Removal of sulfamethazine and sulfathiazole from water using modified bamboo biochar

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USBI: 2016 Conference
Oregon State University, Corvallis, OR, USA
22nd -25th of August, 2016

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Contents

Antibiotics and Their Effects

Antibiotics as emerging contaminants are of global concern due to the development of antibiotic resistant genes potentially causing superbugs. They are unique among medicines in that they act selectively on bacteria, among them the pathogens, while leaving cells and tissues unaffected (Ahmed et al., 2015).

Impacts of antibiotics:

- Significance impacts on aquatic organisms on their survival, growth and body weight at μg L^{-1} – mg L^{-1} concentration level.
- Can alter the microbial communities leading to the antibiotic resistance of some bacteria.
- May be absorbed eventually by humans through food chain and drinking water.
- Geno-toxic effects

Price of Different Adsorbents

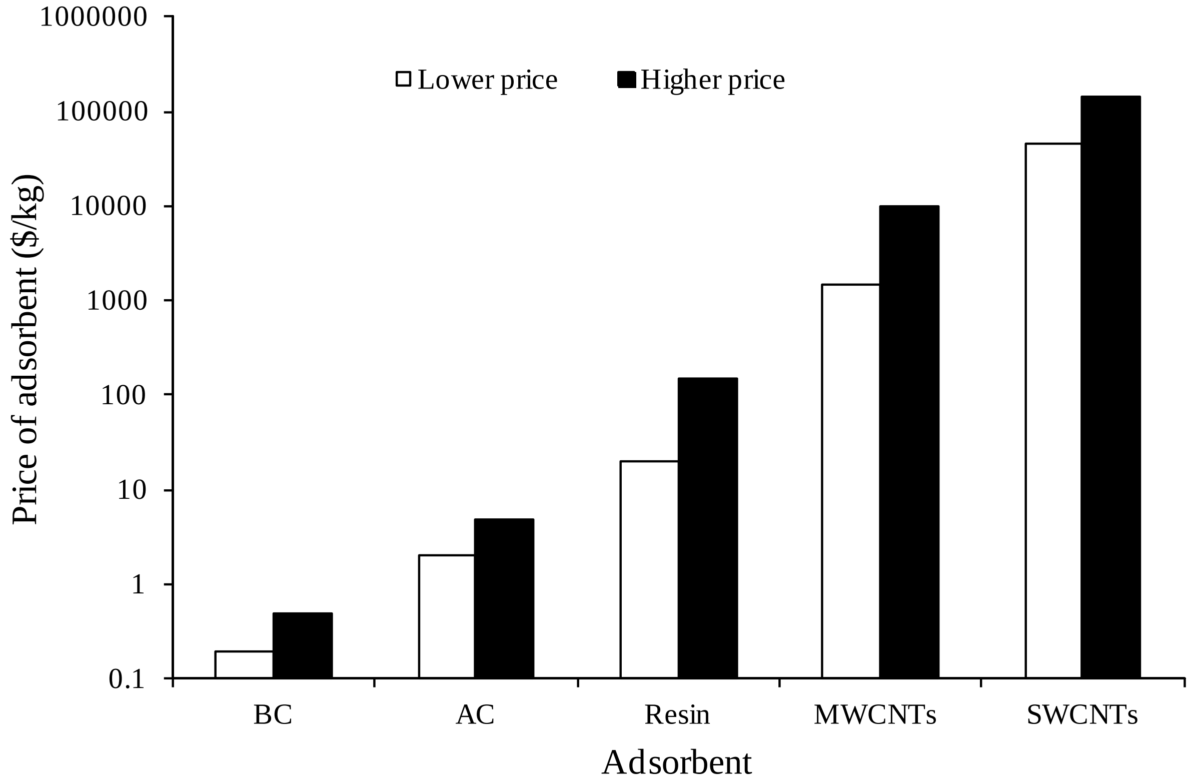


Fig. The price of different adsorbents (BC = Biochar, AC = Activated Carbon, MWCNTs = Multi Wall Carbon Nanotubes, SWCNTs = Single Wall Carbon Nanotubes (Ahmed et al., 2015).

Ahmed, M. B., Zhou, J. L., Ngo, H. H., & Guo, W. (2015). Adsorptive removal of antibiotics from water and wastewater: progress and challenges. ***Sci. Total Environ. 532*****, 112-126.**

Biochar, Modified Biochar and Their Applications

Biochar is a carbon dominant product which is obtained when biomass feedstock's are heated at elevated temperature in a closed reactor with little or oxygen hungry conditions even (Ahmed et al., 2016a).

Modified biochar is obtained when biochar is further activated or modified either chemically or physically in order to improve their sorptive properties of contaminants (Ahmed et al., 2016b).

Applications of Biochar:

- Sorptive removal of heavy metals, anionic contaminants, and organic including emerging contaminants
- Reduction of trace-gas emissions from soil and atmosphere
- Bolster soil fertility agricultural and crop production
- Carbon sequestration

Ahmed, M. B., Zhou, J. L., Ngo, H. H., & Guo, W. (2016a). Insight into biochar properties and its cost analysis. *Biomass Bioenerg. 84*, 76-86.

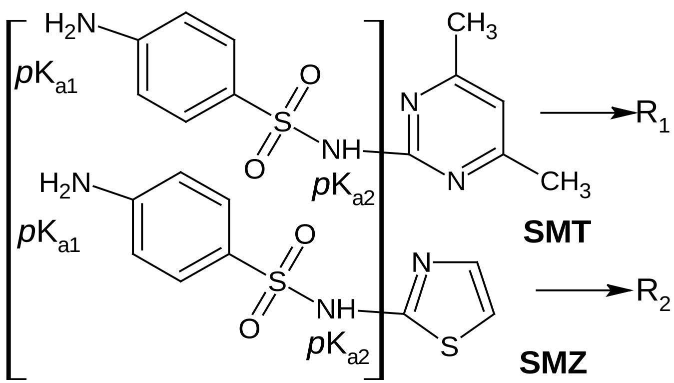
Ahmed, M. B., Zhou, J. L., Ngo, H. H., Guo, W., & Chen, M. (2016b). Progress in the preparation and application of modified biochar for improved contaminant removal from water and wastewater. *Bioresour. Technol. 214*, 836-851.

