Utilization of Biochar For Removing Emerging Contaminants in Water and Wastewater

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Manipulation of Selectivity of Biochar for Sustainable Recovery of Nutrients from Human Urine Containing Antibiotics

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Introduction

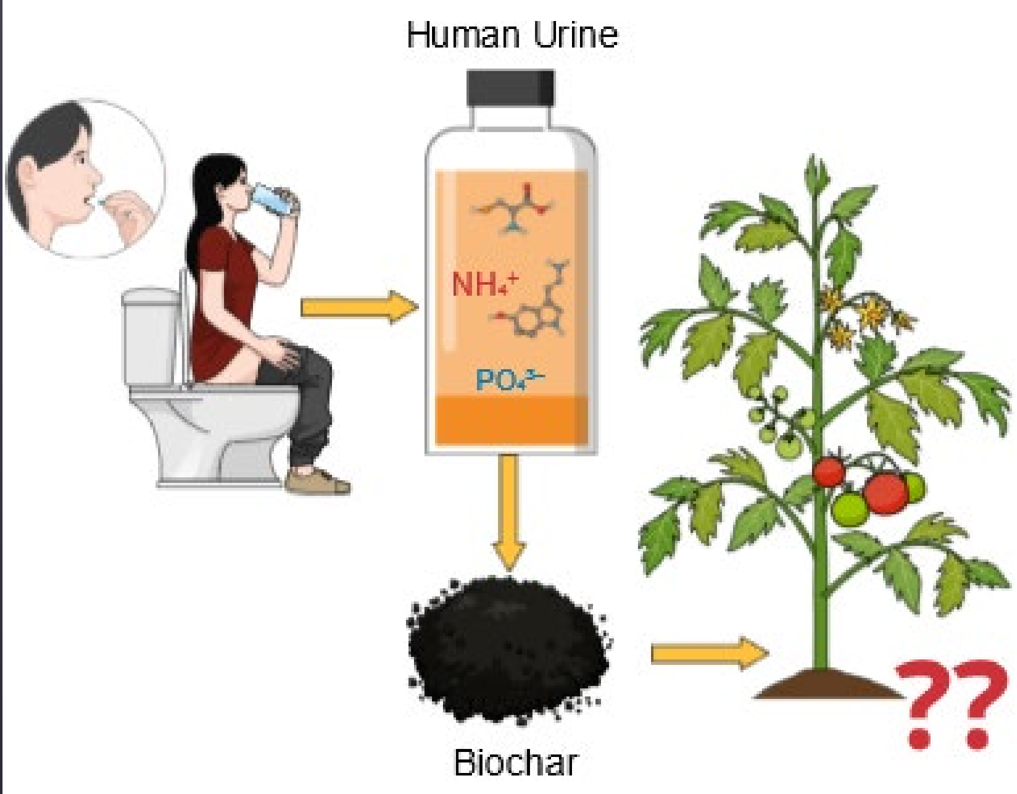
- Human urine is a valuable source of nutrients (N and P)
- Total nitrogen concentration ranges from 1.79 to 2.61 g/L and the total phosphorus concentration is around 0.21 g/L
- pH of the urine solution is generally around 9
- Urine contributes 45-50% of total phosphorus and 75-80% of total nitrogen by mass but accounts for only 1% of the wastewater volume
- Dilution is not a good solution!
- Urine should be separated at the source for beneficial use
- Resource recovery and circular economy paradigms

Introduction

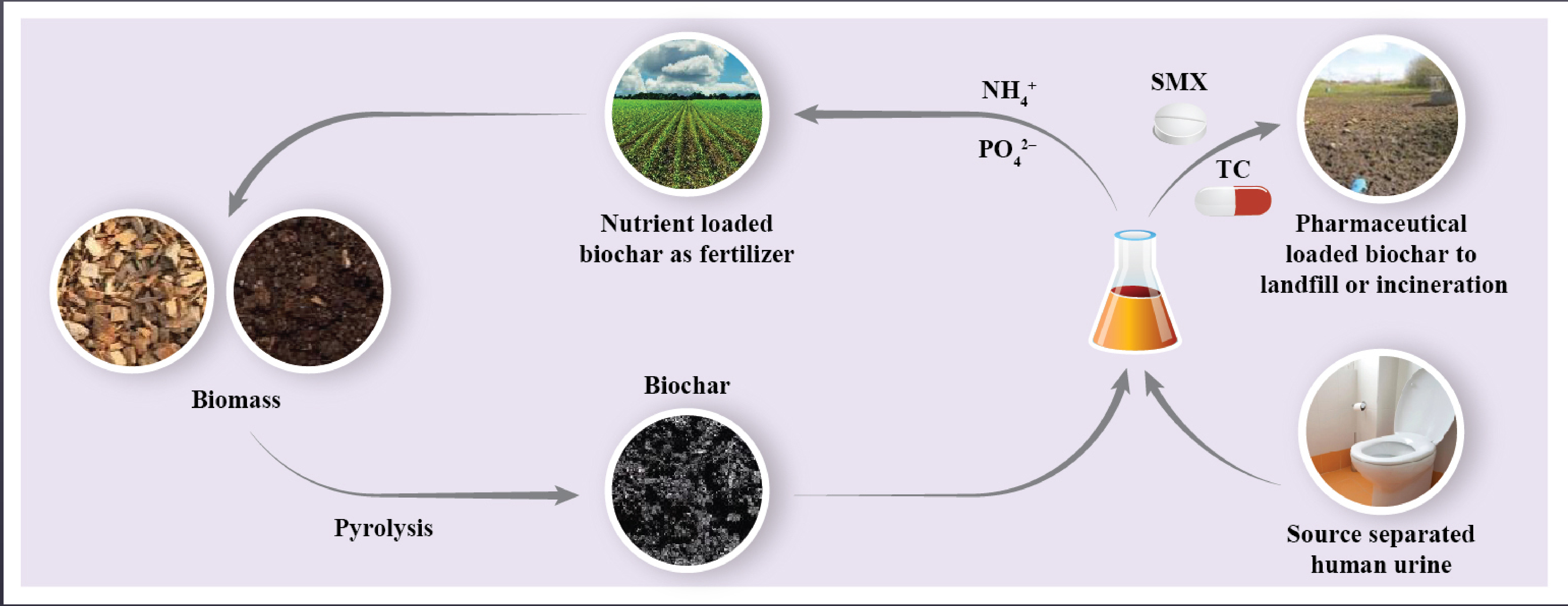
- Increasing consumption of pharmaceuticals leads to their presence in urine
- Source-separated urine detected the presence of sulfamethoxazole, trimethoprim, and diclofenac at 6,800, 1,280, and 72 μg/L, respectively
- Conventional wastewater treatment systems are not designed to eliminate the pharmaceuticals and metabolites
- Dilution is again not a good solution!
- Pharmaceuticals in urine need to be considered prior to the application of source-separated urine as a nutrient product

Introduction

- Biochar, low-cost adsorbent for nutrient recovery from human urine and recycling to uphold agricultural production
- Biochar applied for nutrients recovery can also uptake pharmaceuticals
- Azithromycin (AZ), ciprofloxacin (CPX), tetracycline (TC), trimethoprim (TMP) and sulfamethoxazole (SMX) are the most detected pharmaceuticals in human urine



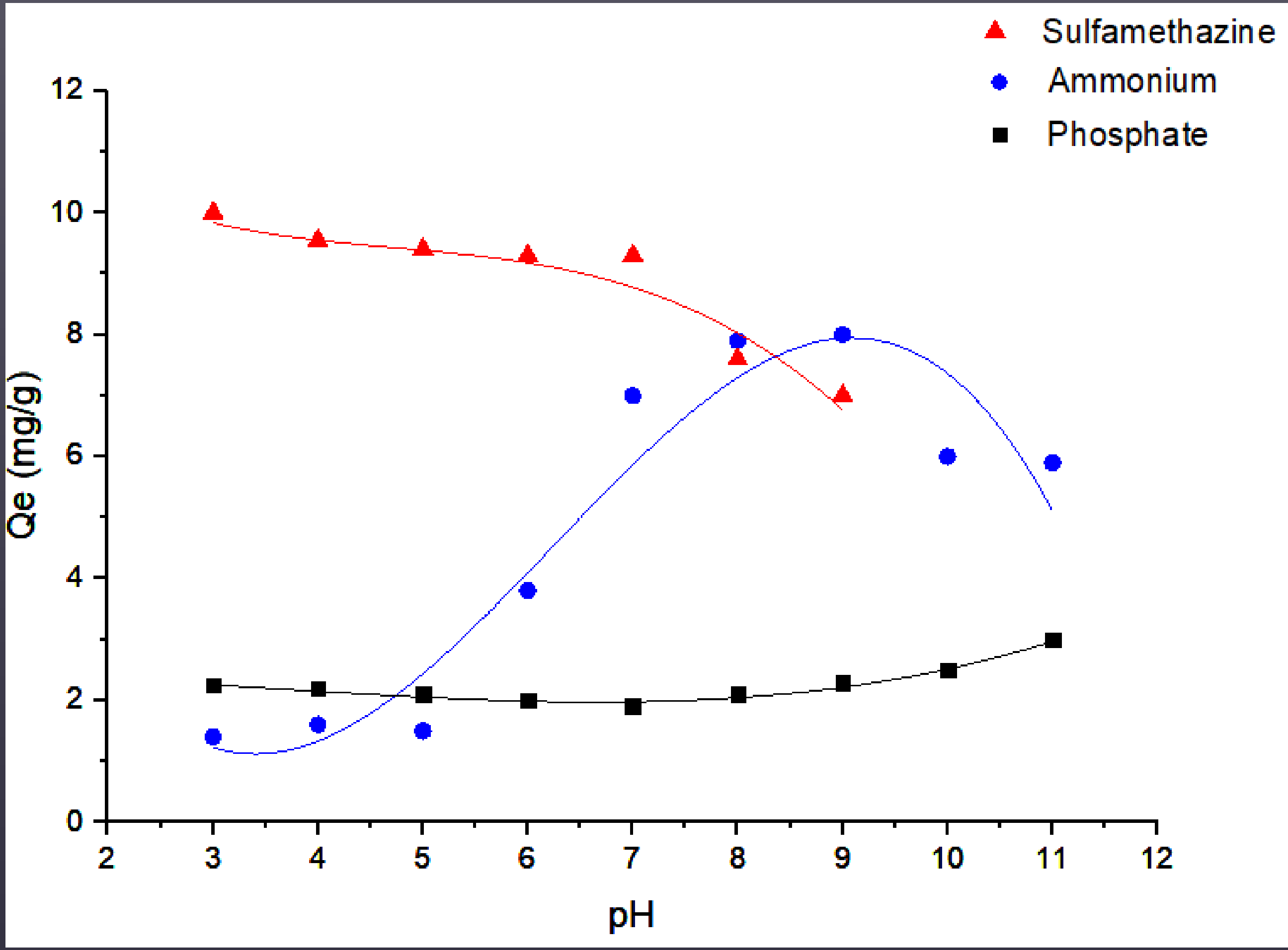
Introduction



Introduction

- Two separate biochars with different characteristics can be applied for separate nutrient and pharmaceutical extractions in sequence
- While nutrients adsorption is effective at pH > 5, pharmaceutical adsorption is promising at low pH < 5
- Biochar pyrolyzed at high temperatures → higher aromaticity → suitable for pharmaceuticals removal
- Biochar pyrolyzed at low temperatures → increase in negatively charged functional groups → suitable for nutrients recovery
- First stage → pharmaceuticals removal → pH < 1
- Second stage → nutrient recovery → pH > 5
- In this way, the problem of environmental release would be substantially less

