Insight into the Role of the Pore Structure and Surface Functional Groups in Biochar on the Adsorption of Sulfamethoxazole from Synthetic Urine

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Article

Abstract: The study assessed the influence of pyrolysis temperature on the properties of hickory sawdust and peanut shells based biochar, particularly its pore structure, surface functional groups, and adsorption capacity. Results from SEM analysis demonstrated that higher pyrolysis temperatures led to an enhanced pore structure and surface roughness in biochars, providing increased adsorption capacity. Raman spectrum analysis revealed higher levels of disorder and graphitization in biochars pyrolyzed at elevated temperatures. Quantification of surface functional groups using the Boehm method indicated a shift in the abundance of basic and acidic groups under high pyrolysis conditions. Employing the FHH model, fractal characteristics were observed in the pore structure of different biochars, with high-temperature biochars displaying increased disorder. The study also explored the mechanism of SMX adsorption onto biochars, revealing higher adsorption capacity for biochars with richer pore structures and rougher surfaces. The Elovich model proved to be the best fit for describing the chemisorption process of SMX onto the biochars. Moreover, the study demonstrated the impact of urine ions on SMX adsorption onto the biochars. These findings provide valuable insights into the properties and potential applications of biochars in environmental remediation.

Keywords: pore structure; surface functional groups; Biochar; sulfamethoxazole removal

1. Introduction

The release of pharmaceutical residues into waterbodies and soils poses a serious ecological and human health threat, largely attributed to the extensive use of pharmaceuticals [1,2]. Primarily expelled through urine, excess pharmaceuticals eventually find their way into wastewater treatment plants (WWTPs) within influent wastewater. Regrettably, the practical treatment technologies are inadequate in effectively eliminating contaminants. Sulfamethoxazole (SMX), for instance, represents a prominent member of the sulfonamide antibiotics extensively employed in addressing bacterial infections among humans, inclusive of prostatitis, bronchitis, and urinary tract infections. Notably, SMX undergoes incomplete metabolism within the human and animal systems, posing challenges for effective elimination through conventional wastewater treatment procedures. Furthermore, the introduction of antibiotics into the biological treatment units of WWTPs could result in the creation of antibiotic resistance genes (ARGs) by the resident microbes. Moreover, there is a burgeoning interest in extracting nutrients, particularly phosphorus, from human urine as an alternative source of fertilizer for agricultural production [3,4]. However, the use of antibiotics in urine hinders its potential use as a fertilizer, resulting in adverse effects on both the environment and human health [5]. Therefore, it is crucial to develop techniques for the elimination of antibiotics. One effective method involves preventing their introduction into WWTPs by removing them from origin.
In recent years, various physico-chemical technologies, such as advanced oxidation processes (AOPs) [6,7], membrane filtration [8], and adsorption [9], have been developed and employed for pharmaceutical treatment. Among these methods, adsorption has shown promise due to its potential for real wastewater treatment, characterized by low-cost, low-energy and low-maintenance [10]. In contrast to chemical oxidation, adsorption could be emphasized for its lower energy requirements and reduced production of harmful by-products. Furthermore, compared to membrane filtration, the authors could emphasize the potential advantages of adsorption in terms of simplicity, lower capital investment, and adaptability to a wide range of contaminants without the need for frequent membrane replacement. Consequently, a range of materials has been developed to remove antibiotics from urine. Carbon-based materials have emerged as potentially favorable alternatives to metal-based adsorbents in urine due to their toxic-free and environmentally benign characteristics. Graphene oxide [11] (GO), carbon nanotubes [12] (single or multi-walled), and activated carbon [13] (AC) have demonstrated high adsorption capacities for pharmaceuticals, the removal efficiency could be over 80% under the neutral pH. However, the need for a more cost-effective adsorbent remains to align with economic considerations.