Physicochemical Properties of Sulfonamide Antibiotics

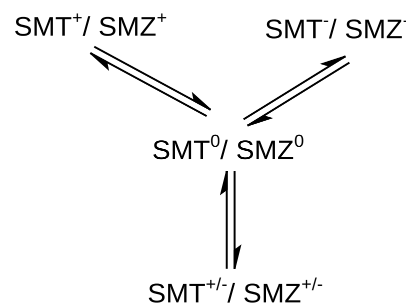
Class	Compound	Acronym	CAS Number	$\log k_{ow}$	pK_a	Molecular mass	Molecular formula
Sulphonamides (SAs)	Sulfamethazine	SMT	57-68-1	0.14	2.65/7.65	278.34	$C_{12}H_{14}N_4O_2S$,
	Sulfathiazole	SMZ	74-14-0	0.05	2.2/7.24	255.32	$C_{10}H_{11}N_3NaO_3S^+$ [1]

K_{ow}: Octanol-water partition coefficient & pK_a : Acid dissociation constant

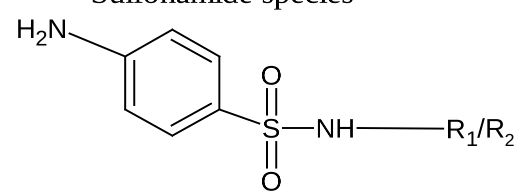
- Moderately soluble in water and the $\log K_{ow}$ indicates that they are moderately hydrophilic



