Ball milled biochar effectively removes sulfamethoxazole and sulfapyridine antibiotics from water and wastewater

UF | IFAS
UNIVERSITY of FLORIDA

Jinsheng Huang
Advisor: Dr. Bin Gao
Agricultural & Biological Engineering
University of Florida
February 2022

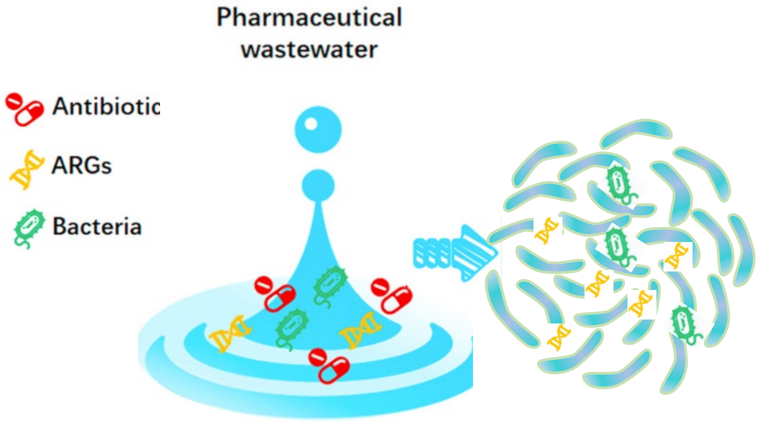
AGRICULTURAL & BIOLOGICAL
ENGINEERING

Background

- **Sulfonamides**
- Disease treatment
- Low metabolization

- **Potential sources**
  - Wastewater
  - Animal excretion

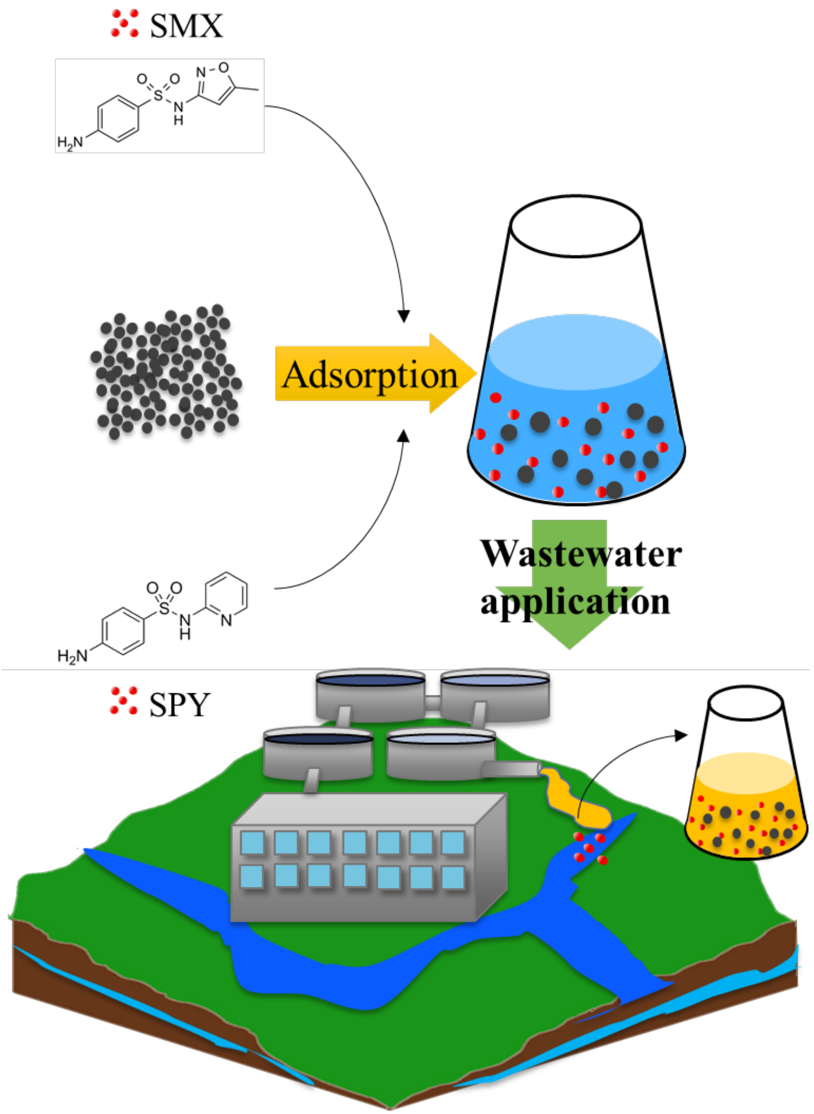
- **Drawbacks**
  - Mobility & biodegradation (S&GW&DW)
  - Carcinogen risk
  - Skin allergic reactions
  - Antibiotic resistance genes (ARGs)



https://waterandhealth.org/safe-drinking-water/drinking-water/antibiotic-resistant-bacteria-and-genes-in-wastewater-and-drinking-water/