Biochar (BC) has emerged as a cost-effective material with a significant specific surface area, demonstrating successful utilization in removing diverse antibiotics from land and water environment [14]. Despite the unique composition of urine in comparison to conventional wastewater influents, BCs present a potential solution to directly adsorb the antibiotics residue in the urine. Our previous study demonstrated that biochar derived from specific feedstocks and prepared at different temperatures showed varying levels of aromaticity, influencing the adsorption of SMX and underscoring the pivotal role of biochar’s aromatic structures in the removal of SMX from hydrolysis urine [15]. However, it is significant to know that while the as-prepared biochar may have similar specific surface areas and pore structures, potential implications of the pore adsorption process cannot be ruled out. This is particularly relevant given that the pore size was calculated based on average pore size, warranting a more detailed analysis of pore structure. Additionally, while qualitative analysis of surface functional groups was carried out using Fourier-transform infrared spectroscopy (FTIR), a quantitative analysis of the surface functional groups would provide further insights. Further research is also needed on adsorption kinetics to offer a more comprehensive explanation of the mechanism.

To further address the key role of pore structure and surface functional groups, four types of biochar were utilized to reveal the mechanism of SMX removal from urine due to its high concentration in human urine. The initial step involved quantitatively analyzing the surface functional groups of the prepared biochars using the Boehm method. Subsequently, the Frenkel Halsey Hill (FHH) model was employed to gain a deeper understanding of the structural properties of the biochars. Finally, the adsorption of SMX by different formulations of the biochars in synthetic urine and PBS solution was evaluated.

2. Materials and Methods
2.1. Materials and Reagents
Sulfamethoxazole (SMX) was purchased from Sigma Aldrich (Shanghai, China), and HPLC grade methanol was obtained from Fisher Scientific (Shanghai, China). The composition of synthetic urine (refer to Table 1) was prepared following the method outlined in the literature [2]. Other chemical reagents were acquired from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).
### Table 1. Composition of synthetic hydrolysis urine matrices.

<table>
<thead>
<tr>
<th>Species</th>
<th>Molecular Weight (g mol⁻¹)</th>
<th>Concentration (mol·L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>58.44</td>
<td>0.06</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>142.04</td>
<td>0.015</td>
</tr>
<tr>
<td>KCl</td>
<td>74.55</td>
<td>0.04</td>
</tr>
<tr>
<td>NH₄OH (conc.)</td>
<td>35.04</td>
<td>0.25</td>
</tr>
<tr>
<td>NaH₂PO₄</td>
<td>119.98</td>
<td>0.0136</td>
</tr>
<tr>
<td>NH₄HCO₃</td>
<td>79.06</td>
<td>0.25</td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td>9</td>
</tr>
</tbody>
</table>

#### 2.2. Preparation of BCs and Their Characteristics

Hickory sawdust (HS) and peanut shells (PS) were selected as biochar feedstock followed by our previous study [15]. Four milligrams of biomasses were taken into a covered 20 mL ceramic crucible to create an oxygen-limited environment. Subsequently, the crucible was placed in a muffle furnace and pyrolyzed it at 350 °C or 700 °C for 2 h. Then, the resulting product was ground into powder using a mortar and pestle. Because the ash had a negative impact on the SMX adsorption onto the biochar, this powder underwent a washing process with 500 mL of deionized (DI) water at least five time to eliminate it until the water was no longer turbid and was subsequently dried in an oven at 60 °C overnight. The resulting biochars were labeled as 350HSBC (Hickory sawdust biochar), 700HSBC, 350PSBC (peanut shells biochar), and 700PSBC, respectively.

The biochars were characterized with a S-4800 scanning electron microscope (Hitachi, Tokyo, Japan) at 10 kV from 400 to 70 K magnification. The Raman spectrum of biochars was conducted on the LabRAM Odyssey instrument (HORIBA, Paris, France). The zeta potential was tested on the NanoBrook 90Plus PALS (Brukers, New York, NY, USA).

#### 2.3. Adsorption Experiments

All the experiments were conducted in covered 100 mL conical flasks. Sulfamethoxazole (SMX) was selected as the target drug for this study due to its high concentration in human urine [16]. In these experiments, 10 mg of prepared biochar and 10 µm SMX were added to synthetic urine, with 5 mM phosphate-buffered saline (PBS) solution used as a control. All conical flasks were placed on a temperature-controlled shaker set at 22 °C and 200 rpm. At a specific time, 1 mL of the solution was sampled and filtered by a 0.45 µm PTFE filter for the next analyzing. The concentration of SMX was determined by our previous method [15]. The results presented are averaged from two repeated experiments.