Sulfonamide structures



Sulfonamide species

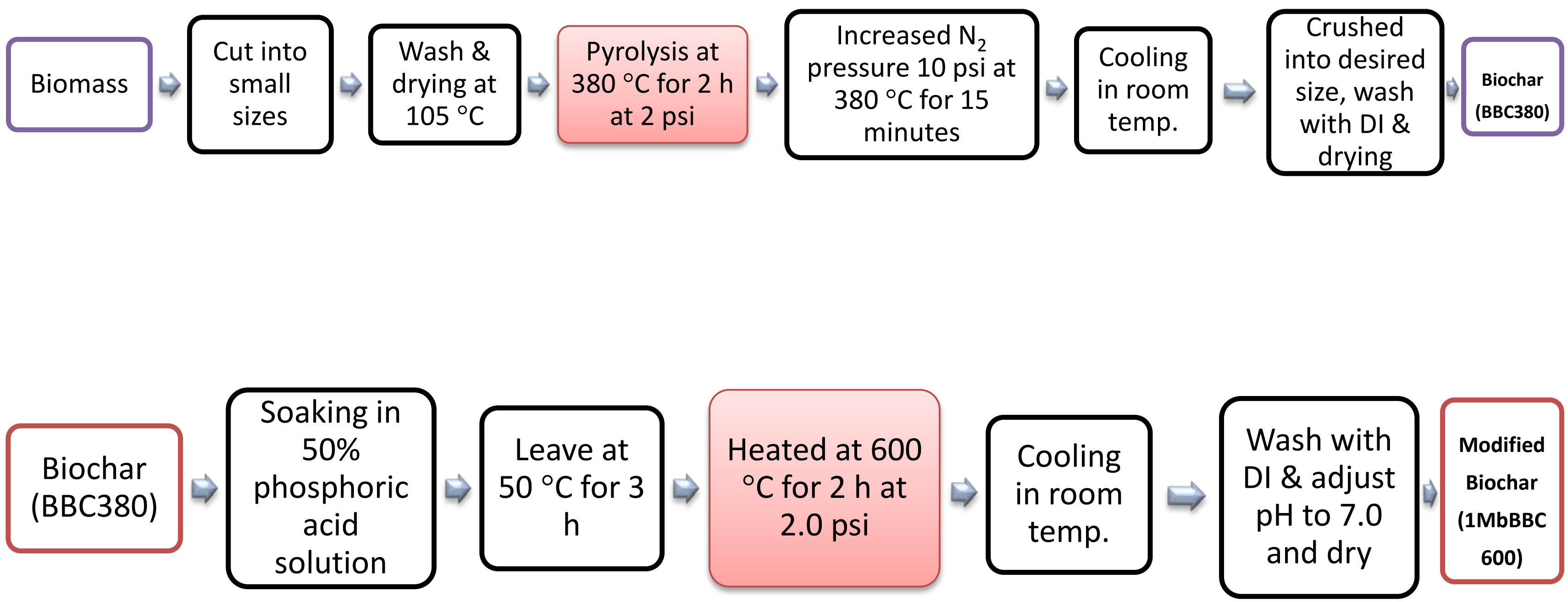


General formula of sulfonamides

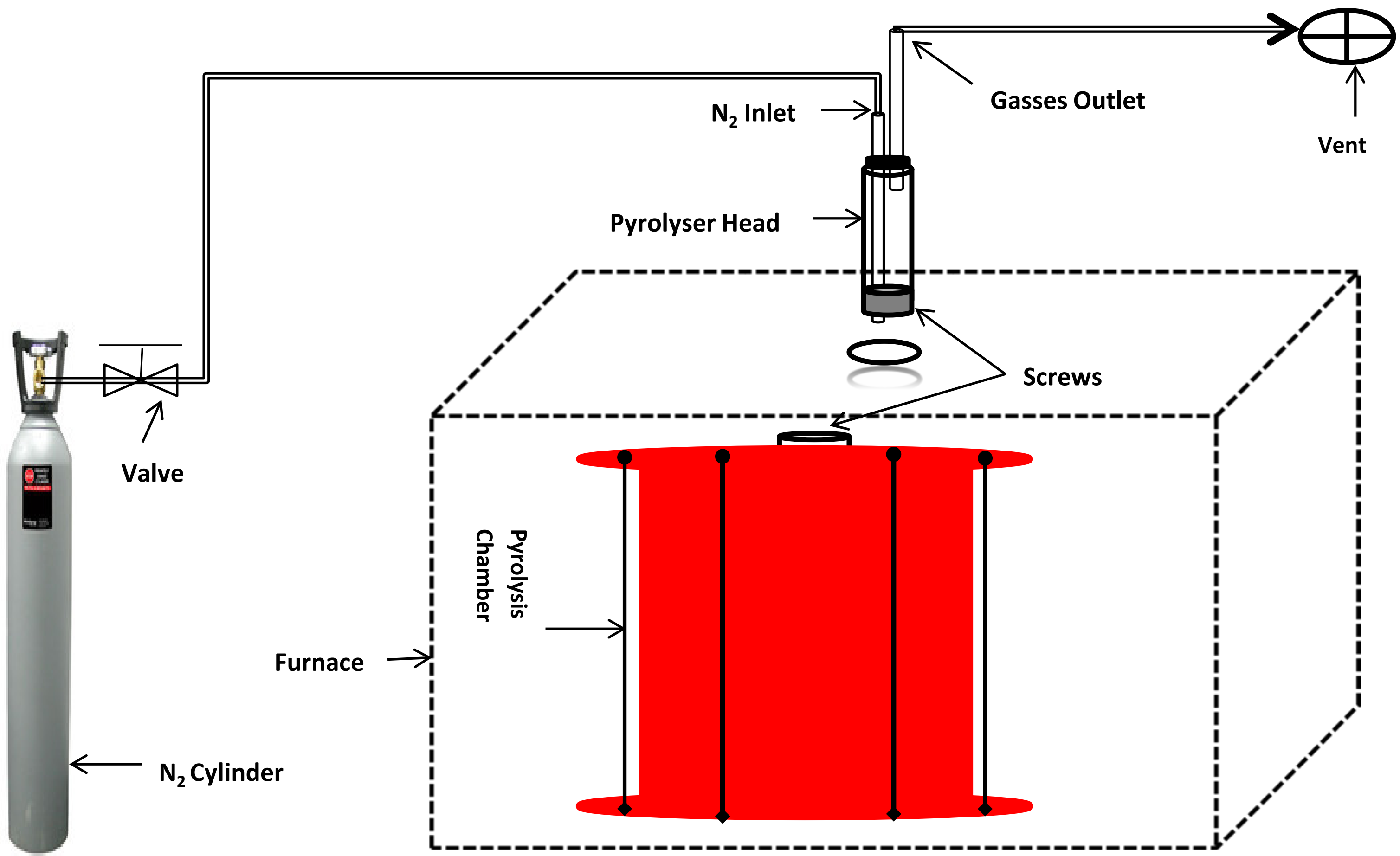
At pH range: 0-3.00, SMT^+ species dominant
At pH range: 3.00-7.50, SMT^o species dominant
At pH range: 7.50-11, SMT^- species dominant (Teixido et al., 2011)

At pH range: 0-3.0, SMZ^+ species dominant
At pH range: 3.00-6.0, SMZ^o species dominant (negligible)
At pH range: 6.00-10, SMZ^- species dominant (Fukahori et al., 2011)