Introduction



Dugdug, A. A., Chang, S. X., Ok, Y. S., Rajapaksha, A. U., & Anyia, A. (2018). Phosphorus sorption capacity of biochars varies with biochar type and salinity level. *Environmental Science and Pollution Research*, *25*(26), 25799–25812. https://doi.org/10.1007/s11356-018-1368-9

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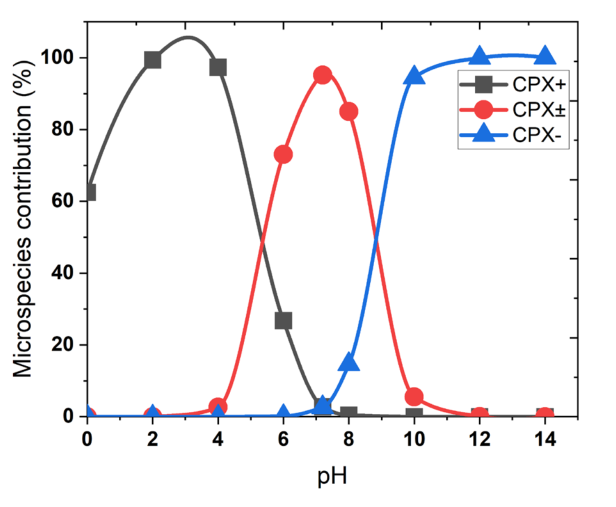
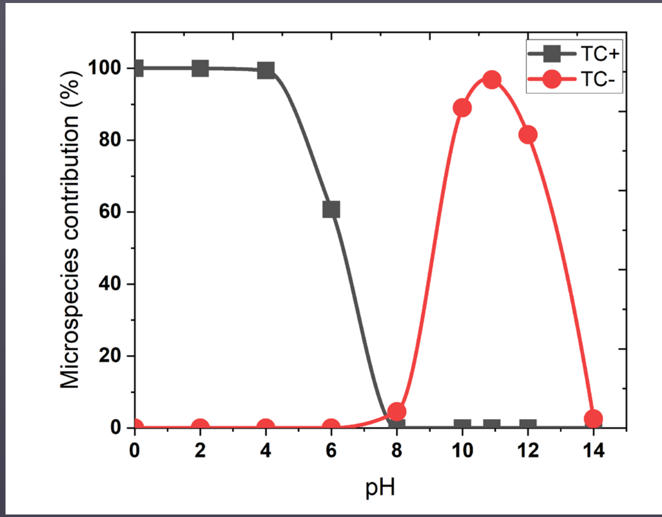
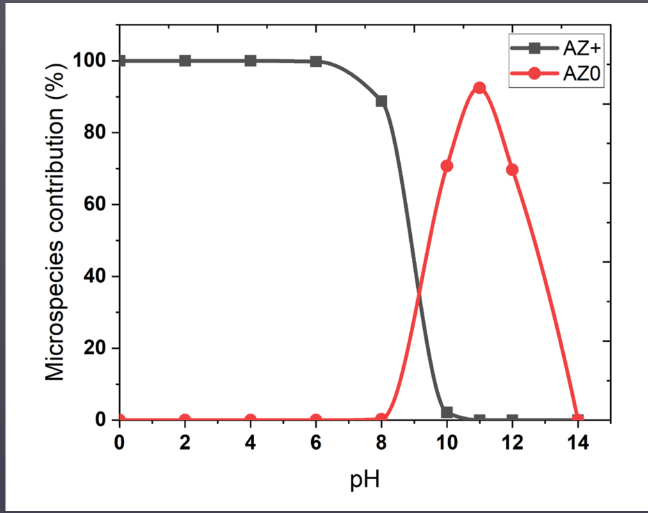
Ionization State of Pharmaceuticals at Different pH



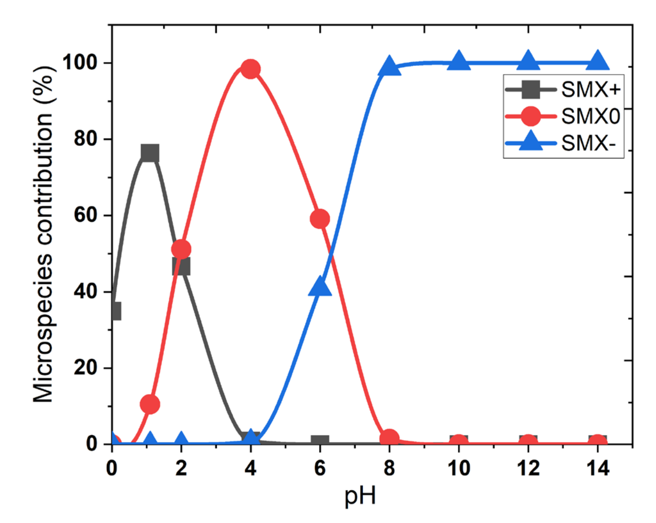
Ciproflaxacin (CPX)



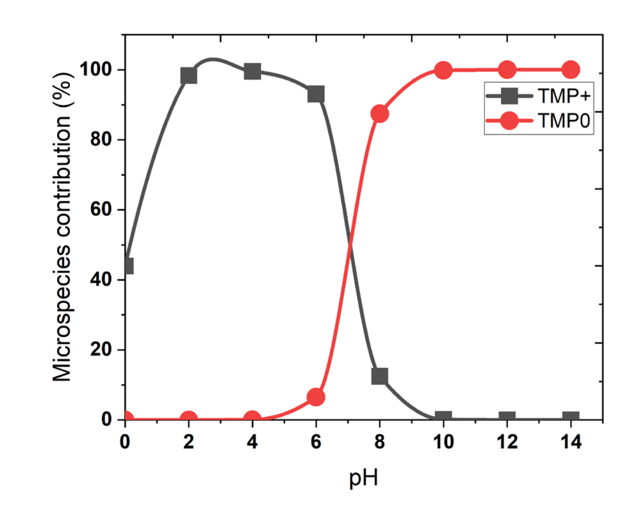
Tetracycline (TC)



Azithromycin (AZ)



Sulfamethoxazole (SMX)



Trimethoprim (TMP)

Objective and Hypothesis

Objective: Apply biochar for the separate adsorption of nutrients and pharmaceuticals from source-separated human urine

Hypothesis: Negatively charged biochar surface will remove positively charged pharmaceuticals at pH 1 at stage-1 leaving nutrients to get adsorbed at pH > 5 at stage-2 by surface precipitation

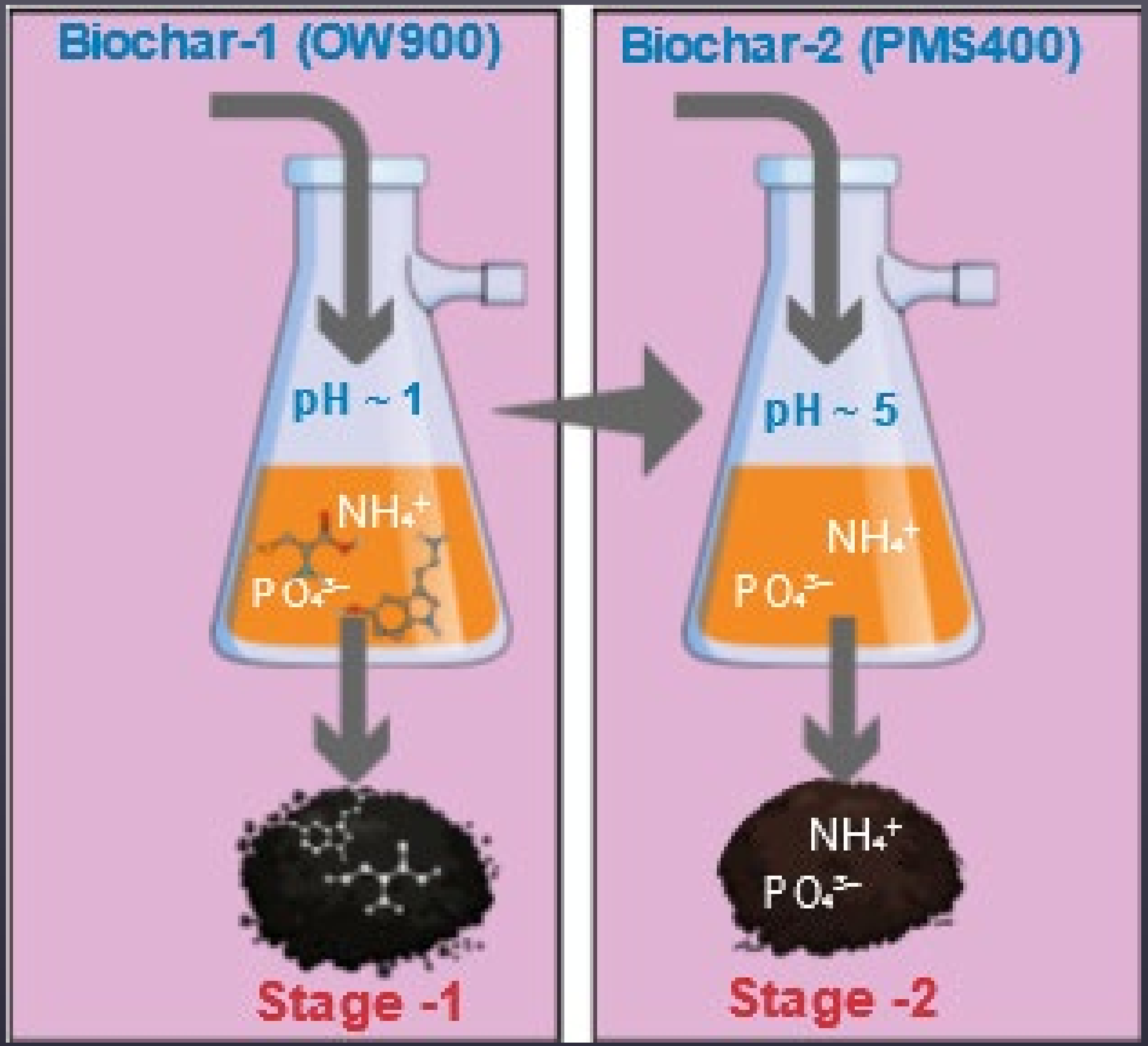
Methodology

- Biochar for pharmaceutical removal (stage-1):
  - Oak wood biochar pyrolyzed at 900°C (OW900)
- Biochar for nutrient recovery (stage-2):
  - paper mill sludge biochar pyrolyzed at 400°C (PMS400)
- Kinetic and isotherm studies
  - Biochar doses (0.1 to 20 g/L)
  - pH ranging from 1 to 11
  - Adsorption time 0 to 24 h
- Optimum biochar dose → 5 g/L
- Analyses of N and P by flow injection analysis (USEPA Method 350).
- Analysis of pharmaceuticals by liquid chromatography mass spectrometry