Pseudo-first-order, pseudo-second-order and Elovich models were then used to evaluate the adsorption mechanism [17–19].

\[
q_t = q_e \left(1 - e^{-k_1 t}\right) \quad \text{pseudo-first-order} \tag{1}
\]

\[
q_t = \frac{q_e^2 k_2 t}{q_e k_2 t + 1} \quad \text{pseudo-second-order} \tag{2}
\]

\[
q_t = \beta \ln(a \beta t) + \beta \ln(t) \quad \text{Elovich} \tag{3}
\]

In the equations, \(q_e\) (mg·g⁻¹) was the adsorption capacity of SMX at equilibrium; \(q_t\) (mg·g⁻¹) was the adsorption capacity of phosphate at time \(t\); \(k_1\) (h⁻¹) and \(k_2\) (g·mg⁻¹·h⁻¹) was the pseudo-first-order and pseudo-second-order models, respectively; \(a\) (mg·g⁻¹·h⁻¹) represented the initial adsorption rate; and, \(\beta\) (g·mg⁻¹) represented the desorption constant.

#### 2.4. Boehm Method

Boehm titration serves as a versatile qualitative and quantitative analysis method, relying on the reactivity of surface oxides with varying acidic and alkaline strengths [20]. This methodology stands as the most widely employed chemical analysis approach for porous carbon surfaces. It effectively discerns the levels of strong acid, medium-strong
acid, weak acid, and basic groups present on the surface of biochar. To conduct testing on a specific carbon sample, it was carefully weighed out 4 samples each weighing 1.0 g and placed in separate 250 mL iodine bottles. It was added 25 mL of 0.1 mol/L HCl solution, 0.1 mol/L NaOH solution, 0.1 mol/L Na$_2$CO$_3$ solution, and 0.1 mol/L NaHCO$_3$ solution into each bottle, followed by shaking for 30 min. Subsequently, it was allowed the samples to stand in a constant temperature bath at 25 °C for 48 h to reach equilibrium, and then proceed with filtering. It was measured 10 mL of each of the four filtrates and dilute to a final volume of 50 mL respectively.

(1) It was utilized a standard 0.1 mol/L NaOH solution to titrate the changes in the HCl solution before and after immersion. This would allow for the measurement of the amount of hydrochloric acid adsorbed by the sample, and subsequently calculated the amount of hydrochloric acid consumed per unit mass of the sample as the number of basic groups on its surface.

\[
\text{Number of basic groups} = \frac{\text{HCl solution consumption}}{m}
\]

(2) It was used a standard 0.1 mol/L HCl solution was used to titrate the changes in the NaOH solution before and after immersion. It was measured the amount of NaOH adsorbed by the sample, and then calculated the amount of NaOH consumed per unit mass of the sample as the number of acidic groups on its surface.

\[
\text{Number of acidic groups} = \frac{\text{NaOH solution consumption}}{m}
\]

(3) It was employed a standard 0.1 mol/L HCl solution was employed to titrate the changes in the Na$_2$CO$_3$ solution before and after immersion. It was measured the amount of Na$_2$CO$_3$ adsorbed by the sample, and the number of phenolic hydroxyl groups on its surface.

\[
\text{Amount of phenolic hydroxyl group} = \frac{\text{NaOH solution consumption}}{m} - \frac{\text{Na}_2\text{CO}_3 \text{ solution consumption}}{m}
\]

(4) It was used a standard 0.1 mol/L HCl solution to titrate the changes in the NaHCO$_3$ solution before and after immersion. It was measured the amount of NaHCO$_3$ adsorbed by the sample, and calculated the number of carboxyl groups on its surface.

\[
\text{Number of carboxyl groups} = \frac{\text{NaHCO}_3 \text{ solution consumption}}{m}
\]