Biochar and Modified Biochar Preparation



Experimental Design: Pyrolyser



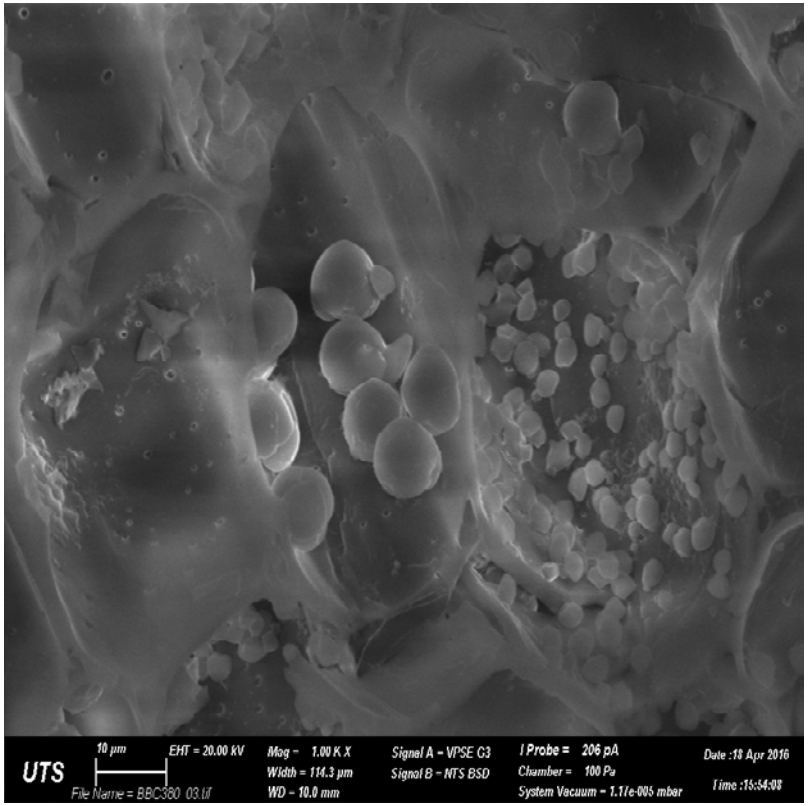
Results

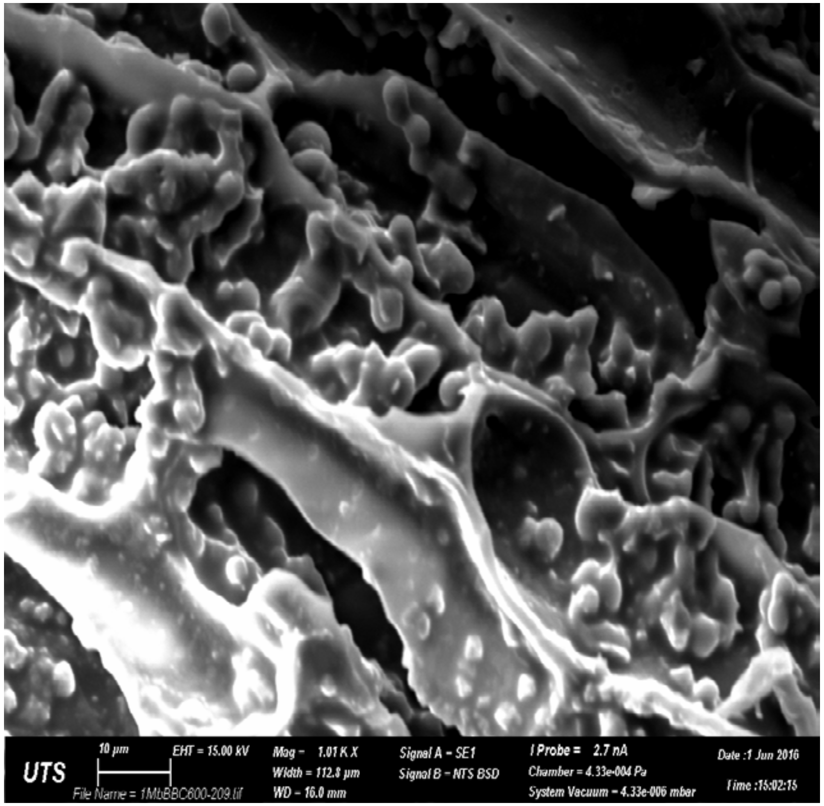
Physicochemical Properties of Biochar and Modified Biochar

Sample	**Composition data**				
	Yield$_{dry\ basis}$ (%)	Moisture content (%)	Ash (%)	Volatile mater (%)	Fixed carbon (%)
Biomass		5.61	12.93	63.83	26.67
Biochar	43.50				
			Modified Biochar		
Initial pH	1.62	3.00	4.35	6.13	10.00
Final pH	1.15	2.74	3.39	4.09	8.28
Zeta potential (mV)	5.34±0.32	-3.25±0.24	-12.76±1.23	-19.6±1.15	-45.9±4.67

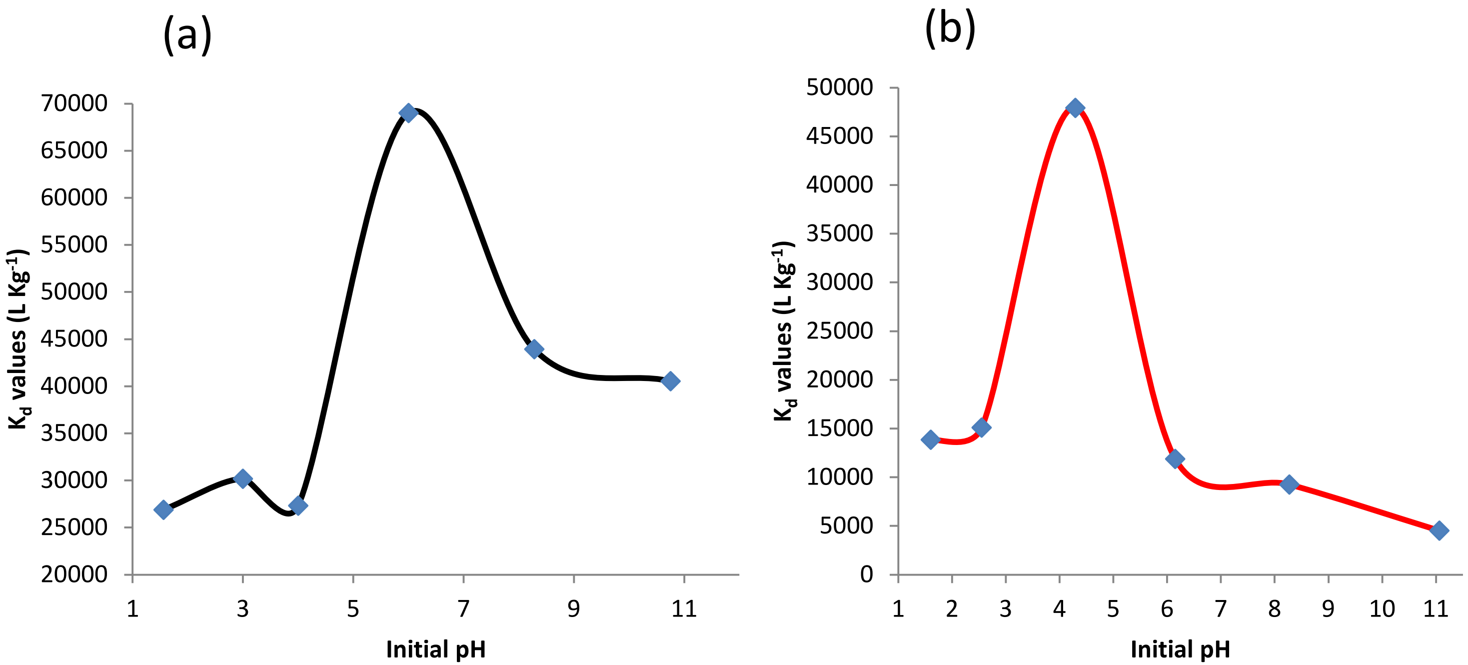
Sample	**EDS analysis**				**BET surface area**	**BJH Adsorption pore diameter**
	C %	O %	P %	Molar O/C		
Biochar	81.18	18.83	-	0.219	0.50 $m^2\ g^{-1}$	113.5 Å
Modified Biochar	51.96	39.52	8.16	0.71	1.12 $m^2\ g^{-1}$	83.8 Å

Scanning Electron Microscopic (SEM) Picture of Biochar and Modified Biochar





Effect of pH on Distribution Coefficient (K_d) for (a)Sulfathiazole (SMZ) and (b) Sulfamethazine (SMT) Sorption