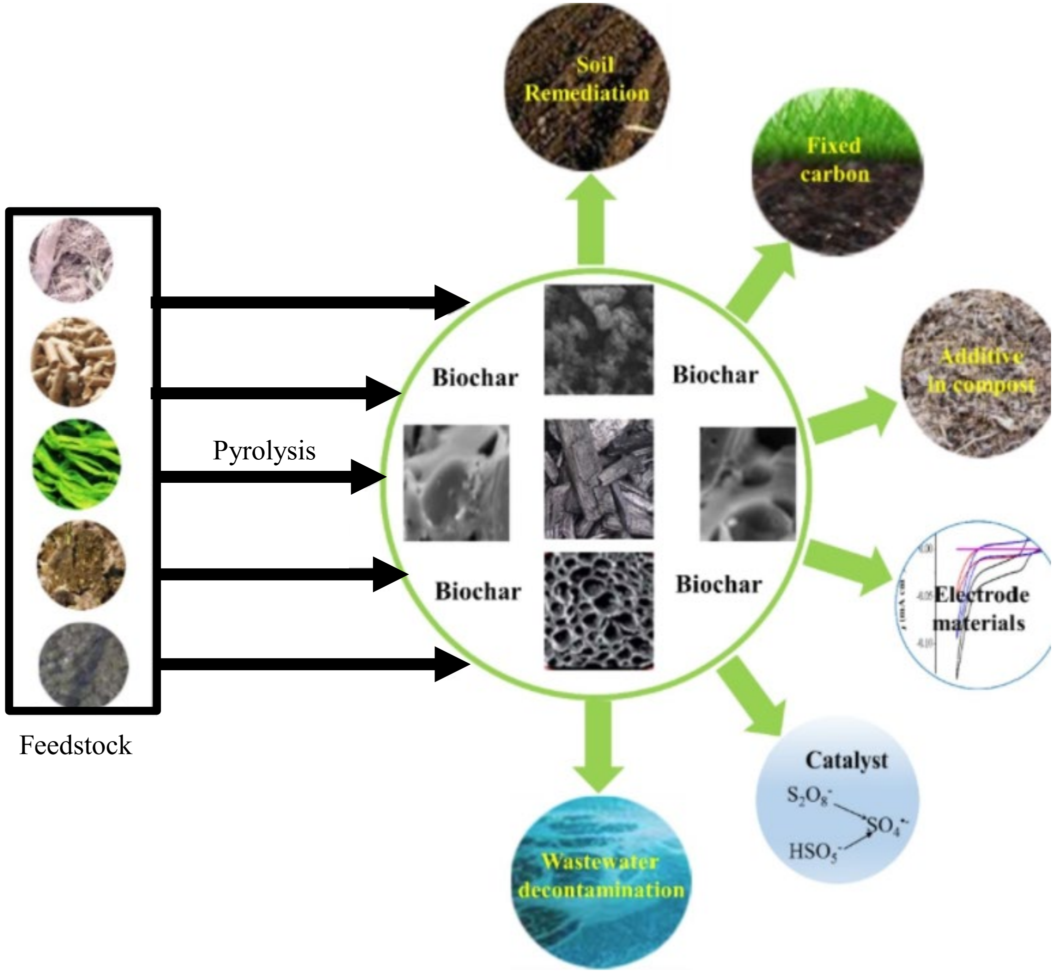
Motivation

- **Removal**
  - Sulfonamide antibiotics
- **Treatment methods**
  - R&O, ion exchange
  - High capital cost
  - Limited operation
- **Adsorption**
  - Convenient
  - Affordable
  - Environment-friendly



Adsorbents

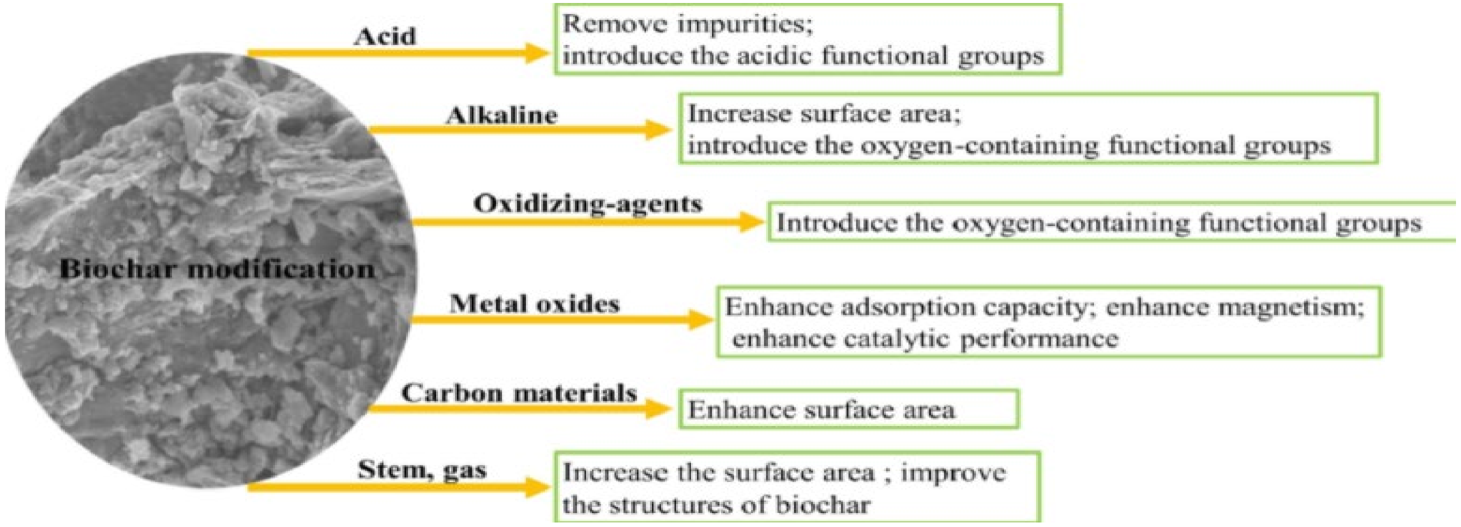
- **Biochar**
  - Low cost (5 times cheaper than activated carbon)
  - A black carbon derived from thermal conversion of biomass
  - Environmental application



Wang, Jianlong, and Shizong Wang. Journal of Cleaner Production 227 (2019): 1002-1022.

Biochar Modification

- **Why**
  - Depends on feedstocks
  - Unmodified
- **Purpose**
  - Physiochemical.
  - Functionality
  - **SAs & FGs**