2.5. Fractal Theory of N$_2$ Adsorption

The pore structure of BCs is inherently irregular and complex [21]. Pore structure characterization is pivotal in materials science and is often achieved through the application of fractal theory. Fractal analysis provides a powerful framework to quantitatively describe the complex and irregular porosity of materials. By utilizing fractal dimensions and scaling laws, it becomes possible to gain insights into the surface roughness, connectivity, and distribution of pores within a material. Furthermore, fractal geometry enables the identification of self-similar patterns at different scales, yielding valuable information about the hierarchical nature of pore networks. The application of fractal theory in pore structure characterization not only facilitates a deeper understanding of material properties but also provides a robust foundation for the development and optimization of various porous materials for diverse applications ranging from catalysis and adsorption to energy storage and filtration [22,23]. The FHH model can be described as follows:

\[
\ln(V) = A \left[ \ln \left( \frac{p_0}{p} \right) \right] + C
\]
where \( V \) represented the volume of adsorbed gas; \( P \) represented the equilibrium pressure; \( P_0 \) represented the saturation pressure of adsorbed gas; \( C \) represented a constant; and \( A \) represented the slope of linear fitting between \( \ln V \) and \( \ln(P_0/P) \).

\[
D_N = A + 3
\]  

where \( D_N \) represented the fractal dimension; \( A \) was calculated by Equation (1). The fractal dimension of adsorption pores should be calculated in Table 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( S_{\text{BET}} ) (m(^2) g(^{-1}))</th>
<th>( V_1 ) (cm(^3) g(^{-1}))</th>
<th>( D_p ) (nm)</th>
<th>( P/P_0: 0–0.4 ) ( A_1 )</th>
<th>( D_{N1} = 3 + A_1 )</th>
<th>( A_2 )</th>
<th>( D_{N2} = 3 + A_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>350HSBC</td>
<td>143.1</td>
<td>0.008714</td>
<td>3.14</td>
<td>–0.215</td>
<td>2.785</td>
<td>–0.016</td>
<td>2.984</td>
</tr>
<tr>
<td>700HSBC</td>
<td>683.4</td>
<td>0.184537</td>
<td>3.56</td>
<td>–0.349</td>
<td>2.651</td>
<td>–0.043</td>
<td>2.957</td>
</tr>
<tr>
<td>350PSBC</td>
<td>75.12</td>
<td>0.007810</td>
<td>7.4</td>
<td>–0.119</td>
<td>2.881</td>
<td>–0.038</td>
<td>2.962</td>
</tr>
<tr>
<td>700PSBC</td>
<td>691.1</td>
<td>0.104923</td>
<td>3.21</td>
<td>–0.436</td>
<td>2.564</td>
<td>–0.027</td>
<td>2.973</td>
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</table>

3. Results and Discussions

3.1. Physicochemical Properties of BCs

To analyze the morphology, SEM was conducted on it and the results are shown in Figure 1. The 700HSBC and 700PSBC exhibit a rich pore structure while the 350HSBC and 350PSBC have a limited pore structure, suggesting that the higher pyrolysis temperature is attributable to the formation of pore structures in biochar [24]. The relationship between temperature and the development of biochar pores is such that higher pyrolysis temperatures contribute to the creation of more intricate and well-defined pore structures in biochars. This leads to an increase in specific surface area and pore volume, ultimately enhancing the adsorption capacity of the biochars. Besides, the higher pyrolysis biochars have a rougher surface than the lower pyrolysis biochars, which could enhance the adsorption capacity of biochars. Therefore, elevated temperatures play a crucial role in shaping biochar pore structures, which in turn impacts their adsorption performance.

![Figure 1. SEM image of (a) 700HSBC, (b) 700PSBC, (c) 350HSBC and (d) 350PSBC with 5 \( \mu \)m magnification.](image)

Figure 2 shows the Raman spectrum of BCs, which can be observed in two peaks. The disorder degree of biochar was corresponding to the D-band (1348 cm\(^{-1}\)) while the G-band (1590 cm\(^{-1}\)) was reflecting the graphitization degree [25,26]. The intensity of D and G peaks of the higher pyrolysis biochars is significantly stronger than that of the lower pyrolysis biochars, while the peak area ratio between D and G bands (ID/IG) of BC are similar.
The results reveal that the high pyrolysis temperature could affect both the graphitization degree and disorder degree of biochar.