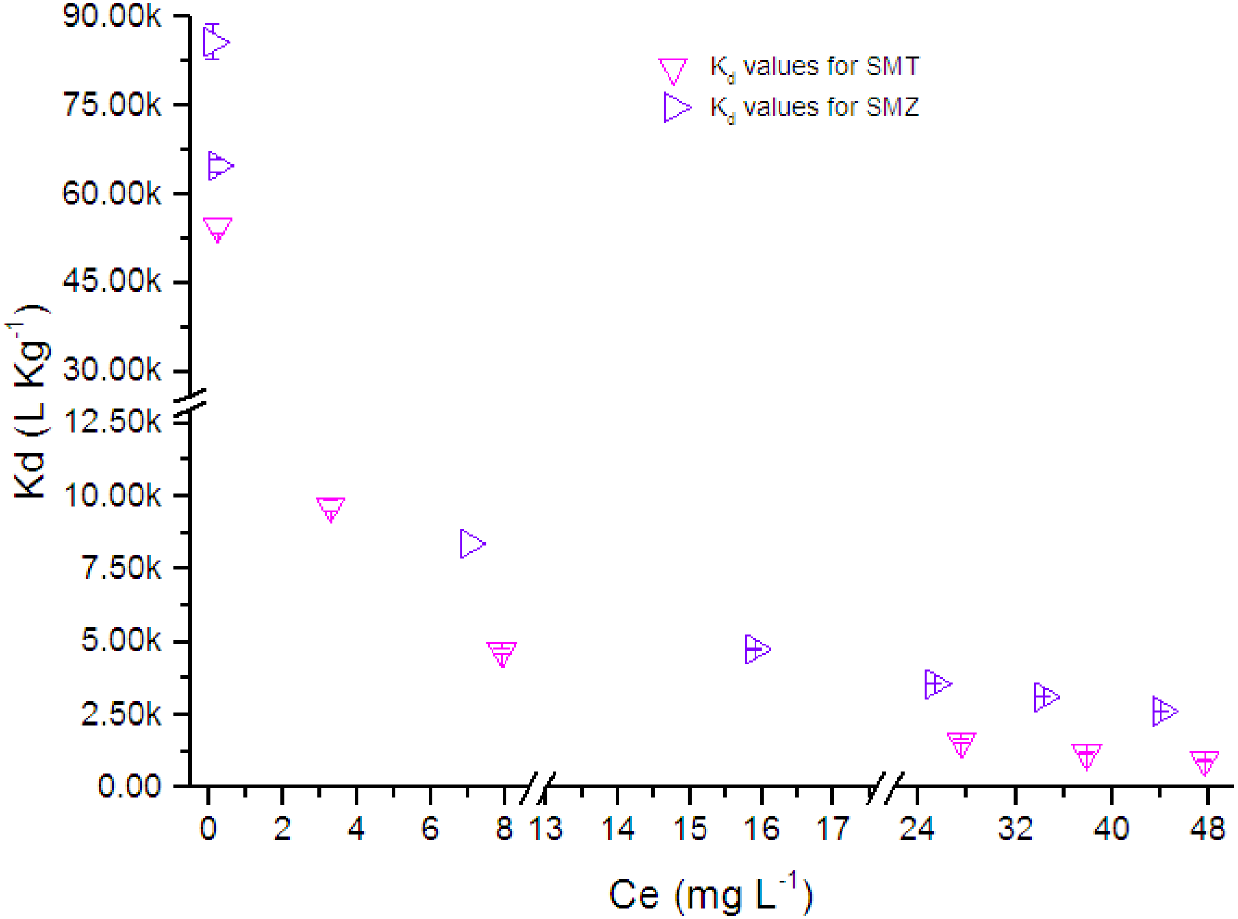
HPLC Analysis Method:

Mobile Phase A (Acetonitrile : Formic Acid = 99.99% : 0.1% , v/v) and

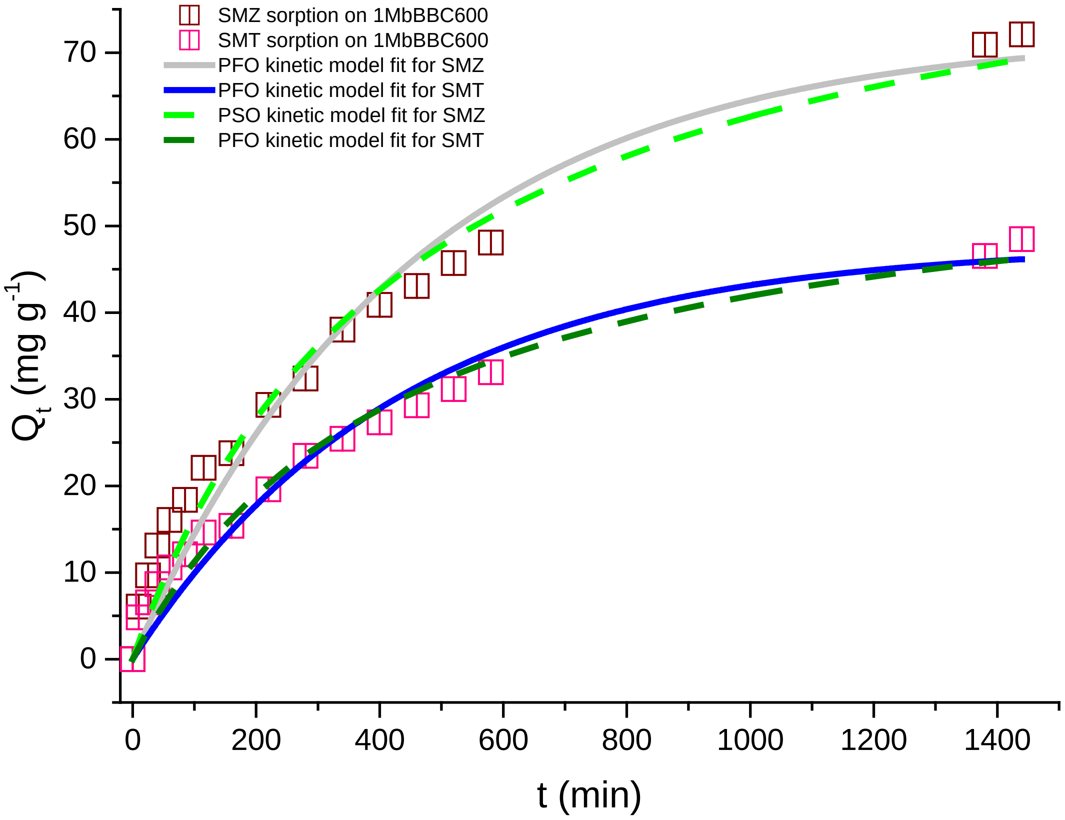
Mobile Phase B (Milli Q Water : Formic Acid = 99.99% : 0.1% , v/v), Measured at 285 nm.

