrievable** from the treated water

Fractional Factorial Design

3 factors at 3 levels

+ AC:Fe salts (*w/w*)
+ Fe^{3+}:Fe^{2+} salts molar ratio
+ Temperature

AND

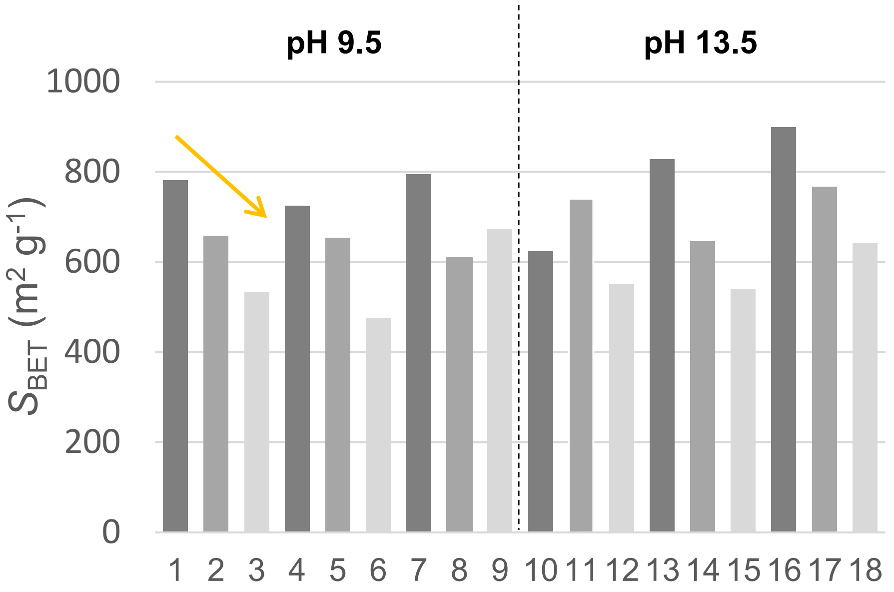
a 4th factor at 2 levels

+ pH

Responses for statistical analysis

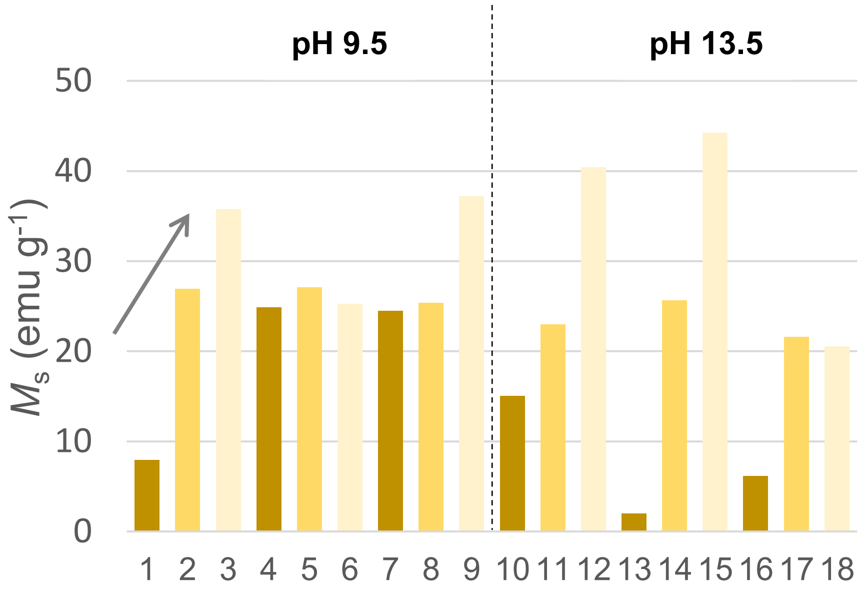
AC:Fe (1:3)
AC:Fe (1:4)
AC:Fe (1:6)

Specific surface area S_{BET}



S_{BET} (1:3) > S_{BET} (1:4) > S_{BET} (1:6)

Saturation magnetization M_S



M_s (1:3) < M_s (1:4) < M_s (1:6)