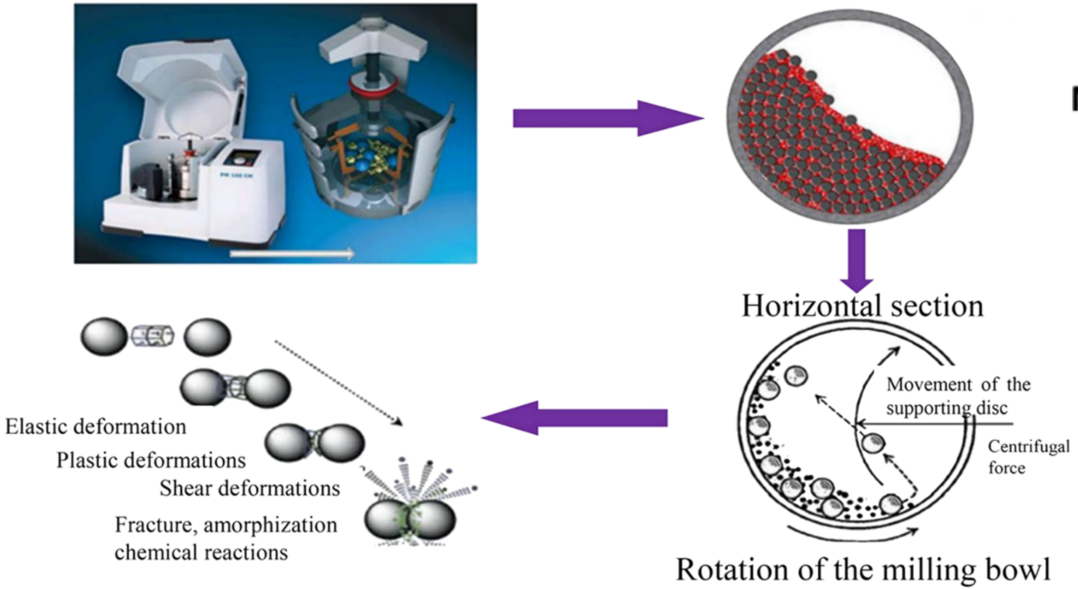


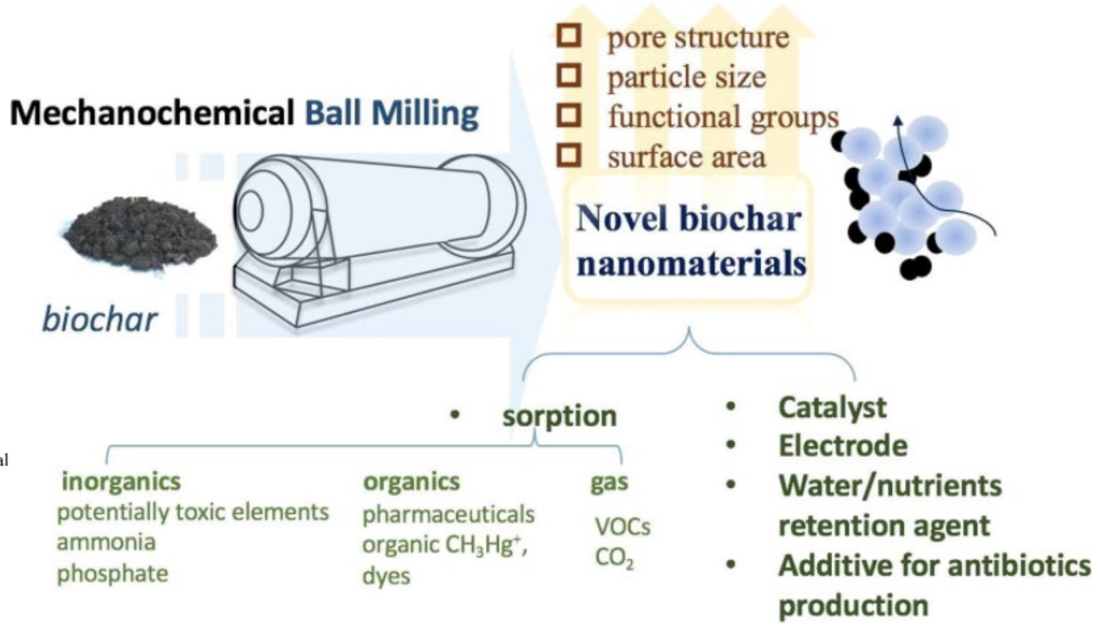
Wang, Jianlong, and Shizong Wang. Journal of Cleaner Production 227 (2019): 1002-1022.

- **Modification**
  - Chemical, biological, and physical pretreatment and post-treatment
  - Harmful by-product pollution

Methodology

- **Ball milling**
  - Mechanochemical approach
  - Top-down nano-synthesis method



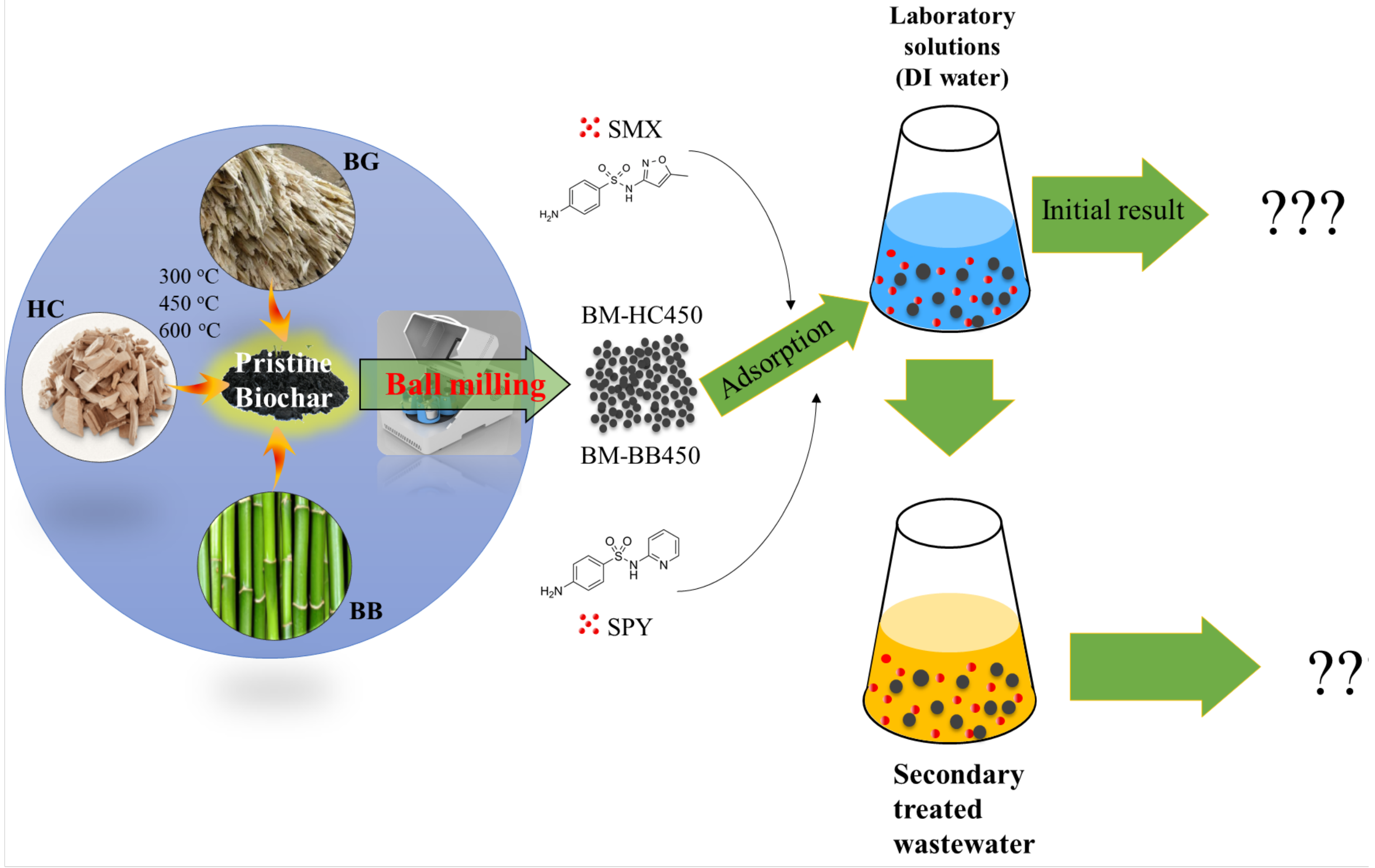


Lyu, H., et al., *ACS Sustainable Chemistry & Engineering*, 5.11 (2017)

Kumar, Manish, et al. Bioresource technology (2020): 123613.