Initial Flow Rate 0.400 mL min^{-1} at 40% A and 60%B and At 0.10 min Flow Rate Change to 0.30 mL min^{-1} over 8 minutes.

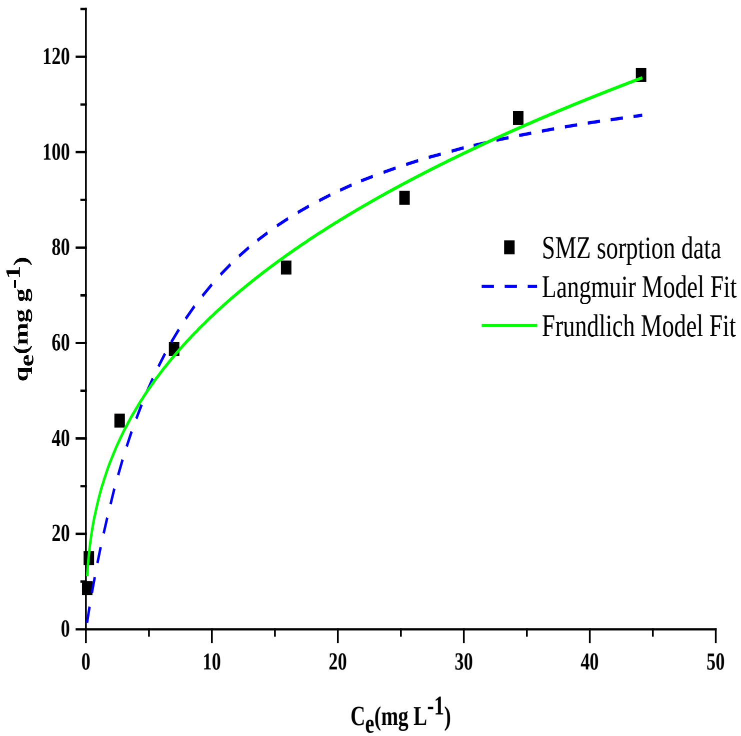
Distribution Coefficient (K_d) values for Sulfamethazine (SMT) and Sulfathiazole (SMZ) Sorption

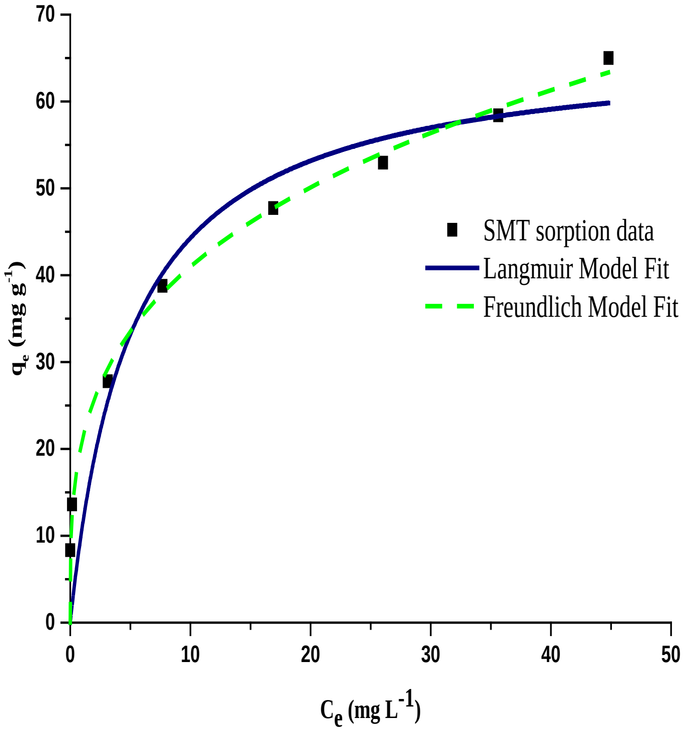


Pseudo first order (PFO) and Pseudo second order (PSO) kinetic model for SMT and SMZ sorption on modified biochar



Sorption Isotherm Models of Sulfamethazine (SMT) and Sulfathiazole (SMZ)