Properties of Biochar

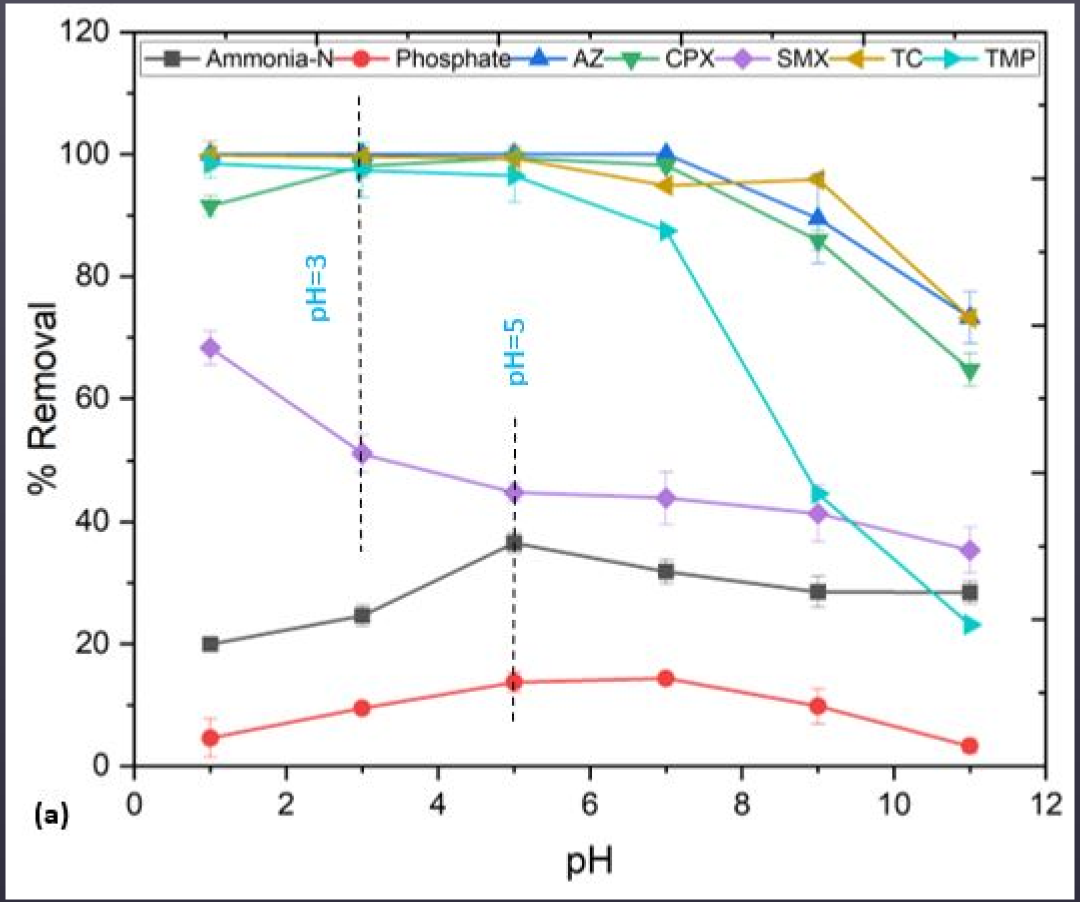
Feedstock	Pyrolysis temperature	Heating rate	pH	*C	*H	*O	*N	Surface area	Zeta potential
	° C	° C/min		%	%	%	%	m^2/g	
Paper mill sludge	400	7	4.82	64	3.80	24	0.42	< 1	-12.60
Oak wood	900	10	11.2	92.1	0.08	7.67	0.17	432	-6.47