Case Study 2 – Multivariable optimization of magnetic AC

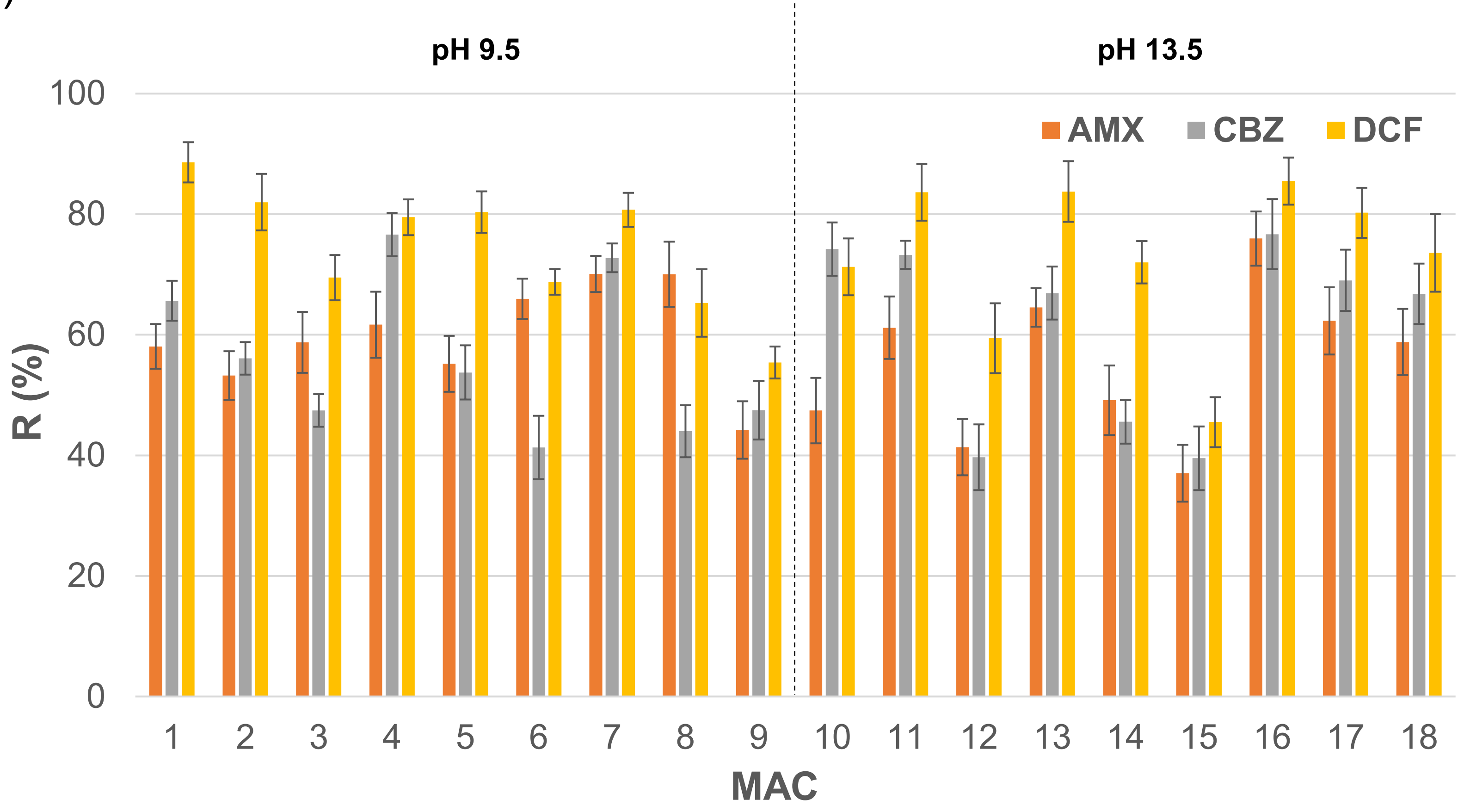
Responses

Removal of selected pharmaceuticals | R (%)*

Amoxicillin (AMX) | Carbamazepine (CBZ) | Diclofenac (DCF)