Methodology

- **Sulfonamides**
  - Sulfamethoxazole (SMX)
  - Sulfapyridine (SPY)
- **Initial assessment**
- **Batch system**
  - Kinetic
  - Isotherm
- **Solution**
  - DI water
  - Wastewater



Wastewater Samples

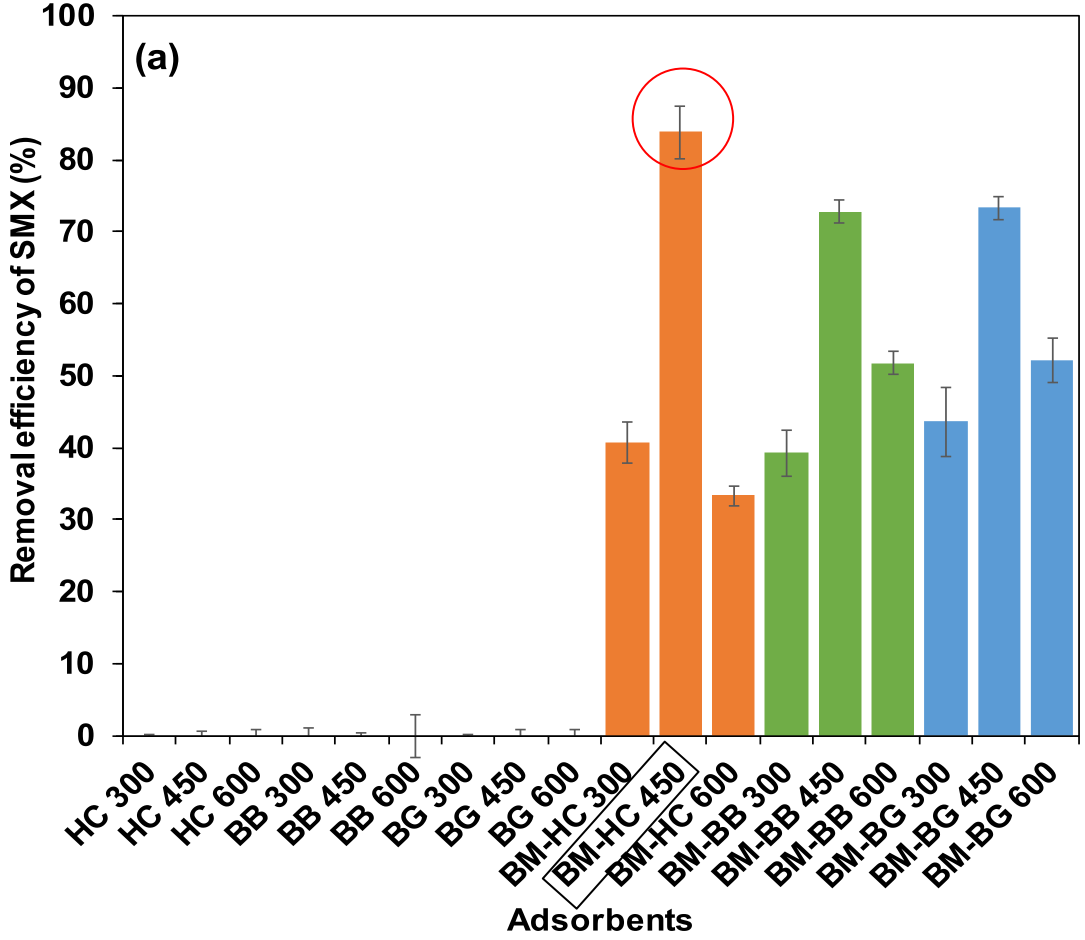
- **Information**
  - 2nd treated
  - WWTPs @ UF
  - Physiochemical property
- **Sample preparation**
  - WW spiked with SMX/SPY
  - 10 ppm
  - Degradation

Parameters	Range	Mean
TOC	4.08–9.40 mg/L	7.11 ± 1.46 mg/L
Na^+	54.18–76.99 mg/L	61.55 ± 5.00 mg/L
K^+	11.94–35.82 mg/L	24.53 ± 9.54 mg/L
Ca^{2+}	44.23–53.26 mg/L	47.81 ± 2.61 mg/L
Mg^{2+}	28.35–44.92 mg/L	31.37 ± 4.21 mg/L
NH_4^+-N	0.04–0.81 mg/L	0.22 ± 0.29 mg/L
NO_3^--N	0.35–2.68 mg/L	1.35 ± 1.02 mg/L
Cl^-	84.97–120.93 mg/L	103.41 ± 14.70 mg/L
Total P	0.90–6.40 mg/L	2.68 ± 1.60 mg/L
pH	7.14–8.16	7.61 ± 0.34

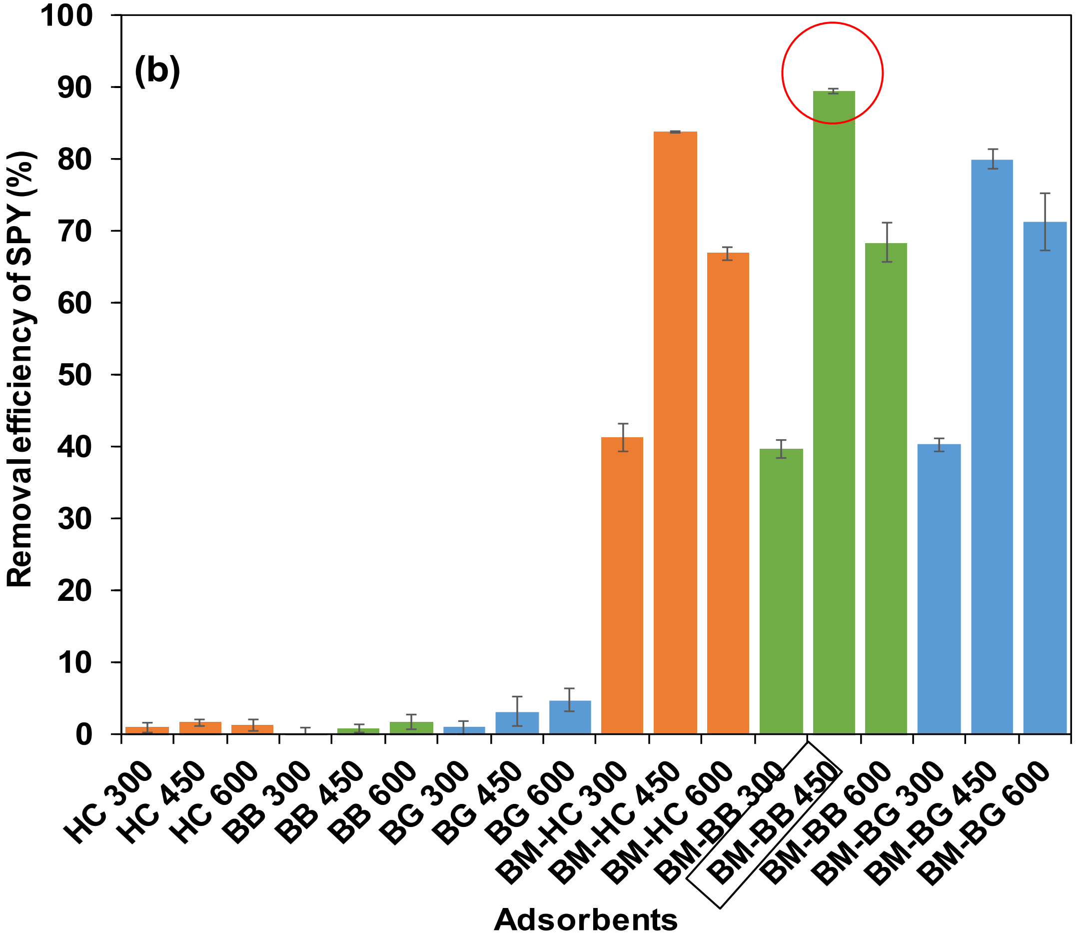
Zheng, Yulin, et al. Chemical Engineering Journal 362 (2019): 460-468.