![Figure 2. Raman spectra of 700HSBC, 700PSBC, 350HSBC and 350PSBC, respectively.](image)

The identification of four distinct functional groups—Basic groups, Acidic groups, Phenolic hydroxyl groups, and Carboxyl groups—on the surface of BCs was established using the Boehm method, as illustrated in Figure 3. The analyses indicate that basic groups dominate as the most abundant groups across all four biochar materials. Subsequent high pyrolysis condition leads to a decrease in the proportion of alkaline groups, with acidic groups assuming the primary fraction, accompanied by an increase in the content of phenolic hydroxyl groups and carboxyl groups. Generally, at higher pyrolysis temperatures, there is a decrease in alkaline groups and an increase in acidic groups, phenolic hydroxyl groups, and carboxyl groups. This indicates that the pyrolysis temperature influences the transformation of functional groups in the biochars, leading to alterations in their chemical composition. Furthermore, the content of functional groups can influence the zeta potential of the biochars. Owing to the low content of acidic groups, all the biochars exhibited a negative zeta potential, even under acidic conditions (Figure 4). When materials are produced at high temperatures such as 700 degrees, fluctuations in their zeta potentials can occur due to various factors. Firstly, the high temperature can lead to changes in the material’s structure, affecting its surface charge distribution and causing fluctuations in the zeta potential. Secondly, the properties of the material, including surface morphology and solubility, may change at high temperatures, which can also influence the zeta potential. Notably, the 700HSBC displayed a notably higher zeta potential than other biochars when the solution pH was 9, potentially contributing to its higher adsorption capacity.

![Figure 3. The contents of the Basic groups, Acidic groups, Phenolic hydroxyl groups, and Carboxyl groups in the 700HSBC, 700PSBC, 350HSBC and 350PSBC, respectively.](image)
As shown in Figure 5, the fitting outcomes demonstrated remarkable fractal characteristics, with R² values exceeding 0.98, in the transition pores of 350HSBC. Similarly, the 350PSBC exhibited pronounced fractal characteristics for micropores, with an R² value of 0.95. In contrast, following high-temperature treatment, the 700HSBC and 700PSBC samples displayed relatively weaker fractal characteristics, indicating an increase in disorder in the biochars at elevated temperatures. Subsequent analysis, as summarized in Table 2, revealed that the Dₙ₁ value for 700HSBC was substantially lower than that of 350HSBC and 350PSBC, although higher than that of 700PSBC. This implies a lower pore surface roughness for 700HSBC compared to 350HSBC and 350PSBC, but a higher roughness than that of 700PSBC. Moreover, the Dₙ₂ value for the biochars was determined to be 2.957, lower than that of other BCs, indicating that the pore volume roughness of 700HSBC was the highest among the four samples.
3.2. Adsorption Results

In order to further investigate the SMX adsorption mechanism onto the BCs, rapid SMX adsorption onto 700HSBC and 700PSBC was observed within the first 10 h, showing a significant decrease in adsorption rates thereafter. This decrease was attributed to the reduction of available adsorption sites in the 700HSBC and 700PSBC, with equilibrium being reached after 160 h. The extended equilibrium time observed in this study compared to most biochars may be attributed to the intricate pore structures and rougher surfaces developed in the biochars at higher pyrolysis temperatures. These features potentially provide more adsorption sites, leading to a longer equilibrium time as the adsorption process takes place more gradually and extensively [27]. Additionally, the presence of specific functional groups, as influenced by the pyrolysis temperature, may also contribute to the extended equilibrium time due to their varied interactions with the adsorbate. More importantly, the extended equilibrium time was attributed to the complex urine matrix. However, both the 350HSBC and 350PSBC demonstrated limited SMX adsorption capacity due to their lower specific surface area. These findings underscore the substantial impact of biochar surface area on SMX adsorption. Additionally, the higher Zeta potential of 700HSBC resulted in a greater adsorption capacity than 700PSBC. Furthermore, the superior performance of 700HSBC was attributed to its pore volume roughness, which enhances the interaction between SMX and the adsorbent [25]. Notably, the distinct surface roughness between 700HSBC and 700PSBC, despite their similar specific surface area and pore structure, was found to underlie the differences in adsorption capacity between 350HSBC and 350PSBC. Previous research has demonstrated that having similar pore size distributions eliminates the impact on adsorption results [15]. However, our current study suggests that the shape and distribution of pores require further investigation using FHH model to comprehensively explain their influence on the adsorption process.