Experimental Approach

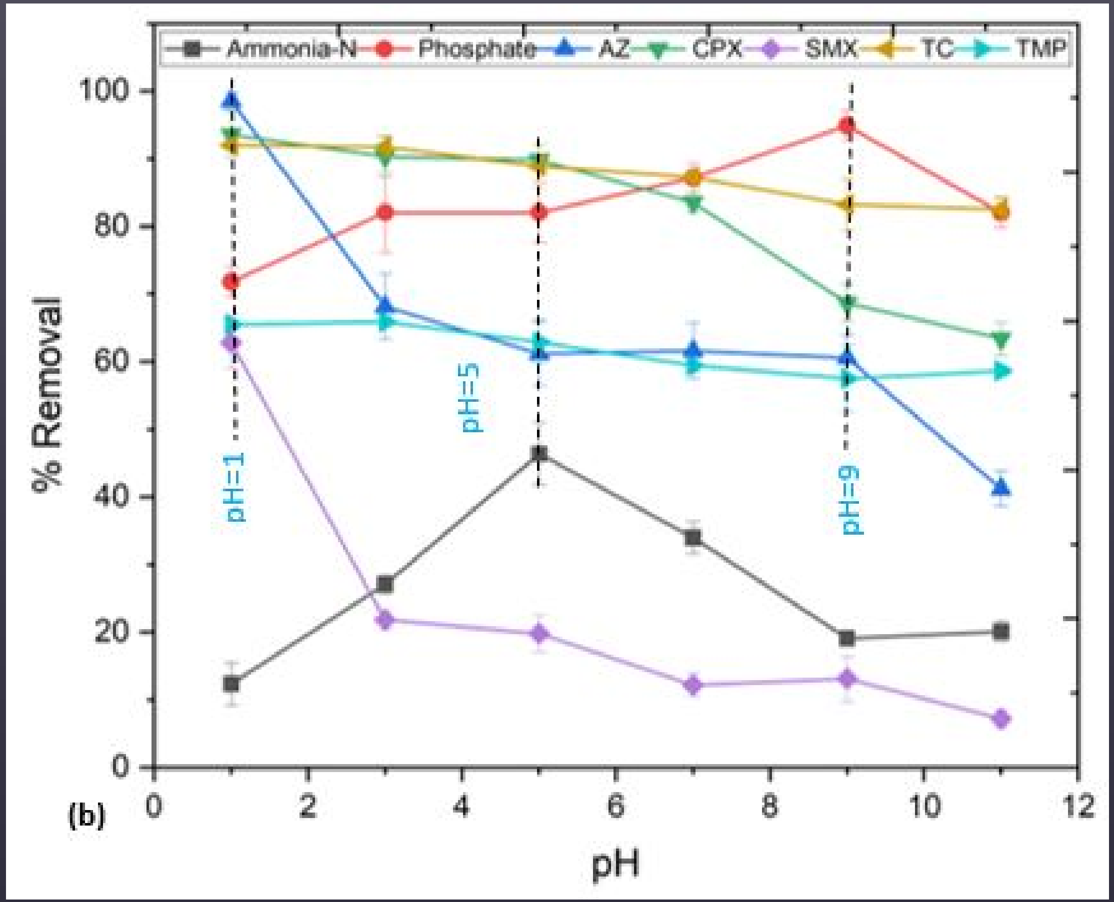


Results: Effect of pH on adsorption

OW 900

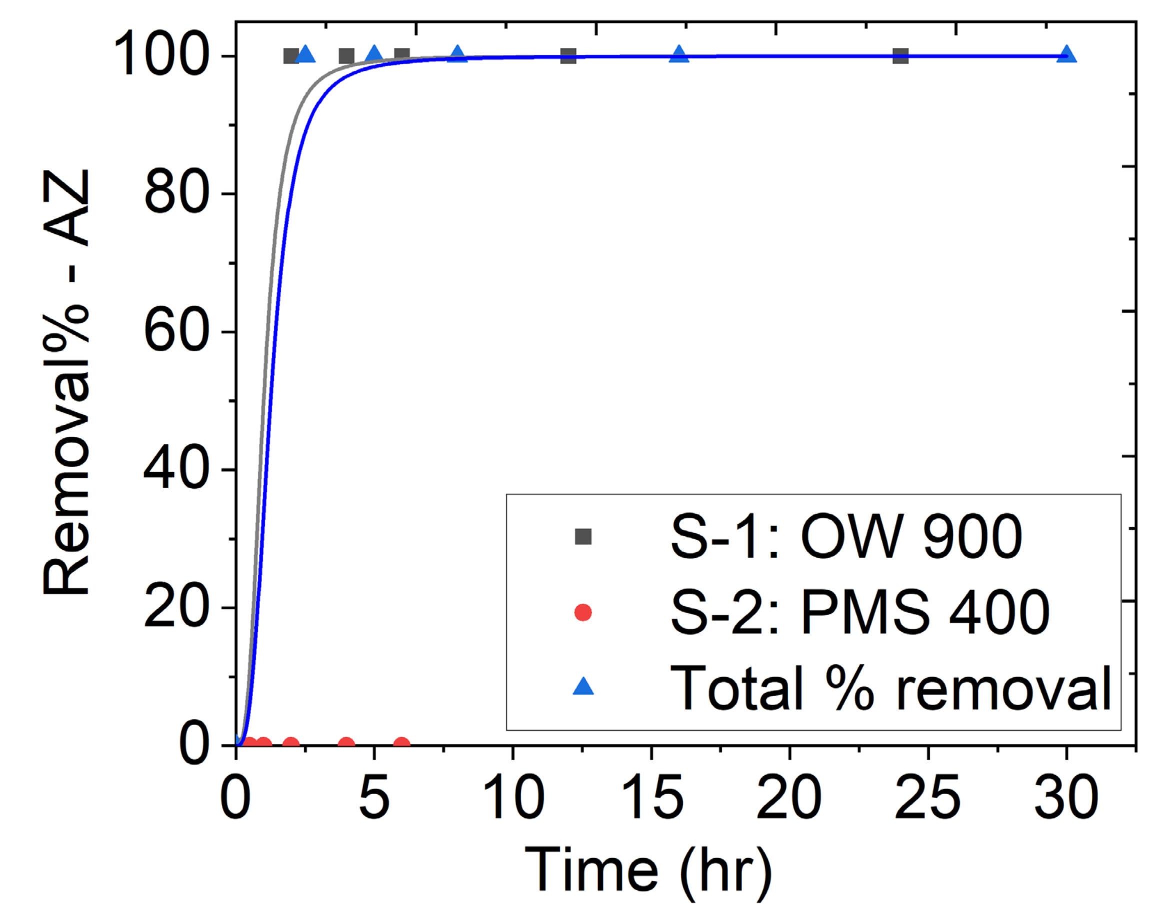


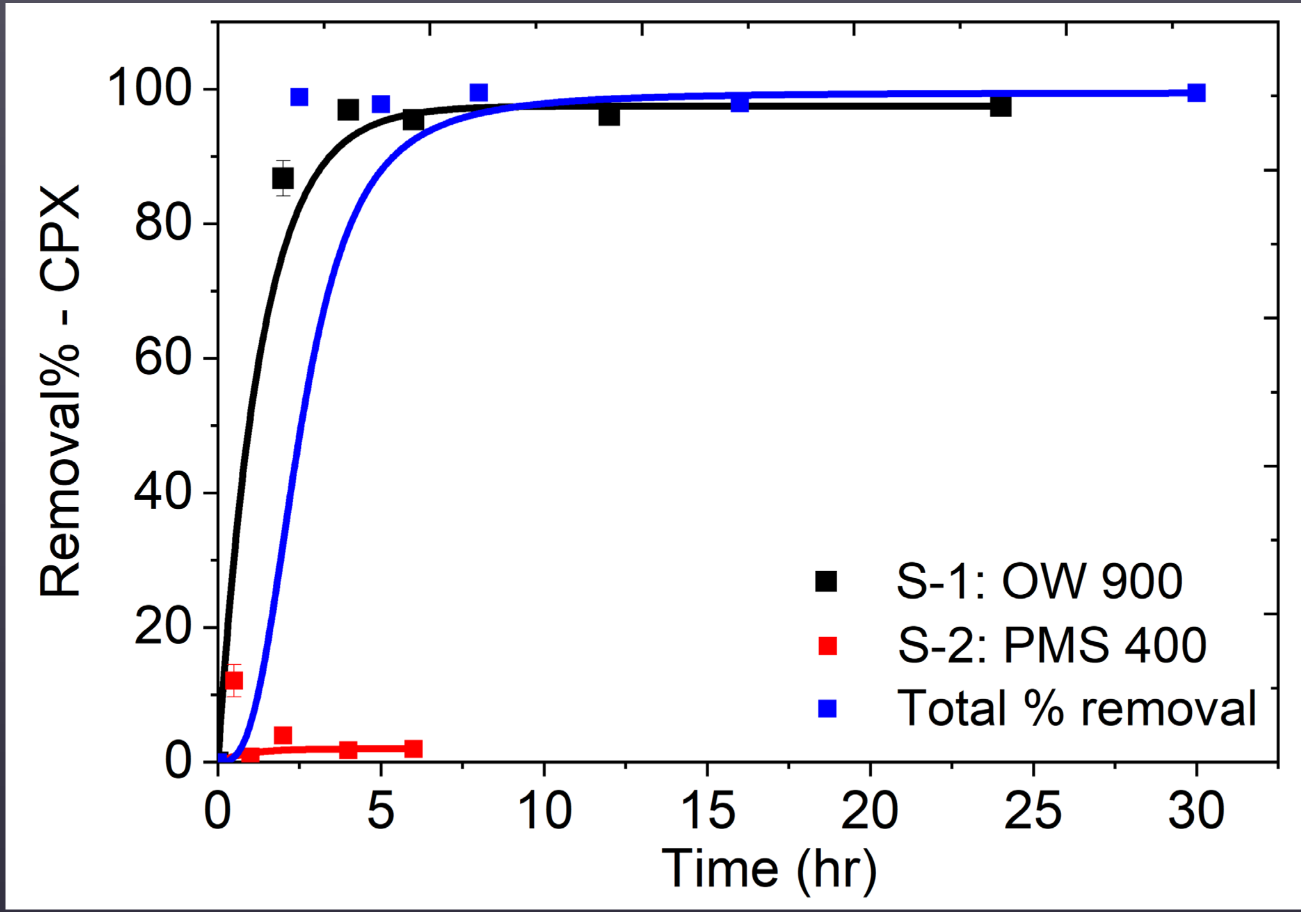
PMS 400



Acidic pH (<5) for pharmaceuticals removal and basic pH (>5) for nutrients recovery

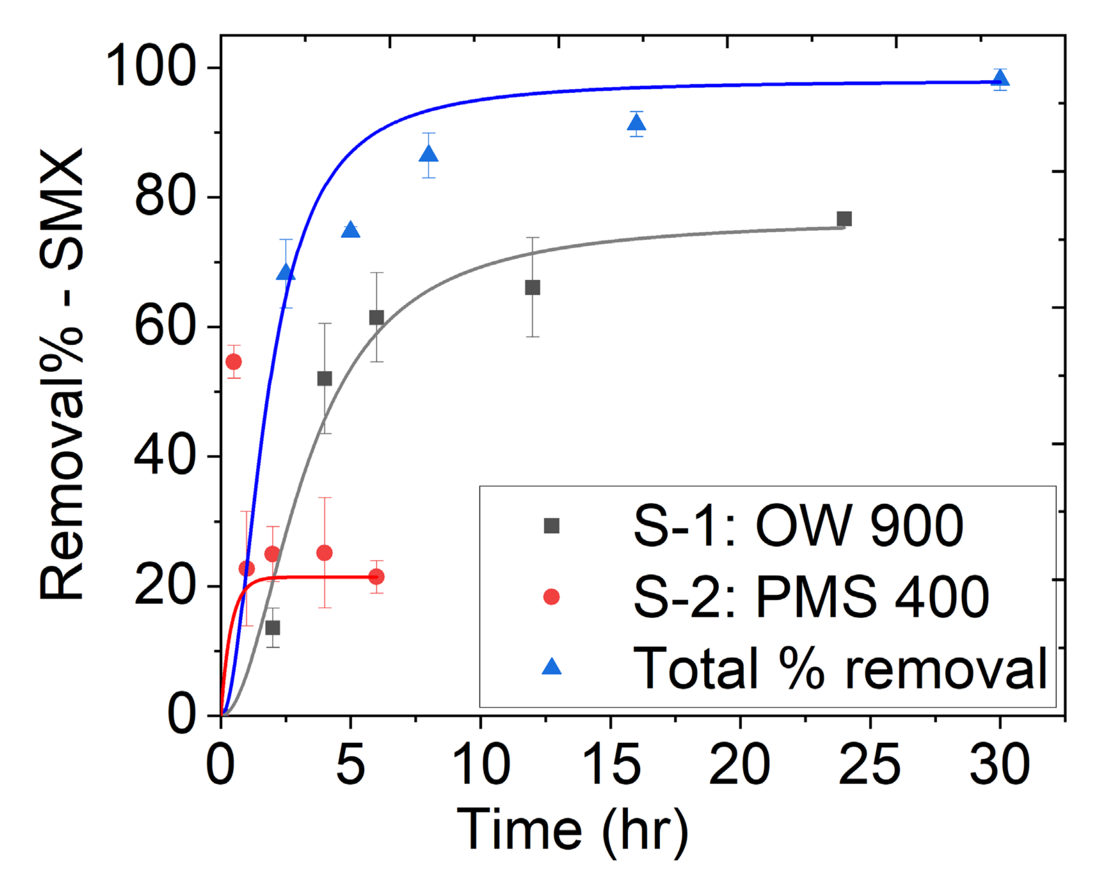
Results: Removal of pharmaceuticals using biochar

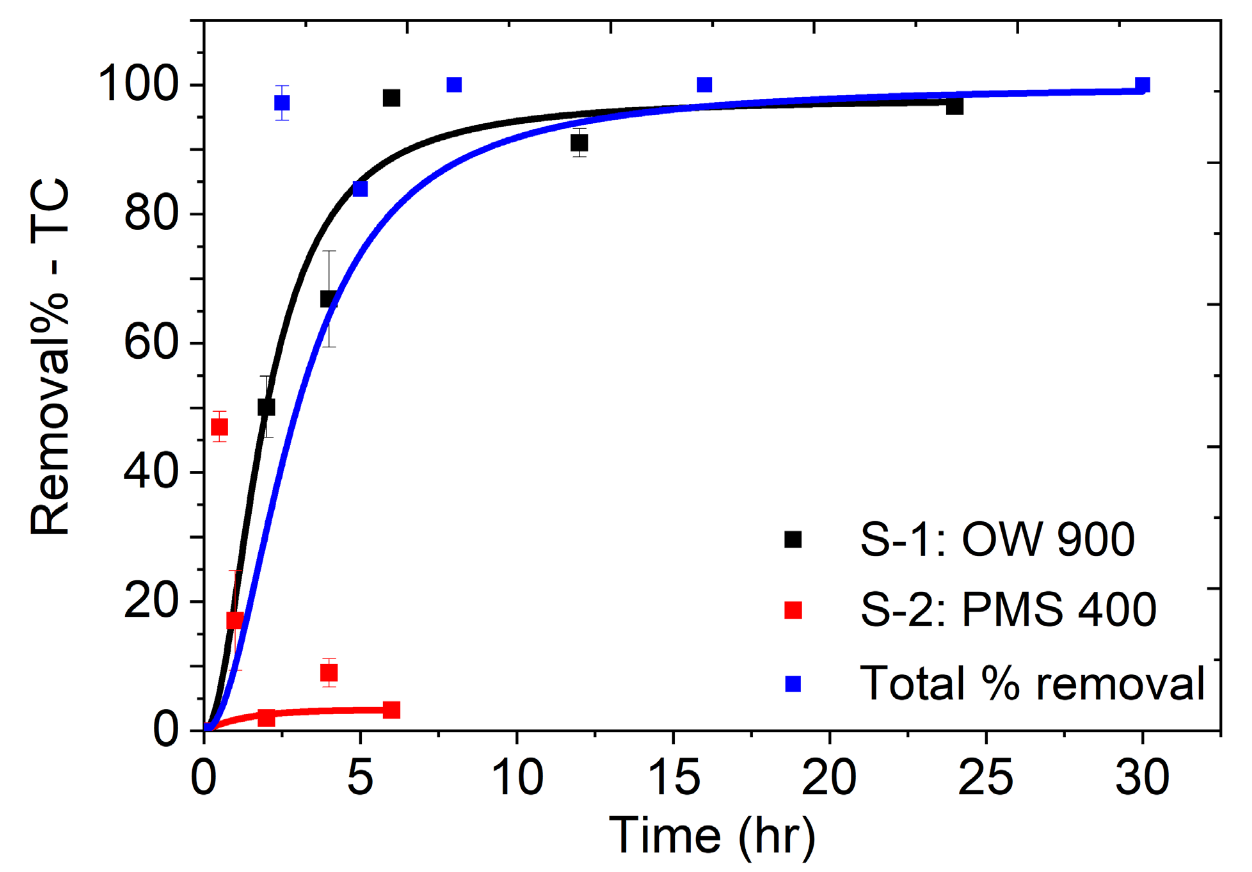




- ❑ 100% adsorption of AZ was achieved at stage 1
- ❑ 97% adsorption of CPX was achieved at stage 1
- ❑ 2% adsorption at stage 2 resulted in 99% removal

Results: Removal of pharmaceuticals using biochar

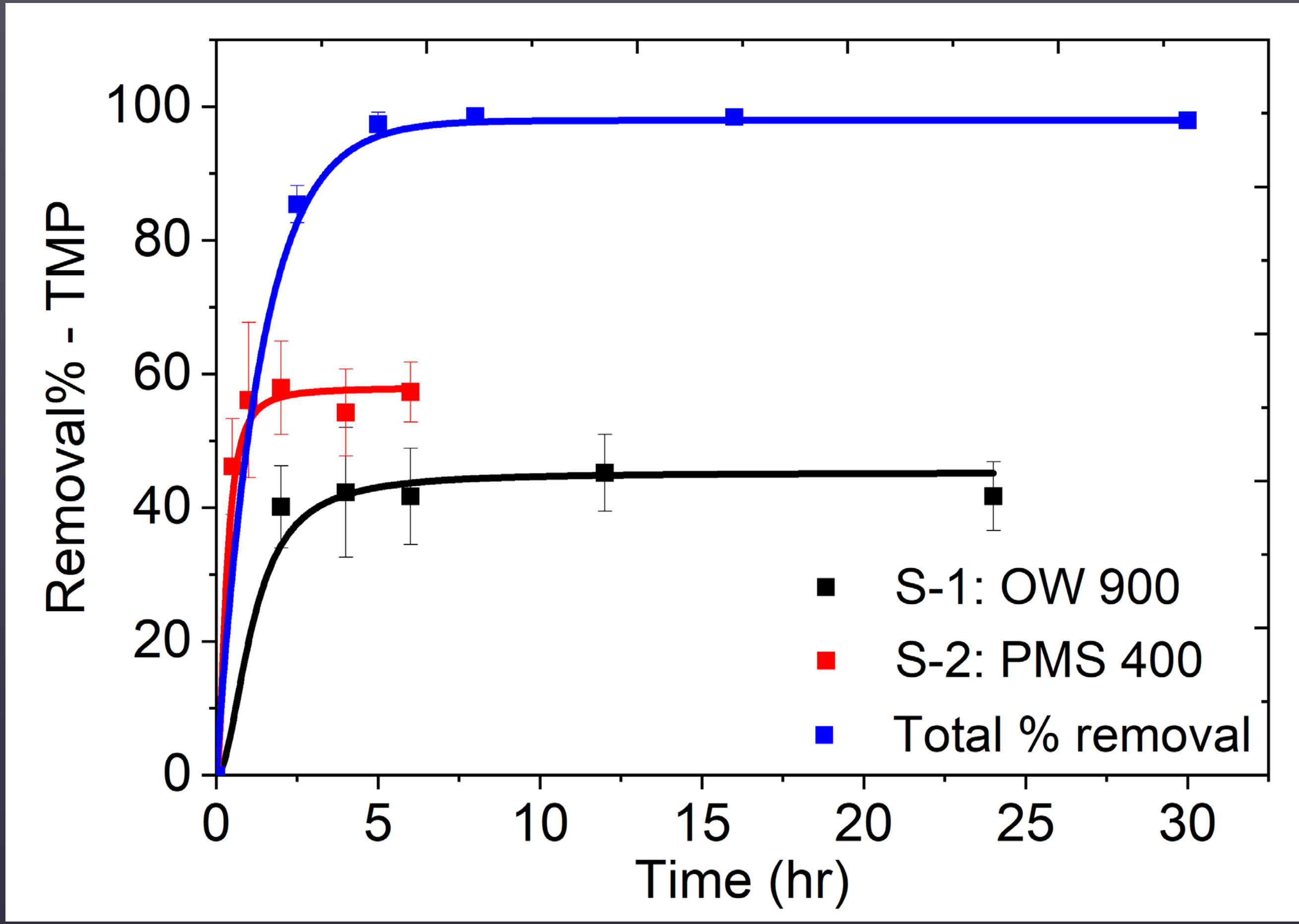




- ❑ 76% adsorption of SMX was achieved at stage 1
- ❑ 21% of the remaining SMX adsorbed at stage 2