Initial Assessment

- **SMX**

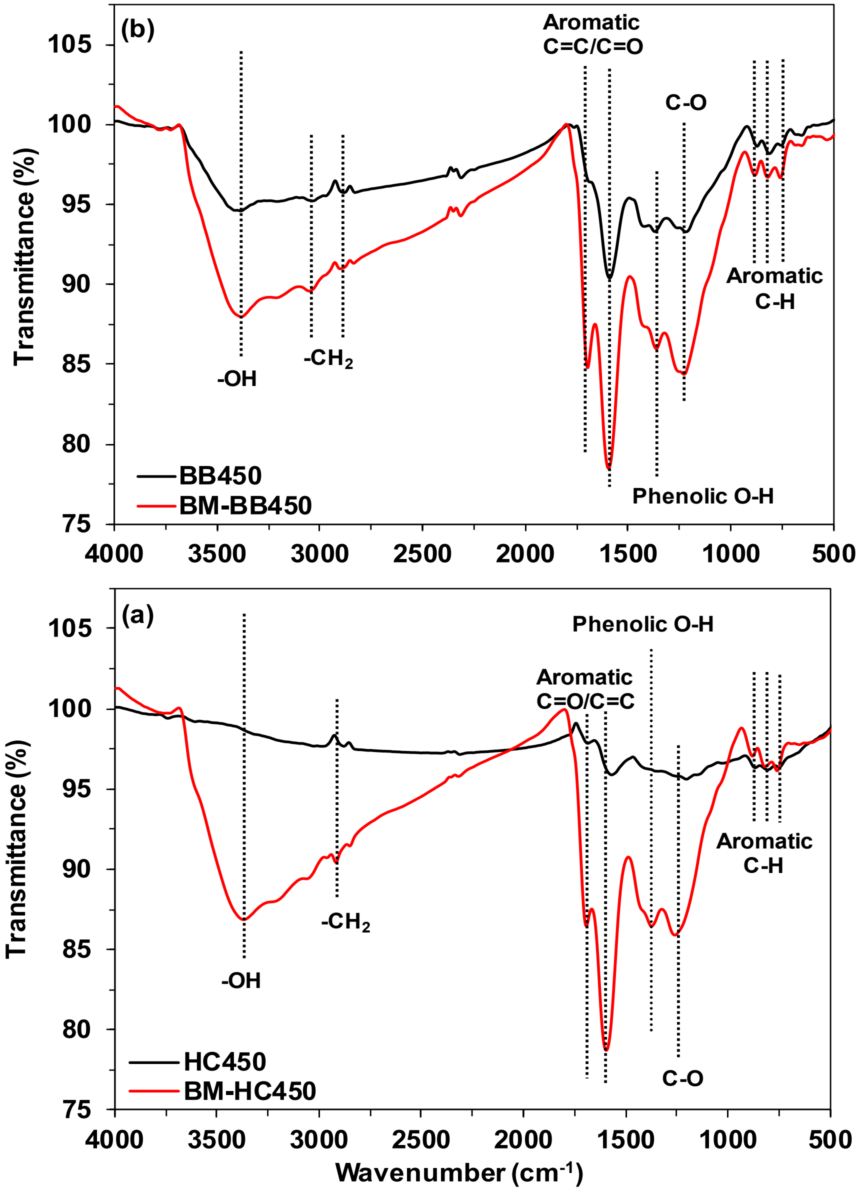


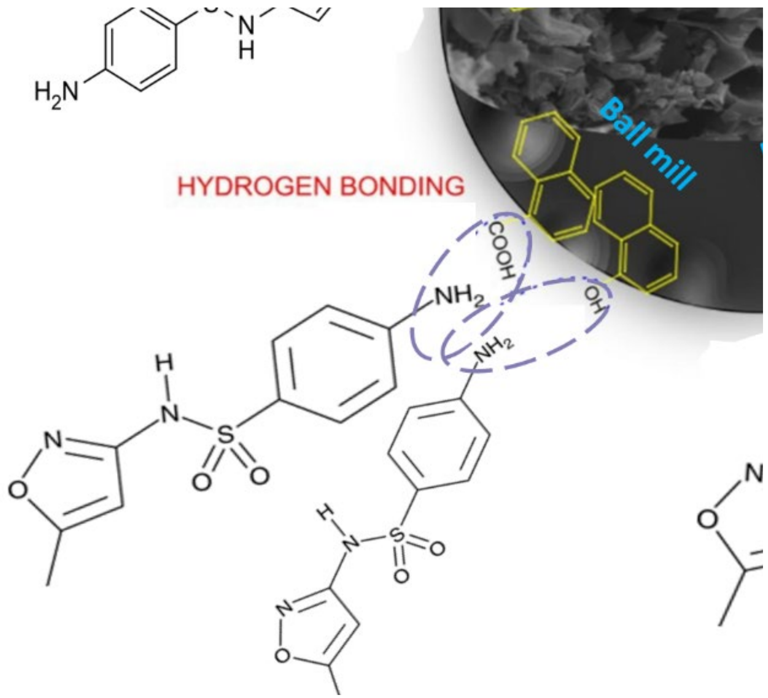
- **SPY**



FTIR

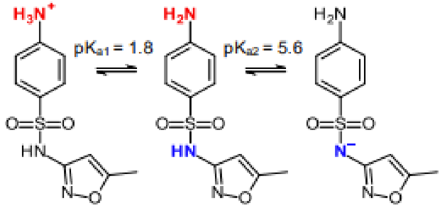
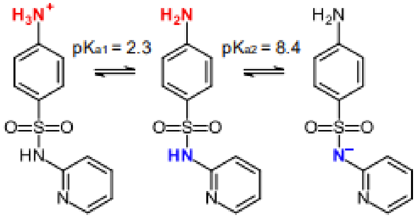
- **BM-BB 450**
- **BM-HC 450**