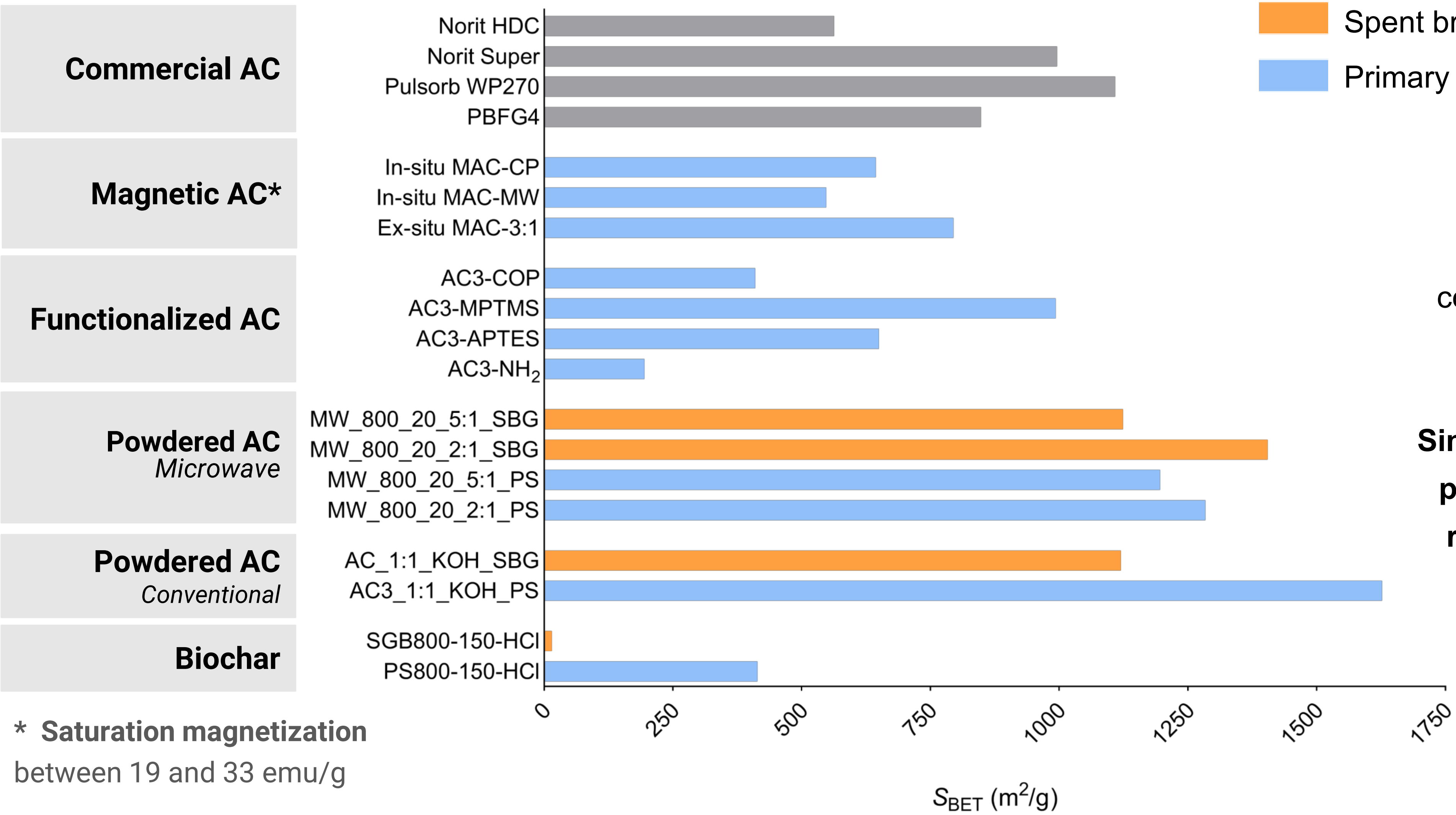
***Batch adsorption studies**

+ MAC dosage: 35 mg L^{-1}
+ $[Pharmaceutical]_i$ = 15 μmol L^{-1}
+ 4 h, 80 rpm, 25 ºC



Overview of selected developed microporous carbons

Specific surface area (S_{BET})



* **Saturation magnetization** between 19 and 33 emu/g

S_{BET} similar or higher to commercial non-functionalized commercial AC

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Similar or superior adsorptive performance concerning the removal of pharmaceuticals from water

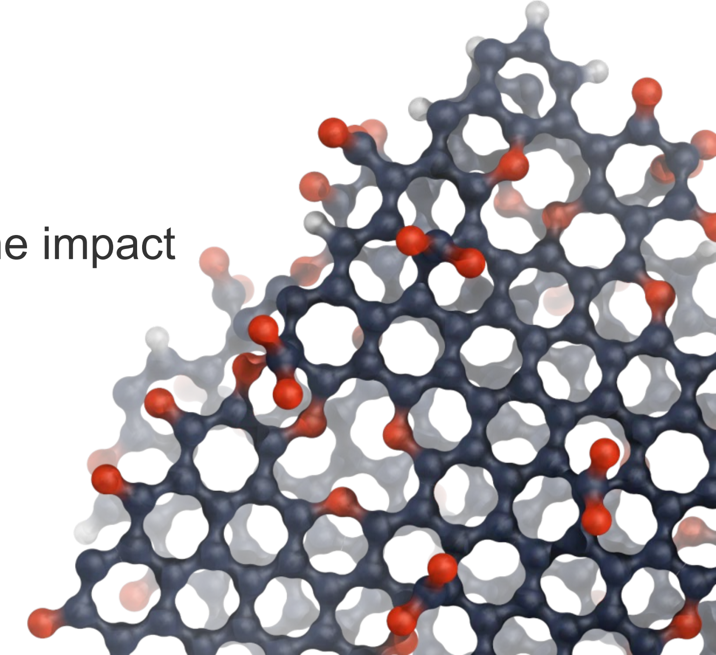
Take-home message

+ **Residual biomass is a valid resource** to produce efficient carbon adsorbents capable to compete in performance with commercial carbons

+ Microwave-assisted pyrolysis can be successfully used in the production of microporous carbons using **significantly lower amounts of chemical activating agents and in just a few minutes**!

+ Biomass-derived AC modified with **magnetic iron oxides allow for immediate recuperation** from the treated water, still maintaining excellent adsorptive properties.

+ It is possible to take advantage of the tunable surface of activated carbon**: grafting, molecular-imprinting and enzyme modifications are being studied** to understand the impact of such modifications on the AC performance in complex matrices



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