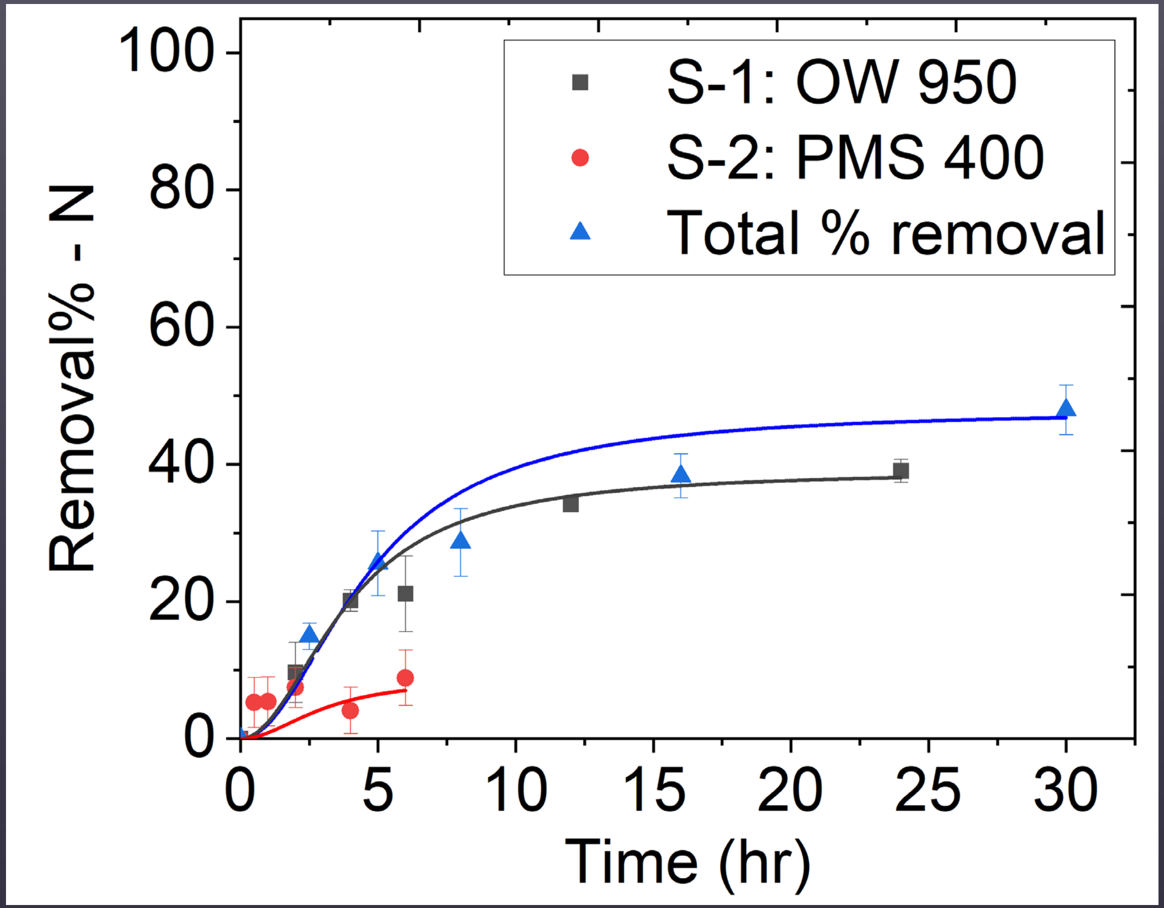
- ❑ 97% adsorption of TC was achieved at stage 1
- ❑ 3% adsorption at stage 2 resulted in 100% removal

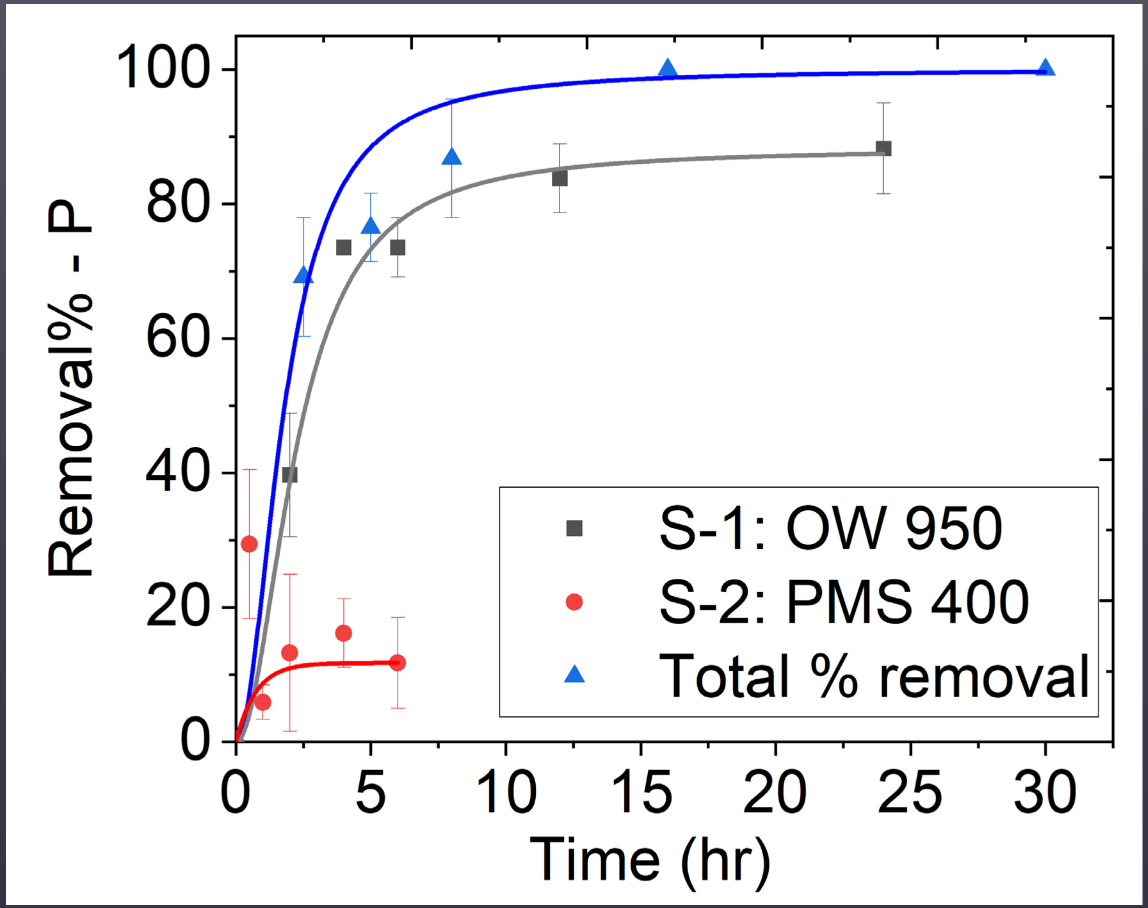
Results: Removal of pharmaceuticals using biochar



- ❑ Stage 2 achieved better adsorption than stage 1
- ❑ Only 41% adsorption of TMP was achieved at stage 1
- ❑ 57% adsorption at stage 2 resulted in total 98% removal

Results: Removal of nutrients on biochar



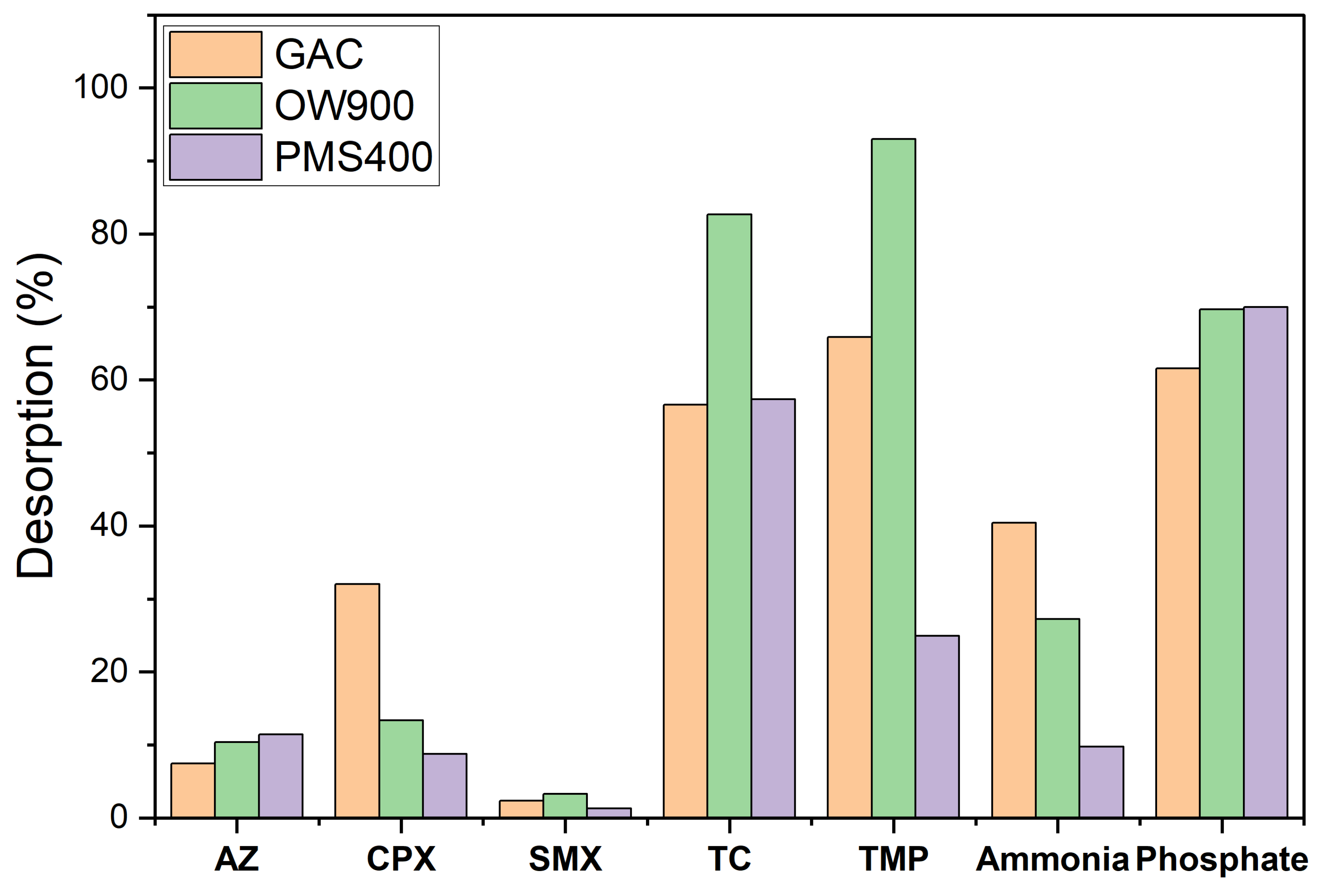


Stage 1 achieved better adsorption than stage 2

- ❑ 39% adsorption of N was achieved at stage 1
- ❑ Only 8% adsorption at stage 2 resulted in total 47% removal

- ❑ 88% adsorption of P was achieved at stage 1
- ❑ 11% adsorption at stage 2 resulted in total 100% removal

Results: Desorption of nutrients and pharmaceuticals



- The highest desorption rate was observed for TMP (92.6 %), and the lowest rate was observed for SMX (3.3 %)
- The more desorption of pharmaceuticals means more contaminants are released into the environment

Conclusions and Future Direction

- Pharmaceuticals being a strong π-acceptor interacts with high temperature biochar which is a π-donor due to less carboxyl functional groups and high content of graphitic carbon (OW900 in stage-1).
- Substantial N and P adsorption achieved at stage-1 did not allow the recovery of nutrients in stage-2 as designed.
- The total removal was close to 100% except N.