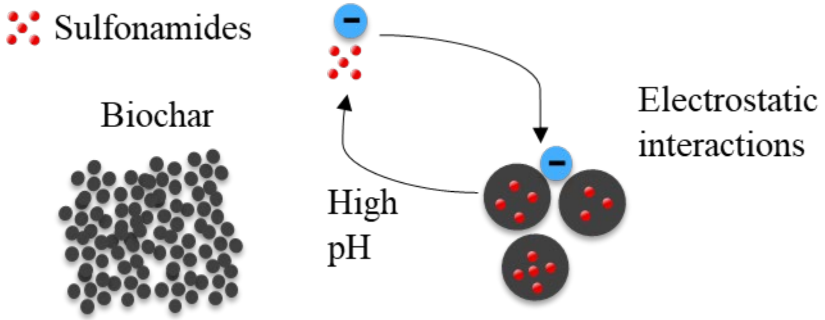




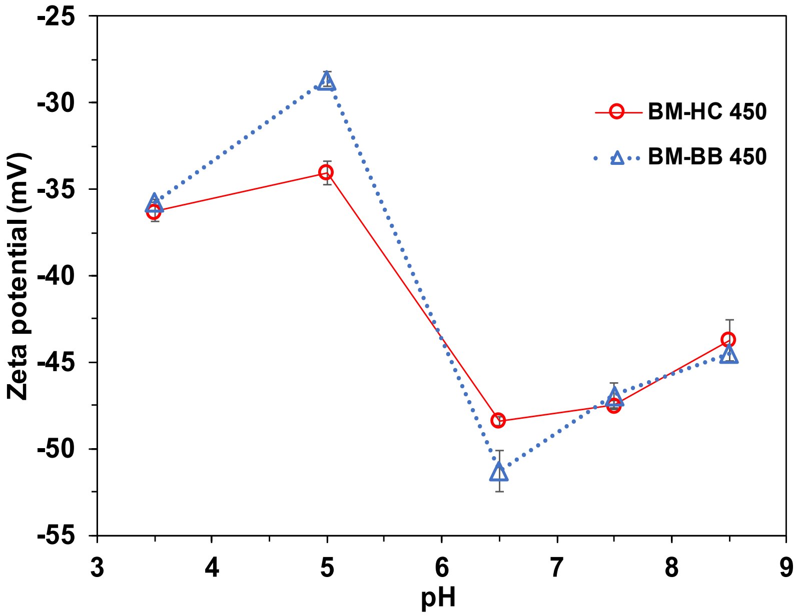
Zeta & pH & Speciation

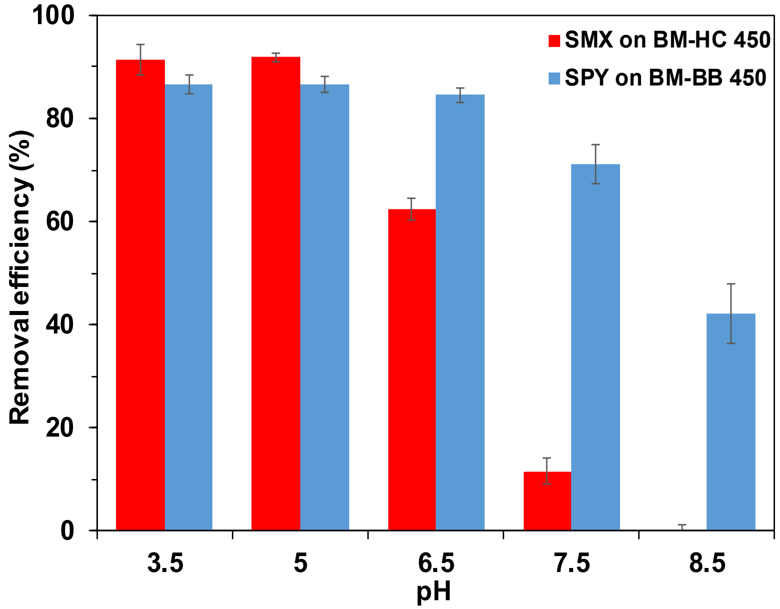
- **Speciation table**

Name	Structure	Molecular weight (g/mol)	Acidity constant pK_a	Speciation pH 3.0	Speciation pH 5.6	Speciation pH 7.0	Speciation pH 9.0
SMX		253.3	$pK_{a1} = 1.8$ $pK_{a2} = 5.6$	SMX^+ (6%) & SMX (94%)	SMX (50%) & SMX^- (50%)	SMX (4%) & SMX^- (96%)	SMX^-
SPY		249.3	$pK_{a1} = 2.3$ $pK_{a2} = 8.4$	SPY^+ (17%) & SPY (83%)	SPY	SPY (96%) & SPY^- (4%)	SPY (20%) & SPY^- (80%)



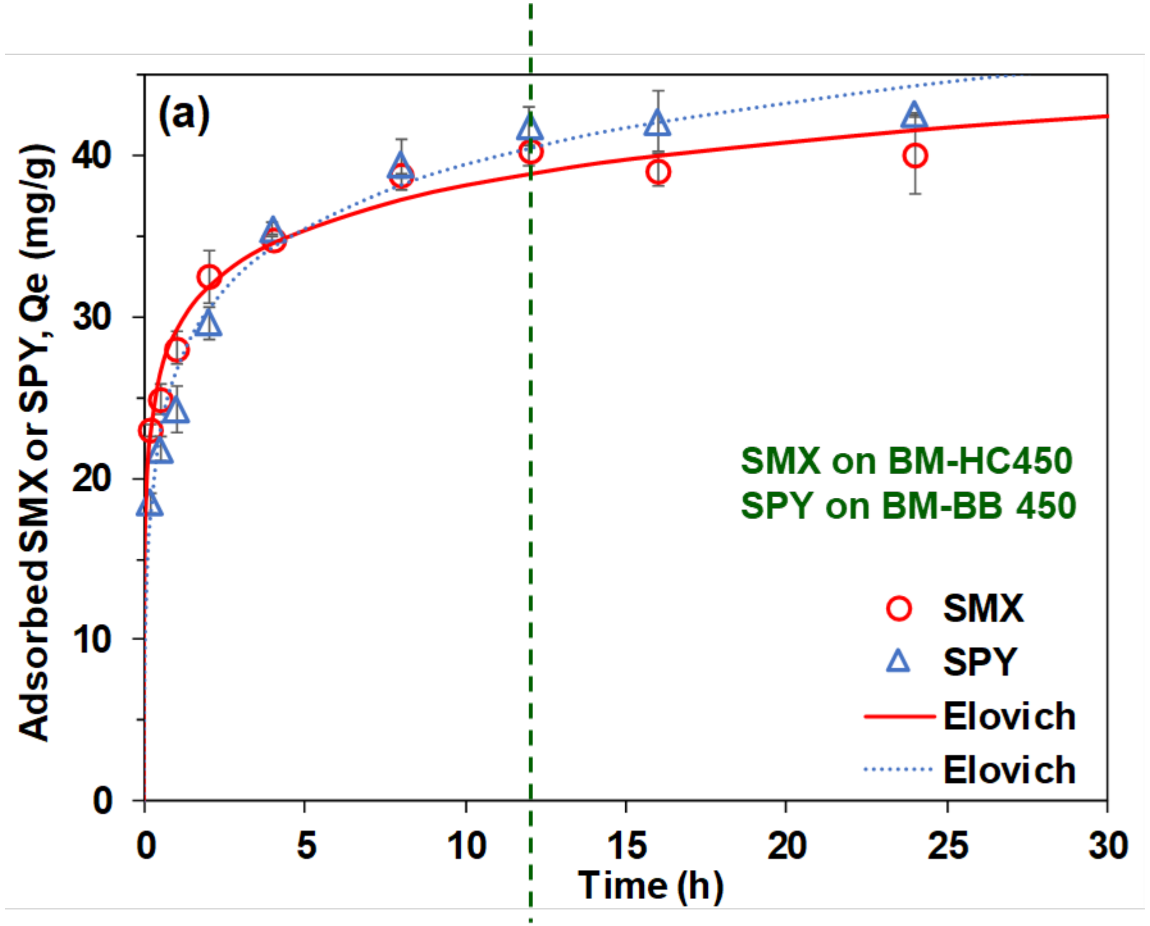
Tian, Yuan, et al., Chemosphere 90.10 (2013): 2597-2605.



