Removal of sulfamethazine and sulfathiazole from water using modified bamboo biochar

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- About Antibiotic Properties and Differents Sorbents
- Biochar and Modified Biochar Preparation
- Properties, Isotherms, Kinetics and Details of Different Sorption Mechanism’s Based on FTIR and Raman Spectroscopy, Resonance Effects and pH Shift Test.
- Summery
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 $\mu$g 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
The price of different adsorbents (BC = Biochar, AC = Activated Carbon, MWCNTs = Multi Wall Carbon Nanotubes, SWCNTs = Single Wall Carbon Nanotubes) (Ahmed et al., 2015).

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

# Physicochemical Properties of Sulfonamide Antibiotics

<table>
<thead>
<tr>
<th>Class</th>
<th>Compound</th>
<th>Acronym</th>
<th>CAS Number</th>
<th>log_{\text{K}_{\text{ow}}}</th>
<th>pK_a</th>
<th>Molecular mass</th>
<th>Molecular formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphonamides (SAs)</td>
<td>Sulfamethazine</td>
<td>SMT</td>
<td>57-68-1</td>
<td>0.14</td>
<td>2.65/7.65</td>
<td>278.34</td>
<td>C_{12}H_{14}N_{4}O_{2}S,</td>
</tr>
<tr>
<td></td>
<td>Sulfathiazole</td>
<td>SMZ</td>
<td>74-14-0</td>
<td>0.05</td>
<td>2.2/7.24</td>
<td>255.32</td>
<td>C_{10}H_{11}N_{3}NaO_{3}S^{+} [1]</td>
</tr>
</tbody>
</table>

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

- Moderately soluble in water and the logK_{\text{ow}} indicates that they are moderately hydrophilic

![Sulfonamide structures](image)

**General formula of sulfonamides**

**Sulfonamide species**

- At pH range: 0-3.00, SMT⁺ species dominant
- At pH range: 3.00-7.50, SMT⁰ species dominant
- At pH range: 7.50-11, SMT⁻ species dominant (Teixido et al., 2011)

- At pH range: 0.30, SMZ⁺ species dominant
- At pH range: 3.00-6.0, SMZ⁰ species dominant (negligible)
- At pH range: 6.00-10, SMZ⁻ species dominant (Fukahori et al., 2011)
Biochar and Modified Biochar Preparation

Biomass
- Cut into small sizes
- Wash & drying at 105 °C
- Pyrolysis at 380 °C for 2 h at 2 psi
- Increased N₂ pressure 10 psi at 380 °C for 15 minutes
- Cooling in room temp.
- Crushed into desired size, wash with DI & drying

Biochar (BBC380)
- Soaking in 50% phosphoric acid solution
- Leave at 50 °C for 3 h
- Heated at 600 °C for 2 h at 2.0 psi
- Cooling in room temp.
- Wash with DI & adjust pH to 7.0 and dry

Modified Biochar (1MbBBC600)
Experimental Design: Pyrolyser
## Results

### Physicochemical Properties of Biochar and Modified Biochar

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition data</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Yield_{dry basis} (%)</td>
<td>Moisture content (%)</td>
<td>Ash (%)</td>
<td>Volatile mater (%)</td>
<td>Fixed carbon (%)</td>
</tr>
<tr>
<td>Biomass</td>
<td>5.61</td>
<td>12.93</td>
<td>63.83</td>
<td>26.67</td>
<td></td>
</tr>
<tr>
<td>Biochar</td>
<td>43.50</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Modified Biochar**

<table>
<thead>
<tr>
<th></th>
<th>Initial pH</th>
<th>Final pH</th>
<th>Zeta potential (mV)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.62</td>
<td>1.15</td>
<td>5.34±0.32</td>
<td>-3.25±0.24</td>
<td>-12.76±1.23</td>
</tr>
<tr>
<td></td>
<td>3.00</td>
<td>2.74</td>
<td></td>
<td></td>
<td>-19.6±1.15</td>
</tr>
<tr>
<td></td>
<td>4.35</td>
<td>3.39</td>
<td></td>
<td></td>
<td>-45.9±4.67</td>
</tr>
<tr>
<td></td>
<td>6.13</td>
<td>4.09</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.00</td>
<td>8.28</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>EDS analysis</th>
<th></th>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C %</td>
<td>O %</td>
<td>P %</td>
<td>Molar O/C</td>
<td>BET surface area</td>
</tr>
<tr>
<td>Biochar</td>
<td>81.18</td>
<td>18.83</td>
<td>-</td>
<td>0.219</td>
<td>0.50 m² g⁻¹</td>
</tr>
<tr>
<td>Modified Biochar</td>
<td>51.96</td>
<td>39.52</td>
<td>8.16</td>
<td>0.71</td>
<td>1.12 m² g⁻¹</td>
</tr>
</tbody>
</table>
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