Way forward: Application of modified biochar to adsorb pharmaceuticals only in stage-1 and let the non-modified biochar to adsorb nutrients only in stage-2.

Development and Testing of a Deep-Eutectic Solvent Coated Biochar Adsorbent for Treating Dimethyl Sulfone in Wastewater on the International Space Station

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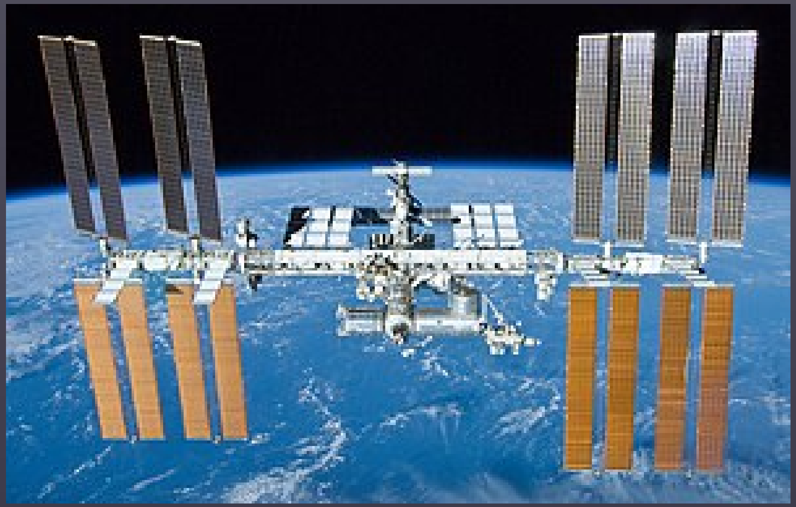
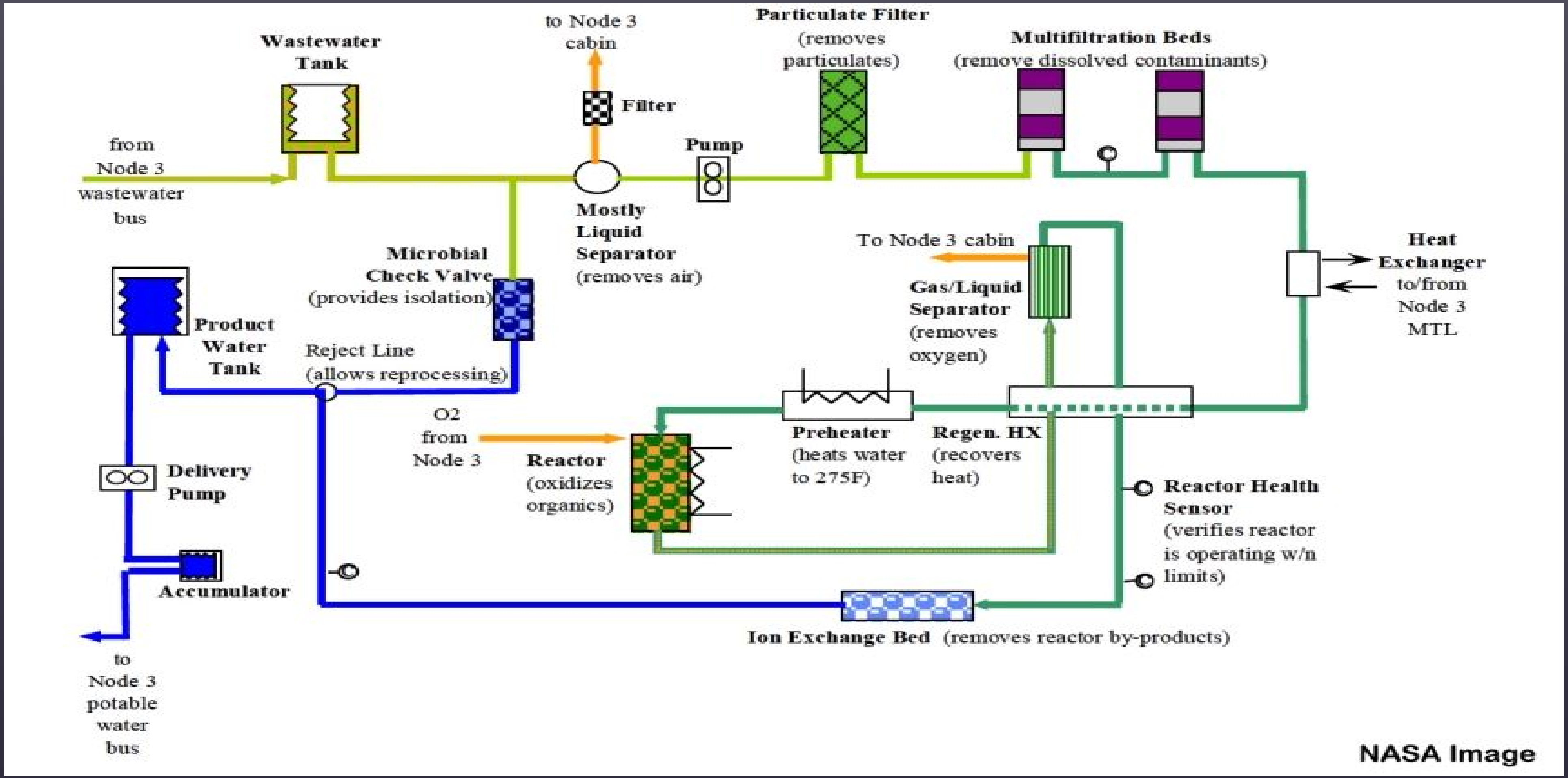
Outline

- Background and Problem Statement
- Ideas and Research Approaches
- Project Objectives
- Methodology
- Findings
- Summary



Source: nasa.gov

International Space Station (ISS) Water Process Assembly (WPA)



Source: www.tested.com

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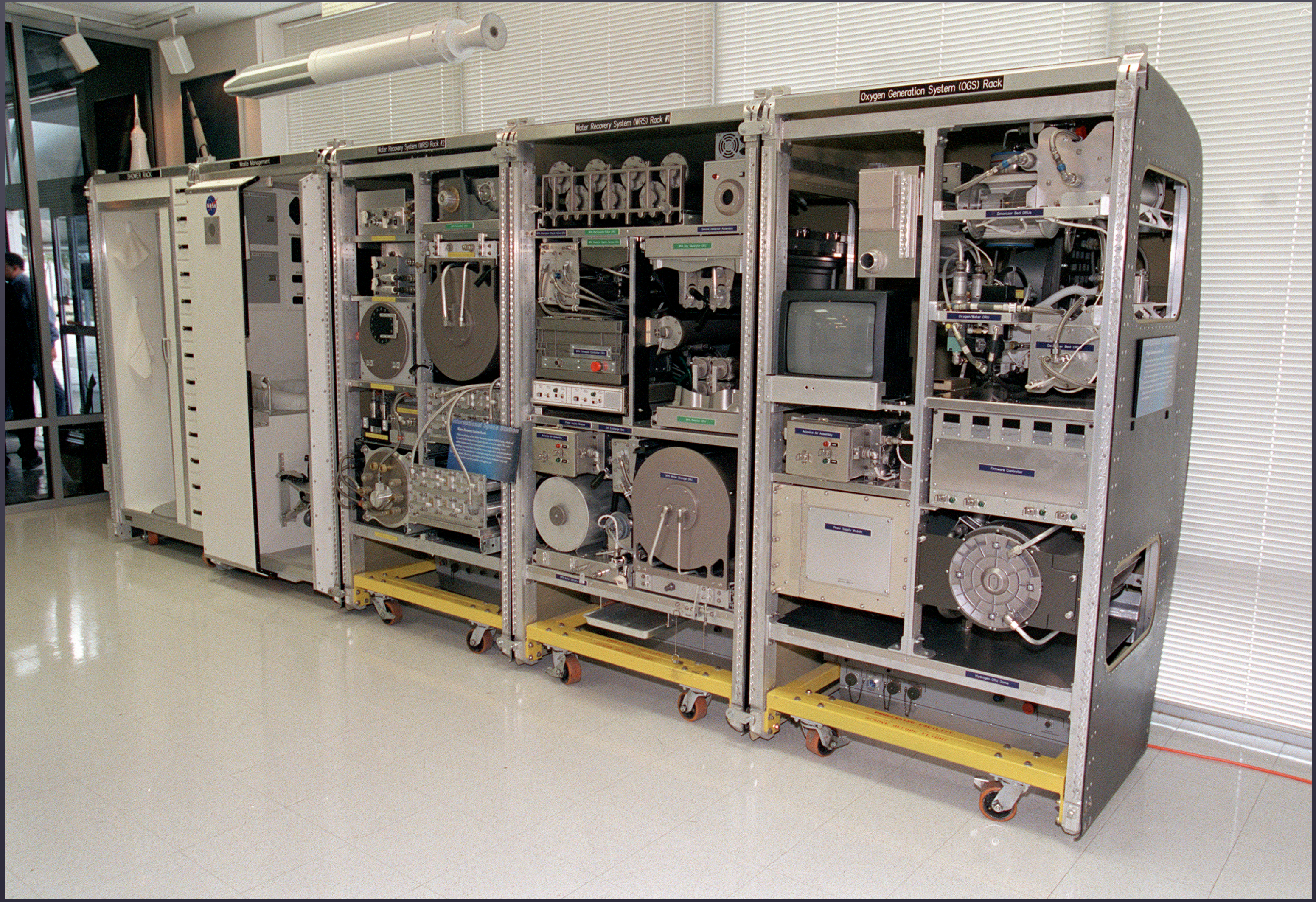