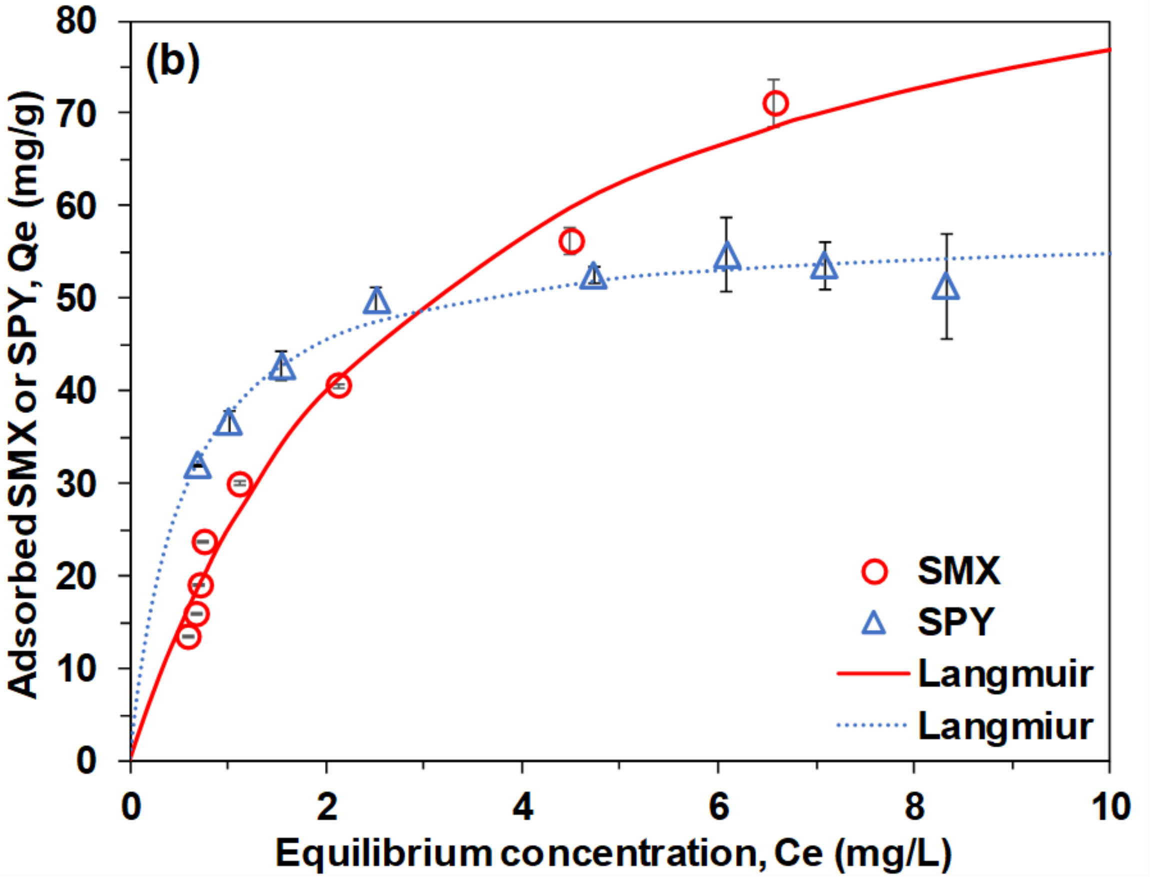


Batch Sorption in Water (pH 6)

- **Kinetics**



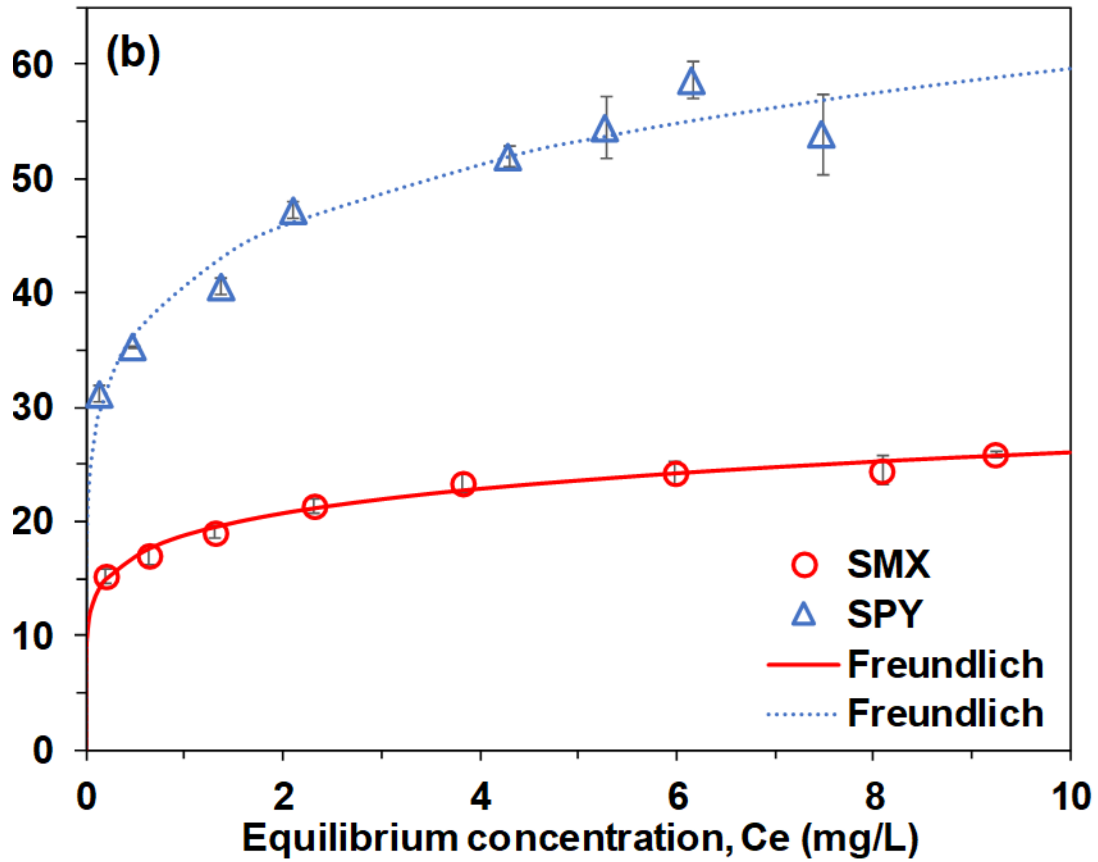
- **Isotherm**



Batch Sorption in Wastewater (~pH 7.6)