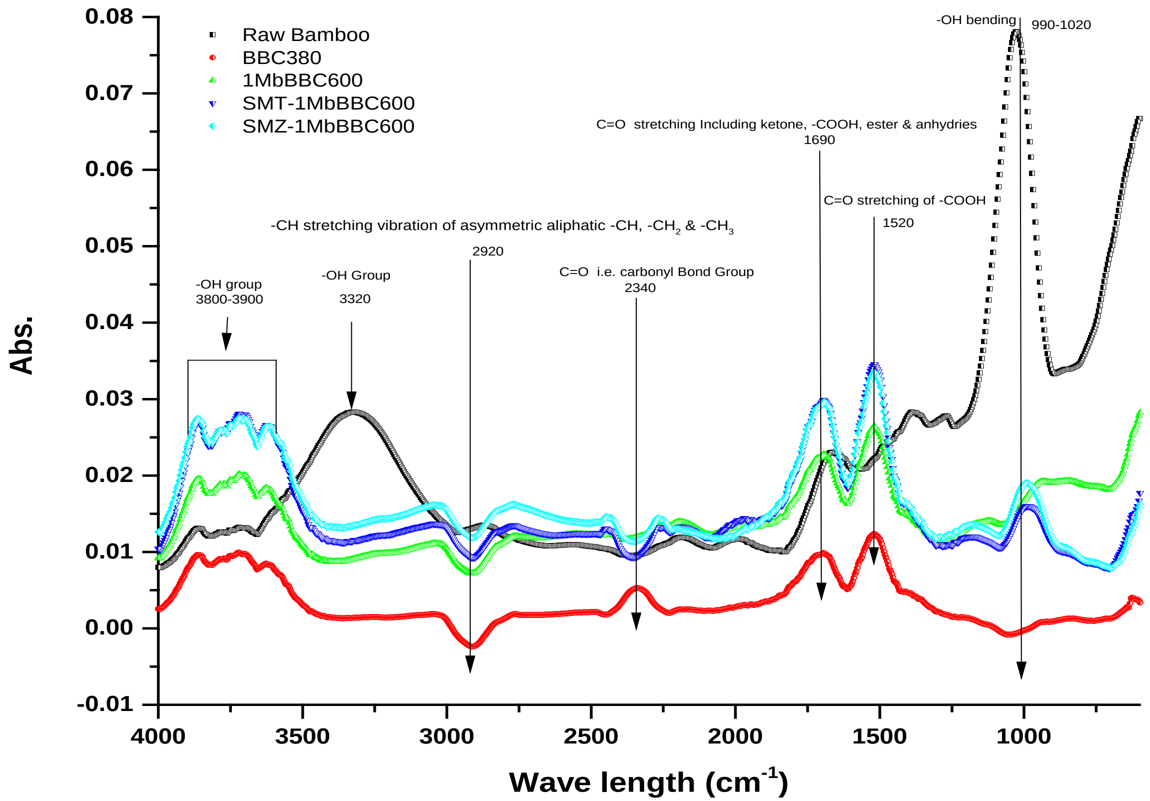
Sorption Isotherm Data Using Modified Biochar

Antibiotics	Freundlich Isotherm Parameter's At 21 ± 0.5 °C Temperature			Langmuir Isotherm Parameters At 21 ± 0.5 °C Temperature		
	K_F	n	R^2	Q_{max}	K_L	R^2
SMZ	27.03±0.946	2.6±0.072	0.998	127.7±18.87	0.058±.0105	0.995
SMT	24.81±2.77	5.94±1.253	0.915	65.74±6.25	0.208±0.087	0.897

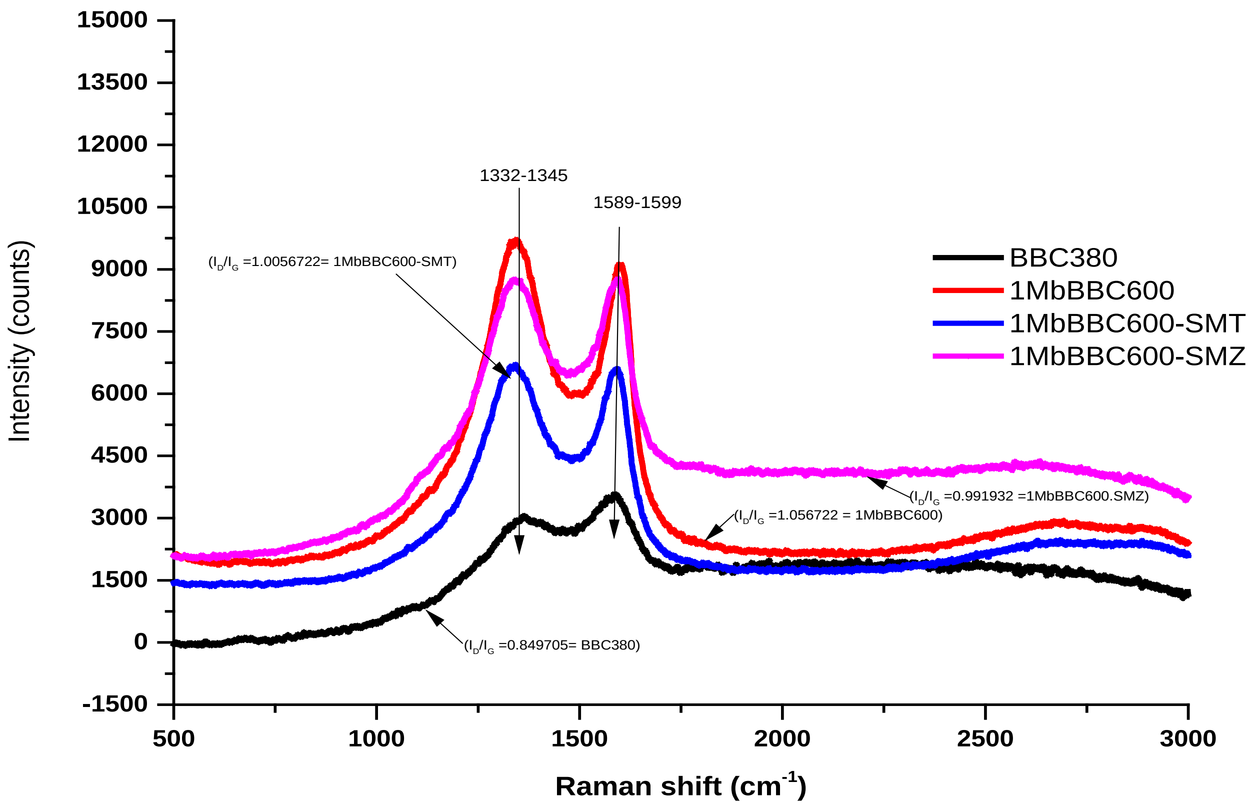
Kinetic Parameters

Name	PFO at 21 ± 0.5 °C			PSO at 21 ± 0.5 °C			Intra-particle Diffusion Model		
	$Q_{e\ cal}$ (mg g^{-1})	K_1 (min^{-1})	R^2	$Q_{e\ cal}$ (mg g^{-1})	K_2 (g mg^{-1} min^{-1})	R^2	C (mg g^{-1})	K_i (mg g^{-1} $min^{-0.5}$)	R^2
SMZ	56.71±1.70	0.00783	0.960	66.08±1.17	0.0001412	0.992	12.01±3.2	1.66±0.18	0.857
SMT	37.46±1.84	0.00627	0.907	43.30±1.18	0.0001840	0.963	7.25±1.49	1.08±0.08	0.921