![Graph showing distribution coefficient values for Sulfamethazine (SMT) and Sulfathiazole (SMZ)]
Pseudo first order (PFO) and Pseudo second order (PSO) kinetic model for SMT and SMZ sorption on modified biochar

\[ Q_t = \frac{Q_e}{1 + k_2 t} \]

\[ Q_t = \frac{Q_e}{1 + \left( \frac{k_1}{k_2} \right) t} \]
Sorption Isotherm Models of Sulfamethazine (SMT) and Sulfathiazole (SMZ)
**Sorption Isotherm Data Using Modified Biochar**

<table>
<thead>
<tr>
<th>Antibiotics</th>
<th>Frendlich Isotherm Parameter’s</th>
<th>Langmuir Isotherm Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>At 21 ± 0.5 °C Temperature</td>
<td>At 21 ± 0.5 °C Temperature</td>
</tr>
<tr>
<td></td>
<td>K_F</td>
<td>Q_max</td>
</tr>
<tr>
<td></td>
<td>n</td>
<td>K_L</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>R²</td>
</tr>
<tr>
<td>SMZ</td>
<td>27.03±0.946</td>
<td>127.7±18.87</td>
</tr>
<tr>
<td></td>
<td>2.6±0.072</td>
<td>0.058±0.0105</td>
</tr>
<tr>
<td></td>
<td>0.998</td>
<td>0.995</td>
</tr>
<tr>
<td>SMT</td>
<td>24.81±2.77</td>
<td>65.74±6.25</td>
</tr>
<tr>
<td></td>
<td>5.94±1.253</td>
<td>0.208±0.087</td>
</tr>
<tr>
<td></td>
<td>0.915</td>
<td>0.897</td>
</tr>
</tbody>
</table>

**Kinetic Parameters**

<table>
<thead>
<tr>
<th>Name</th>
<th>PFO at 21 ± 0.5 °C</th>
<th>PSO at 21 ± 0.5 °C</th>
<th>Intra-particle Diffusion Model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Q_{e cal} (mg g⁻¹)</td>
<td>K₁ (min⁻¹)</td>
<td>R²</td>
</tr>
<tr>
<td>SMZ</td>
<td>56.71±1.70</td>
<td>0.00783</td>
<td>0.960</td>
</tr>
<tr>
<td>SMT</td>
<td>37.46±1.84</td>
<td>0.00627</td>
<td>0.907</td>
</tr>
</tbody>
</table>
FTIR Spectra Based Sorption Mechanisms

- OH bending 990-1020

Abs.

Wave length (cm^{-1})

- OH group 3800-3300

-CH stretching vibration of asymmetric aliphatic -CH, -CH2 & -CH3

-CH stretching vibration of asymmetric aliphatic -CH, -CH2 & -CH3

- OH Group 3320

C=O stretching including ketone, -COOH, ester & anhydrides

1690

C=O stretching of -COOH

1520

C=O i.e. carbonyl bond group

2340

2920

2500

2000

1500

1000

4000

3500

3000

2500

2000

1500

1000

-0.01

0.00

0.01

0.02

0.03

0.04

0.05

0.06

0.07

0.08

Raw Bamboo
BBC380
1MbBBC600
SMT-1MbBBC600
SMZ-1MbBBC600
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

Sorption affinities and $K_d$ values
trend: SMZ$>$SMT

Diffusion

Higher electron density

CAHB

at higher pH where negative species exist (less favorable)

at higher pH where negative species exist (mostly favored)

Where, $R=R_1/R_2$

electron acceptor

For neutral molecules

Lewis acid base interaction

At low pH

For neutral molecules

At high pH

Sorption affinities and $K_d$ values

Where, $R=R_1/R_2$
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, \(\pi^+\text{-}\pi\) electron-donor-acceptor (EDA), and by Lewis acid-base interaction at neutral region. Sorption at very low pH followed \(\pi\text{-}\pi\) EDA interaction. At high pH, sorption was favored through –OH exchange with water molecule leading to formation of \(\pi\text{-}\pi\) EAA interaction.
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Thanks !!

Questions ???

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