Source: nasa.gov

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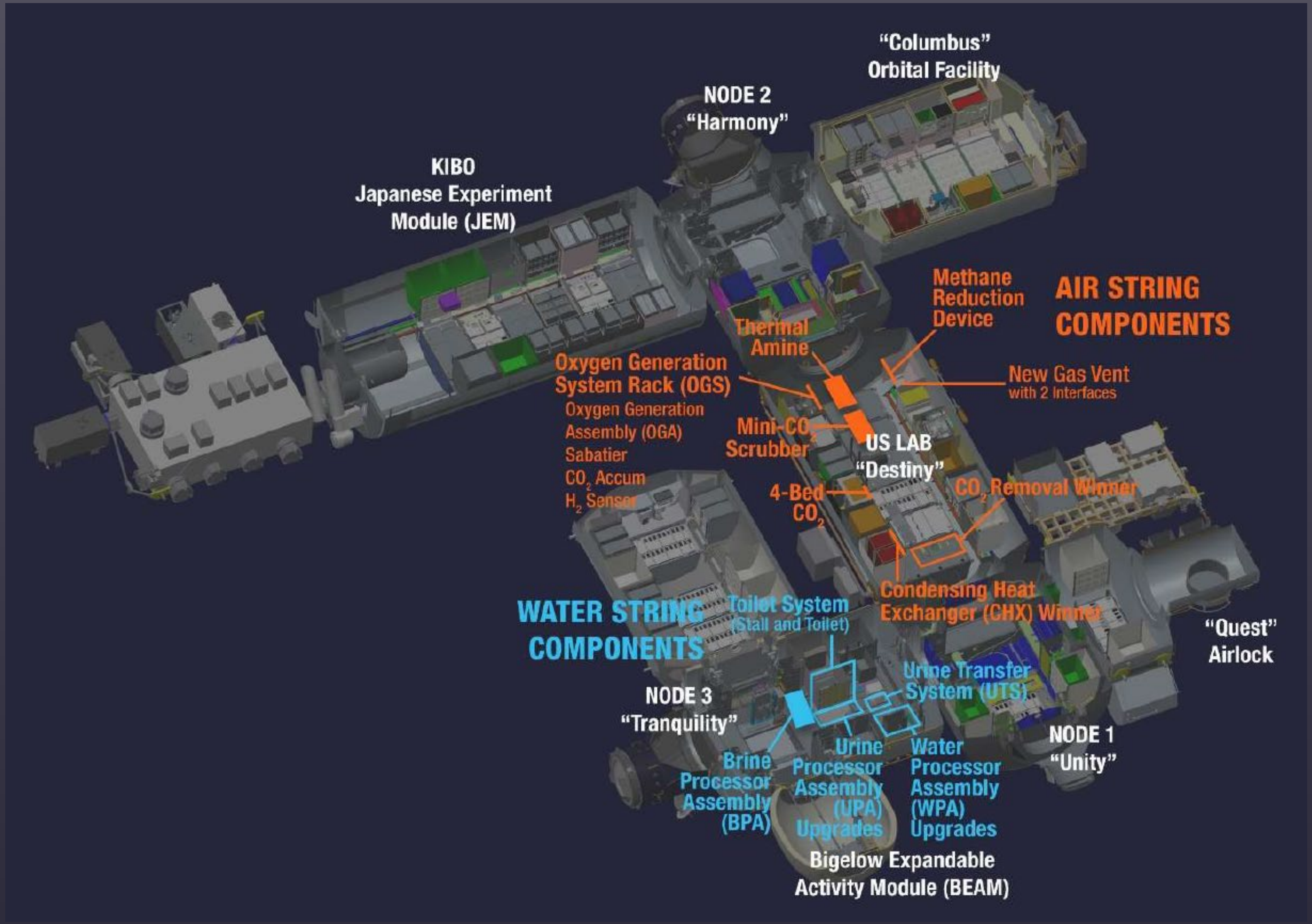
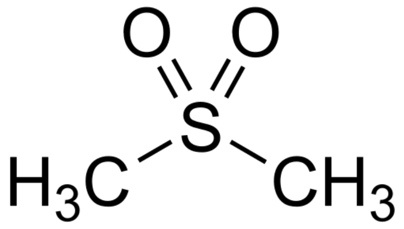


Source: Shaw et al. (2020)

Problem Statement

- The analysis of water samples in a recirculation loop of oxygen generation assembly showed measurable (few ppm) total organic carbon (TOC) levels
- Analysis of water samples revealed that dimethyl sulfone ($DMSO_2$) was one of the main sources of the TOC
- $DMSO_2$ is naturally present in many food products and passes through human body unchanged
- $DMSO_2$ is not effectively removed by any of the existing treatment technologies on the ISS because of its inert nature and low affinity towards many sorbents
- A recent investigation of a failed Sabatier reactor revealed that sulfur from $DMSO_2$ is the culprit



Ideas and Research Approaches

- Deep eutectic solvents (DES): binary or ternary mixtures of compounds that are able to associate mainly via hydrogen bonds
- Properties: chemically and thermally stable, nonflammable, low vapor pressure and volatility
- Tunability: variation of hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) in DES structure allows to synthesize task specific DES
- Synthesis and evaluation of DES: time consuming but molecular simulations can help with that
- DES coated biochar: easily fit in the existing WPA on the ISS and in general a promising approach to treat water contaminants

Project Objectives

- To screen and identify task specific DES for $DMSO_2$ removal from water
- To synthesize and evaluate DES for $DMSO_2$ removal from water
- To synthesize and evaluate biochar supported DES for $DMSO_2$ removal from water

Methodology

- Molecular simulation: Turbomole and COMSO-RS
- Solid support: Various types of biochar
- Batch study
  - $DMSO_2$ concentration: (110 µg/L), volume: 10 mL, time: 24 h, and neat DES: 0.1 g/60 mL
  - Amount of sorbent (DES coated biochar and uncoated biochar): 2 g/L

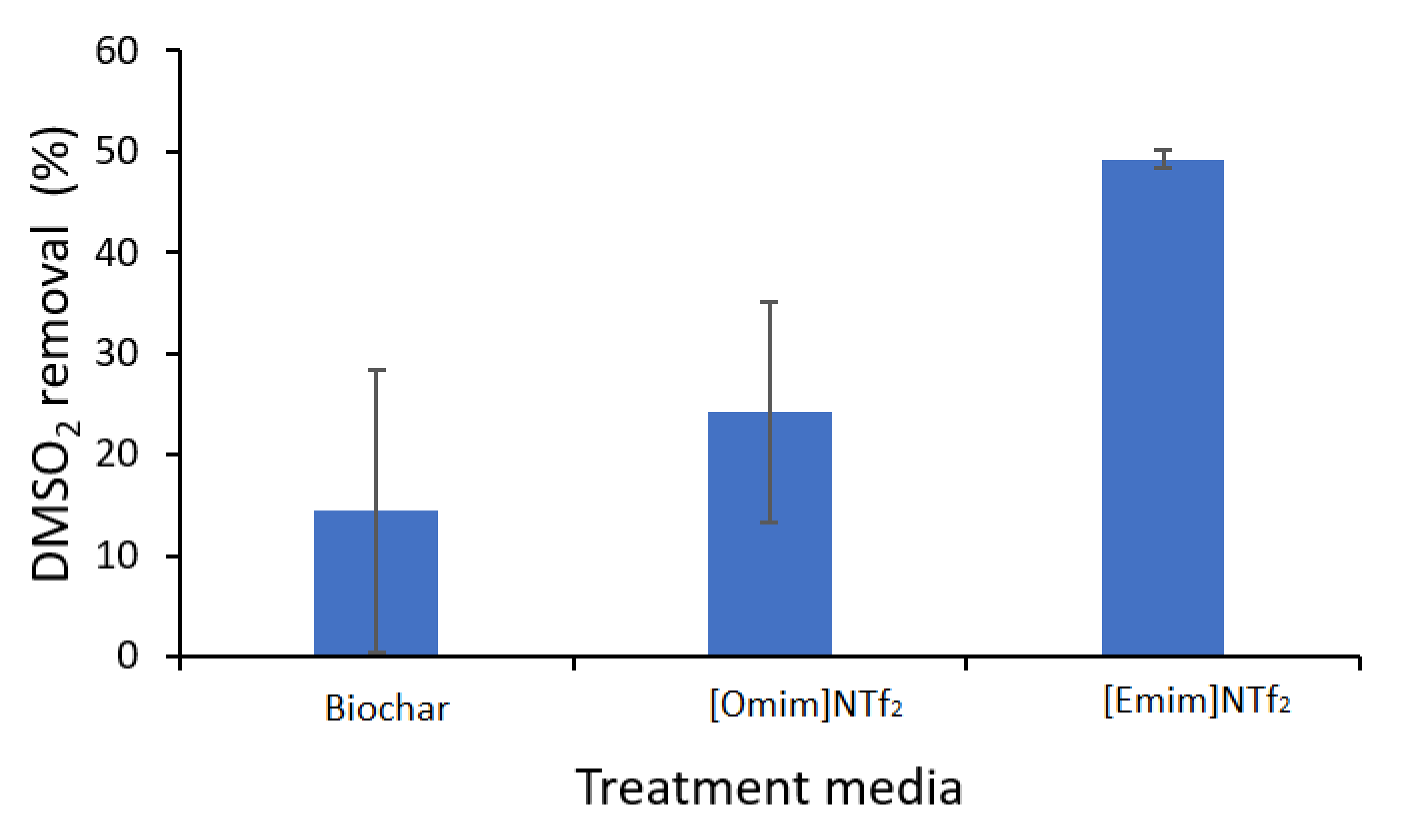
COSMO-RS: Selectivity and Capacities of $DMSO_2$ for Hydrophobic DES

[Cation][Anion](HBA)	HBD	Capacity ($DMSO_2$) $(1/\gamma_{DES}^{bin})$	K_i ($DMSO_2$) $(\gamma_{H20}^{bin}/\gamma_{DES}^{bin})$
[Emim][NTf_2]	Octanoic acid	2.970795	1.689682
[Emim] [NTf_2]	Nonanoic acid	2.529385	1.536519
[Bmim][pentafluoroethyltrifluoroborate]	Octanoic acid	2.680518	1.475559
[Bmim][pentafluoroethyltrifluoroborate]	Nonanoic acid	2.274835	1.33993
[Bmim][NTf_2]	Octanoic acid	2.660937	1.558455
[Bmim] [NTf_2]	Nonanoic acid	2.276803	1.421892