FTIR Spectra Based Sorption Mechanisms

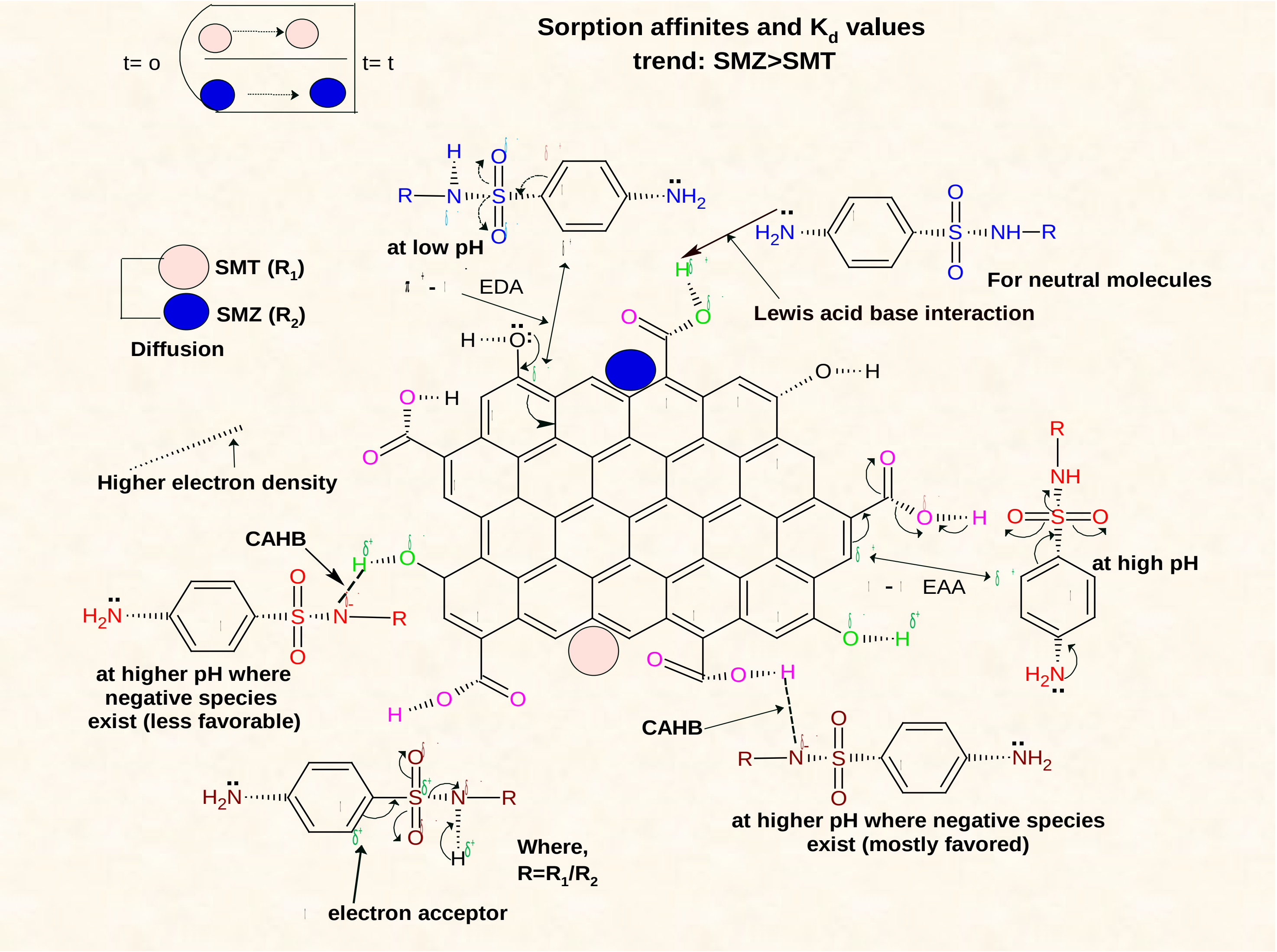


Sorption Mechanisms Inferred from Raman Spectra



D and G bands refer to carbon SP^3 and SP^2 hybridization, respectively. Intensity ratio (I_D/I_G) indicate the degree of graphitization

Schematic Sorption Mechanism



Summery

- Phosphoric acid modified biochar (1MbBBC600) can be used as an alternate adsorbent to effectively remove emerging contaminants such as antibiotics.
- Adsorption distribution coefficient (K_d) values followed the trend of SMZ > SMT.
- Freundlich isotherm sorption parameters slightly better fits than Langmuir isotherm sorption parameters
- Mechanism of the sorption largely pH dependent and mostly governed by strong H-bond formation, π^+-π electron-donor-acceptor (EDA), and by Lewis acid-base interaction at neutral region. Sorption at very low pH followed π-π EDA interaction. At high pH, sorption was favored through –OH exchange with water molecule leading to formation of π-π EAA interaction.

Acknowledgements

- ❖ Professor John L. Zhou
- ❖ Professor Huu Hao Ngo
- ❖ Dr Wenshan Guo
- ❖ IRS, FEIT Scholarships and Blue Sky Funding
- ❖ FEIT, Centre for Technology in Water and Wastewater (CTWW), and my colleges' support in University of Technology Sydney (UTS), Sydney, Australia.

Thanks !!

Questions ???

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