The kinetic results of SMX adsorption by the four adsorbents were analyzed using three different models, and the findings are presented in Table 3. The fitting parameters ($R^2$) indicate that the Elovich model provides a better description of SMX adsorption onto the 700HSBC, 700PSBC, 350HSBC, and 350PSBC compared to the other models, suggesting that SMX adsorption is a chemisorption process [28,29]. This phenomenon was influenced by the pore structure and surfaced function groups. The heterogeneity of the BCs’ surface favours the superior fit of the Elovich model to the data. Due to the amorphous structure of 700HSBC, SMX adsorbed onto it show a more rapid rate, attributing to the improvement of SMX diffusion.

### Table 3. Parameters of pseudo-first-order, pseudo-second-order and Elovich for SMX adsorption by 700HSBC, 700PSBC, 350HSBC and 350PSBC, respectively.

<table>
<thead>
<tr>
<th></th>
<th>350HSBC</th>
<th>350PSBC</th>
<th>700HSBC</th>
<th>700PSBC</th>
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</thead>
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<tr>
<td><strong>hydrolysis urine</strong></td>
<td></td>
<td></td>
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<tr>
<td>Pseudo-first-order</td>
<td>$K_1$ (h$^{-1}$)</td>
<td>0.0103</td>
<td>0.0074</td>
<td>0.1768</td>
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<tr>
<td></td>
<td>$Q_e$ (mg·g$^{-1}$)</td>
<td>1.33</td>
<td>0.82</td>
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<tr>
<td></td>
<td>$R^2$</td>
<td>0.6946</td>
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<td>0.8358</td>
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<tr>
<td></td>
<td>$K_2$ (g·mg$^{-1}$·h$^{-1}$)</td>
<td>0.0047</td>
<td>0.0036</td>
<td>0.0084</td>
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<tr>
<td>Pseudo-second-order</td>
<td>$Q_e$ (mg·g$^{-1}$)</td>
<td>1.84</td>
<td>1.32</td>
<td>33.69</td>
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<tr>
<td></td>
<td>$R^2$</td>
<td>0.6968</td>
<td>0.5274</td>
<td>0.9212</td>
</tr>
<tr>
<td>Elovich</td>
<td>$A$ (mg·g$^{-1}$·h$^{-1}$)</td>
<td>1.0982</td>
<td>0.9730</td>
<td>4.3268</td>
</tr>
<tr>
<td></td>
<td>$B$ (mg·g$^{-1}$)</td>
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<td>0.1603</td>
<td>4.4199</td>
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<tr>
<td></td>
<td>$R^2$</td>
<td>0.7962</td>
<td>0.6349</td>
<td>0.9967</td>
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<td></td>
<td>$K_1$ (h$^{-1}$)</td>
<td>1.8004</td>
<td>0.1634</td>
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<td></td>
<td>$Q_e$ (mg·g$^{-1}$)</td>
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<td>4.0471</td>
<td>39.53</td>
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<td></td>
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<td>0.8551</td>
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<td>Pseudo-first-order</td>
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<td></td>
<td>$Q_e$ (mg·g$^{-1}$)</td>
<td>4.5474</td>
<td>4.3216</td>
<td>41.76</td>
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<td></td>
<td>$R^2$</td>
<td>0.8958</td>
<td>0.9254</td>
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<tr>
<td>Elovich</td>
<td>$\alpha$ (mg·g$^{-1}$·h$^{-1}$)</td>
<td>1.5678</td>
<td>7.4423</td>
<td>1.9781</td>
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<td></td>
<td>$\beta$ (g·mg$^{-1}$)</td>
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<tr>
<td></td>
<td>$R^2$</td>
<td>0.8627</td>
<td>0.8508</td>
<td>0.9930</td>
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</table>
A comparable trend was observed in the adsorption of SMX onto the BCs in the PBS solution, with the fitting trend remaining consistent (Figure 6b). However, it is evident that SMX adsorption in the PBS solution markedly surpassed that in the hydrolysis urine. The SMX removal rate in the PBS by the biochars was significantly higher than that in the hydrolysis urine. As shown in Figure 7, the SMX removal rate could be improved by 20% for high temperature biochar while only 9% improvement was achieved by low temperature biochar. This discrepancy suggests that the ions present in the urine may exert a detrimental effect on the adsorption of SMX onto the BCs.