COSMO-RS: Selectivity and Capacities of $DMSO_2$ for Hydrophobic DES

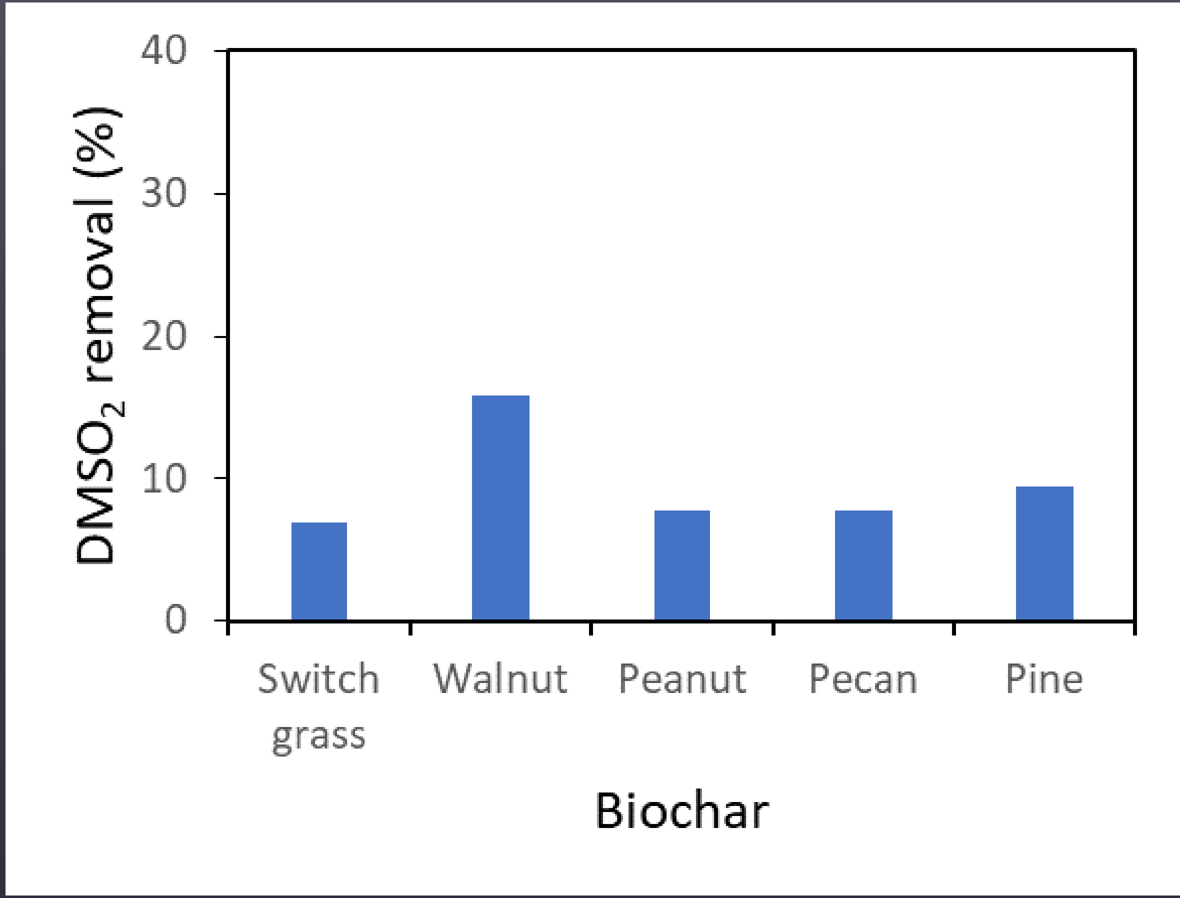
[Cation][Anion] (HBA)	HBD	Capacity ($DMSO_2$) ($1/\gamma_{DES}^{bin}$)	K_i ($DMSO_2$) ($\gamma_{H20}^{bin}/\gamma_{DES}^{bin}$)
[Omim][pentafluoroethyltrifluoroborate]	Octanoic acid	2.262241	1.319381
[Omim][pentafluoroethyltrifluoroborate]	Nonanoic acid	1.939174	1.205861
[Omim][NTf_2]	Octanoic acid	2.263297	1.399274
[Omim][NTf_2]	Nonanoic acid	1.954409	1.284297
[Ethyl-trihexyl-phosphonium][pentafluoroethyltrifluoroborate]	Octanoic acid	1.054055	0.710658
[Ethyl-trihexyl-phosphonium][pentafluoroethyltrifluoroborate]	Nonanoic acid	0.917047	0.655948
[Ethyl-trihexyl-phosphonium] [NTf_2]	Octanoic acid	1.079468	0.766672

Performance Verification of Top Two DES and Walnut Biochar



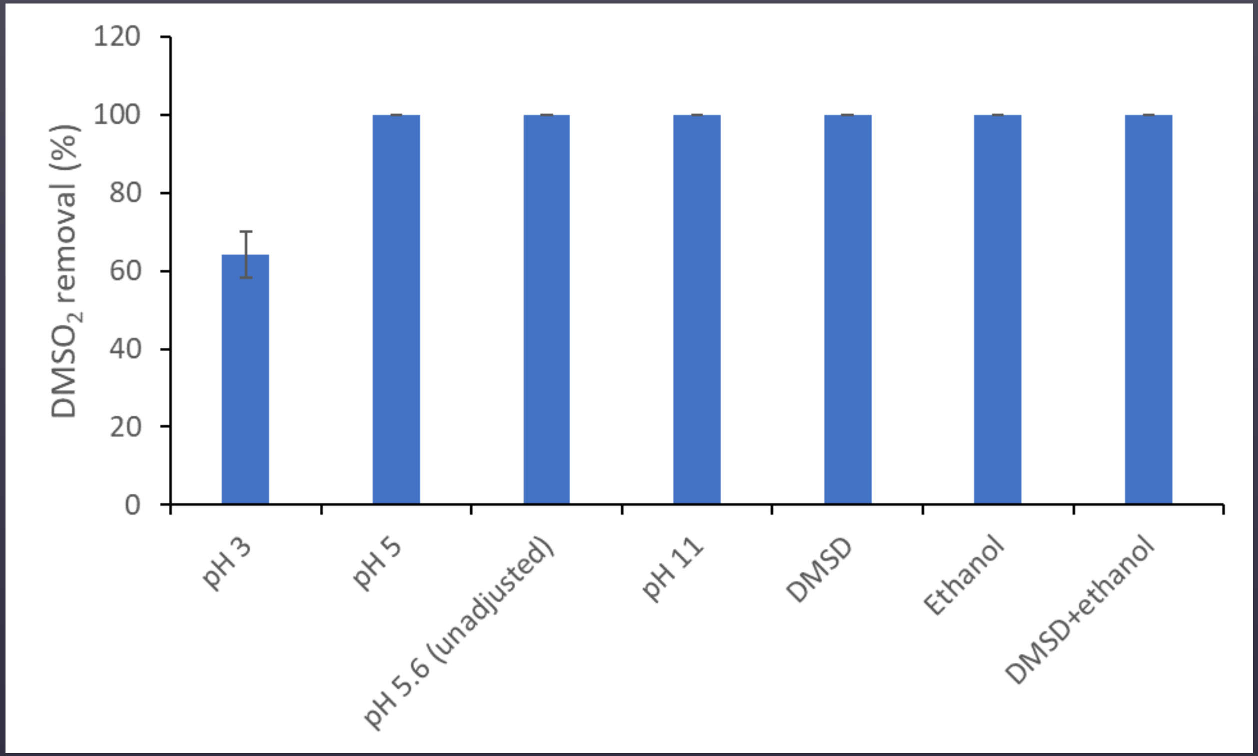
$DMSO_2$ concentration: (110 µg/L), volume: 60 mL, time: 24 h, neat DES: 0.1 g/60 mL, and biochar: 0.12 g/60 mL
[Omim]NTf_2: 1-methyl-3-*n*-octylimidazoliumbis(trifluoromethylsulfonyl)imide + octanoic acid
[Emim]NTf_2: 1-ethyl-3-methylimidazoliumbis(trifluoromethylsulfonyl)imide + octanoic acid

Batch Experiments: $DMSO_2$ Removal Using Different Biochars



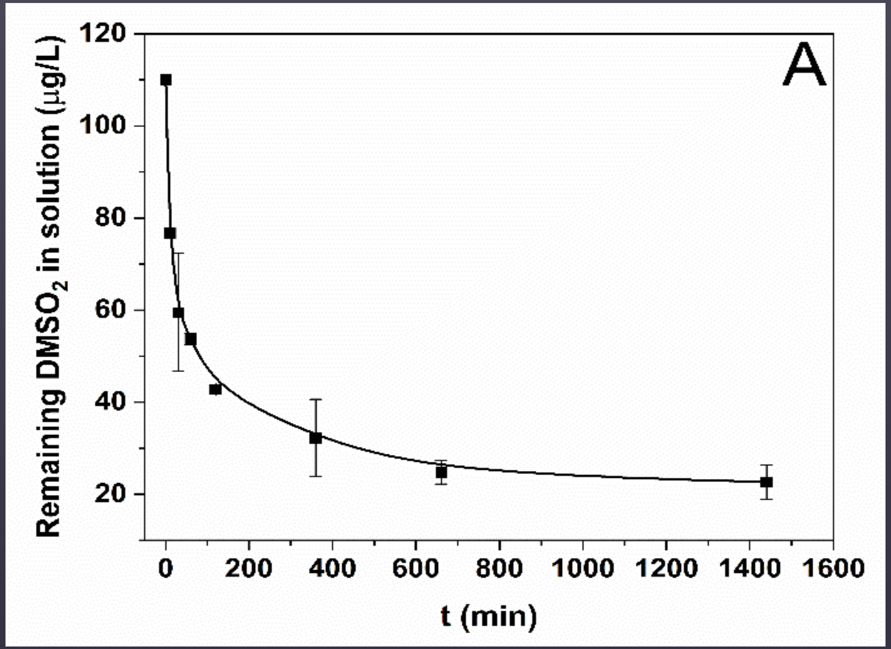
$DMSO_2$ concentration: (110 µg/L), volume: 60 mL, time: 24 h, and biochar: 2 g/L

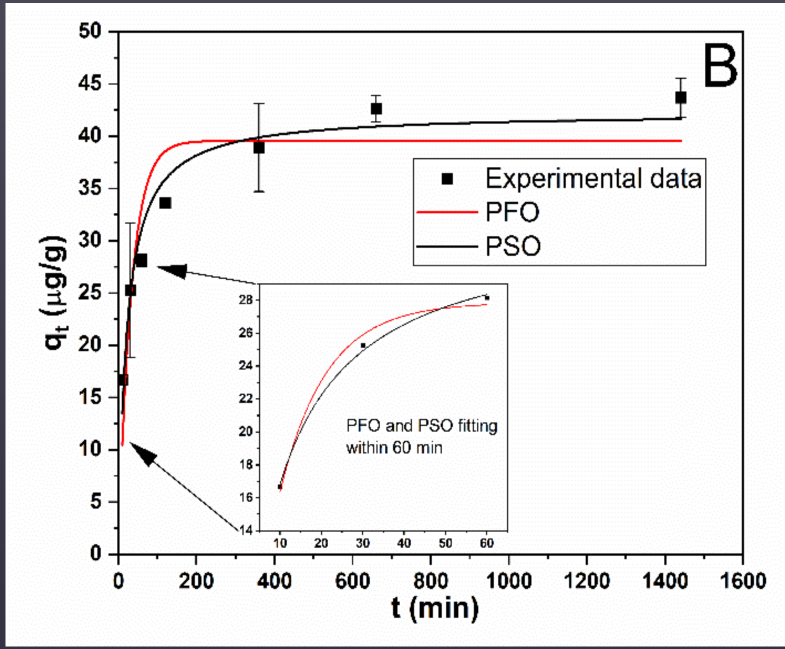
Batch Experiments: $DMSO_2$ Removal Using [Emim] NTf_2 Coated Biochar



$DMSO_2$ concentration: (110 µg/L), volume: 60 mL, time: 24 h, and biochar: 2 g/L

Batch Experiments: $DMSO_2$ Removal Using [Emim]NTf_2 Coated Biochar





(A) Adsorption kinetics of $DMSO_2$ onto [Emim]NTf_2 coated biochar, (B) Pseudo first order (PFO) and Pseudo second order (PSO kinetics)

$DMSO_2$ concentration: (110 μg/L), volume: 60 mL, time: 24 h, and biochar: 2 g/L

Kinetics and Isotherms Parameters

PFO	**q_e (µg/g)**	**39.54**
	k_1 (min^{-1})	0.031
	R^2	0.800
PSO	q_e (µg/g)	42.23
	k_2 (g/µg.min)	0.001
	R^2	0.945
Langmuir	q_m (µg/g)	34.86
	b (L/µg)	0.671
	R^2	0.775
Freundlich	K_F ((µg/g)(L/µg)$^{1/n}$)	23.67
	n	12.53
	R^2	0.752

Summary

- Molecular simulation is an effective tool to identify the task specific hydrophobic DES for emerging contaminant treatment
- Traditional biochar is not effective for $DMSO_2$ treatment
- DES coated biochar completely removed $DMSO_2$ even in the presence of co-contaminants
- The developed DES coated biochar has the potential to treat emerging contaminants in water/wastewater

Thank you for your attention!
Questions/Comments:

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