Parameters	Range	Mean
TOC	4.08–9.40 mg/L	7.11 ± 1.46 mg/L
Na^+	54.18–76.99 mg/L	61.55 ± 5.00 mg/L
K^+	11.94–35.82 mg/L	24.53 ± 9.54 mg/L
Ca^{2+}	44.23–53.26 mg/L	47.81 ± 2.61 mg/L
Mg^{2+}	28.35–44.92 mg/L	31.37 ± 4.21 mg/L
NH_4^+-N	0.04–0.81 mg/L	0.22 ± 0.29 mg/L
NO_3^--N	0.35–2.68 mg/L	1.35 ± 1.02 mg/L
Cl^-	84.97–120.93 mg/L	103.41 ± 14.70 mg/L
Total P	0.90–6.40 mg/L	2.68 ± 1.60 mg/L
pH	7.14–8.16	7.61 ± 0.34

- Isotherm

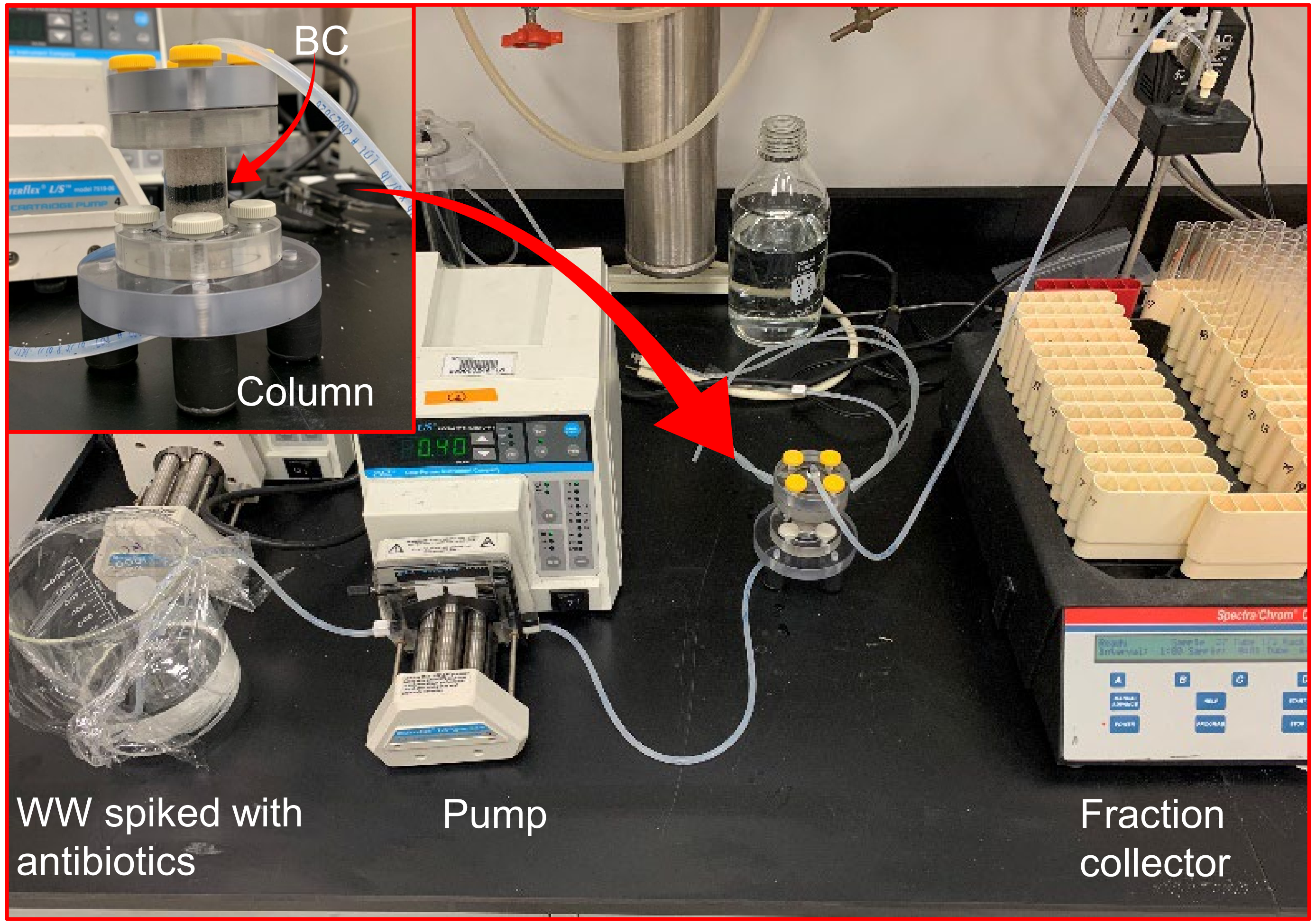


Conclusion

- Ball milling greatly enhanced the ability of biochar to sorb SMX and SPY in water (pH of 6.0). For each biomass, 450 ^{o}C ball milled biochar showed the best removal efficiency.
- Solution pH strongly affected sulfonamide adsorption through variations in electrostatic interaction
- In wastewater, the 450 ^{o}C ball milled biochar still performed well, especially for SPY adsorption. Due to the greater pH of wastewater, SMX sorption capacity of BM-HC450 dramatically declined but still in a considerable amount.

Future Works

- Regeneration & stability
- Fixed bed column
  - Large-scale operations of sulfa- treatment in wastewater
  - Dosage & Flow rate
  - Model & Breakthrough



Reference

- Huang, Jinsheng, et al. "Ball milled biochar effectively removes sulfamethoxazole and sulfapyridine antibiotics from water and wastewater." Environmental Pollution 258 (2020): 113809.
- Kumar, Manish, et al. "Ball milling as a mechanochemical technology for fabrication of novel biochar nanomaterials." Bioresource technology (2020): 123613.
- Lyu, Honghong, et al. "Ball-milled carbon nanomaterials for energy and environmental applications." ACS Sustainable Chemistry & Engineering 5.11 (2017): 9568-9585.
- Wang, Jianlong, and Shizong Wang. "Preparation, modification and environmental application of biochar: a review." Journal of Cleaner Production 227 (2019): 1002-1022.
- Tian, Yuan, et al. "Removal of sulfamethoxazole and sulfapyridine by carbon nanotubes in fixed-bed columns." Chemosphere 90.10 (2013): 2597-2605.
- Liu, Ni, et al. "Synthesis a graphene-like magnetic biochar by potassium ferrate for 17β-estradiol removal: Effects of Al2O3 nanoparticles and microplastics." Science of The Total Environment 715 (2020): 136723.
- Zheng, Yulin, et al. "Reclaiming phosphorus from secondary treated municipal wastewater with engineered biochar." Chemical Engineering Journal 362 (2019): 460-468.

Table S3. Specific surface area of biochar samples used in this study (Lyu et al., 2018).

Pristine Biochar	Surface area (m^2/g)	Ball milled biochar	Surface area (m^2/g)
HC300	0.8	BM-HC300	5.6
HC450	9.8	BM-HC450	309
HC600	221	BM-HC600	270
BB300	2	BM-BB300	8.3
BB450	4.7	BM-BB450	299
BB600	59	BM-BB600	276
BG300	0	BM-BG300	10.8
BG450	51	BM-BG450	331
BG600	359	BM-BG600	364