![Figure 6](image_url)

**Figure 6.** SMX adsorbed onto the 700HSBC, 700PSBC, 350HSBC and 350PSBC, respectively, in the synthetic urine (a) and PBS solution (b).

![Figure 7](image_url)

**Figure 7.** SMX removal rate by the 700HSBC, 700PSBC, 350HSBC and 350PSBC, respectively, in the synthetic urine and PBS solutions.

The findings from the rapid adsorption of SMX onto various biochar samples and the associated factors, such as specific surface area and pore structure, underline the potential practical application of biochar in wastewater treatment. The observed differences in
adsorption capacity among the biochar samples emphasize the need for a thorough understanding of their surface properties when considering their implementation in treatment processes. Moreover, the superior performance of 700HSBC, attributed to its pore volume roughness enhancing the interaction with SMX, provides insight into the economic aspects of biochar application. By optimizing the selection of biochar types based on their surface characteristics, the efficiency of SMX removal can be maximized, thus potentially reducing the overall costs of wastewater treatment. Furthermore, the influence of solution chemistry, as evidenced by the difference in SMX adsorption between PBS solution and hydrolysis urine, highlights the necessity to account for the composition of the wastewater being treated. Considering the potential detrimental effect of urine ions on SMX adsorption onto biochar, economic analyses should encompass the costs associated with adjusting treatment processes to accommodate varying wastewater compositions. In summary, the results obtained provide valuable insights into the practical application of biochar in wastewater treatment, emphasizing the need for careful selection of biochar types and consideration of solution chemistry, to ensure both efficacy and cost-effectiveness in real-world scenarios.

4. Conclusions

Based on the aforementioned research findings, it is evident that the pyrolysis temperature plays a significant role in shaping the pore structure and surface properties of biochars, thereby impacting their adsorption capabilities. Analysis using scanning electron microscopy (SEM) indicated that higher pyrolysis temperatures lead to the development of intricate pore structures and rougher surfaces, thereby enhancing the adsorption capacity of the biochars. Furthermore, Raman spectroscopy analysis revealed that elevated pyrolysis temperatures result in increased levels of graphitization and disorder in the biochars. Additionally, the application of the Boehm method demonstrated that basic functional groups are predominant across all biochar samples, although intensified pyrolysis conditions resulted in a reduction of alkaline groups and an increase in acidic groups, phenolic hydroxyl groups, and carboxyl groups. As a result, the adsorption of SMX onto the biochars is influenced by specific surface area and pore volume roughness, leading to significantly higher adsorption rates and equilibrium capacities for biochars with more pronounced pore structures and rougher surfaces. Kinetic modeling further affirmed the preference for the Elovich model in describing the chemisorption process of SMX onto the biochars, with the 700HSBC biochar displaying the highest adsorption rate, attributable to its amorphous structure. Furthermore, notable disparities were observed in the adsorption of SMX onto the biochars when comparing PBS solution and hydrolysis urine, indicating the differential impact of ions present in urine on the adsorption process. It is pertinent to note that our previous research validated that similar pore size distributions negate their influence on the adsorption results. Nevertheless, this study underscores the necessity for additional exploration using fractal theory to comprehensively expound on the impact of pore shape and distribution on adsorption. The comprehensive findings underscore the critical role of pyrolysis temperature and surface properties of biochars in influencing their adsorption capacities, offering valuable insights for potential environmental remediation applications.

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