Using corncob-based biochar to intercept BTEX in stormwater filtration systems
Huannan Wang, Dandan Yan, Huan Zeng and Jiajie He

ABSTRACT
A biochar material made from corncobs was tested for its capability in BTEX adsorption/interception in stormwater filtration systems. Batch experiments were conducted to examine the adsorption kinetics, adsorption isotherms, and adsorption thermodynamics of BTEX onto this biochar. The feasibility of applying this biochar in stormwater filtration was studied by dynamic transport experiments and model simulations. The result showed that this biochar can adsorb BTEX and the adsorption is a thermodynamically spontaneous, and endothermic process. The BTEX adsorption kinetic experiment and adsorption retarded BTEX transport experiment indicated that the BTEX adsorption kinetics can be changed by the driving force between the BTEX concentrations and the active adsorption site as well as the contact time between BTEX and the biochar. In terms of applying this biochar in stormwater filtration, the Monte Carlo uncertainty analysis indicated that the BTEX interception is sensitive to the hydraulic conductivity of the biochar filter and the adsorption kinetics of the biochar material. Although this corncob-made biochar demonstrated effective pollutant adsorption capability, the biochar adsorption capability should be utilized to retain the pollutant long enough for biodegradation to take effect for ultimate pollutant attenuation.

Key words | biochar, BTEX, HYDRUS, storm runoffs

HIGHLIGHTS
- A corncob-made biochar material demonstrates BTEX adsorption capabilities.
- The adsorption is thermodynamically spontaneous, and endothermic.
- Adsorption kinetics are different between batch and dynamic experiments.
- Lowering hydraulic loading rate can offset the influence of system uncertainties.

INTRODUCTION
Human society can not live without energy, and fossil fuels are the backbone of the current human civilization (Smil 2017). However, the ever-increasing consumption of fossil fuels has caused environmental concerns in various aspects (McCauley & Heffron 2018). The suite of benzene, toluene, ethylbenzene, and xylenes (BTEX) has often been used as the fingerprint for chemical pollution since BTEX are natural constituents of crude oil and gasoline (Bolden et al. 2015). Furthermore, BTEX are also listed among the priority pollutants by the US EPA due to their adverse health effects (ATSDR 2020).

Another sign of human civilization’s advancement is urbanization, but a rapid urbanization process is often accompanied by degrading urban water resources, and ineffective urban stormwater management has been proven as a major cause (McQueen et al. 2010; Hering et al. 2013). Stormwater management is not only flood reduction but also pollution control (Nguyen et al. 2019), and the first flush of storm runoffs is often highly contaminated (Zeng et al. 2019). Therefore, it is crucial to maintain an adequate pollutant interception/treatment capability of stormwater management systems (Hering et al. 2013; Liu et al. 2015; William et al. 2019).

In recent years, biochar has demonstrated potential in stormwater treatment such as interception/removal of organic contaminants, metals, nutrients, and pathogens,
and alternating soil hydraulic properties and redox conditions (Mohanty et al. 2018). As for a commonly used medium in stormwater treatment units, coarse sand does not contain internal pores and has limited adsorption over pollutants in comparison to black carbon materials (Erickson et al. 2016). Furthermore, compared to activated carbon, biochar has the advantage of lower cost and better hydraulic characteristics for pollutant removal (Ulrich et al. 2017). Biochar is a carbon-rich solid product made by anoxic and/or anaerobic pyrolysis of biomass under high temperatures. Biochar also has a wide potential for environmental applications such as pollutant adsorption, soil amendment, carbon sequestration, and greenhouse gas emission mitigation (Weber & Quicker 2018). Nevertheless, the production cost of biochar still presents as an economic challenge for biochar applications, and thus the use of agricultural wastes as raw materials for biochar production could offset some of those high costs (Cha et al. 2016; Panwar et al. 2019).

Corncobs, a high volume, low-cost agricultural by-product, are a good source of biochar (Liu et al. 2014). Corncob-based biochar has been used in stripping BTEX from contaminated air (Rahul et al. 2013), and effective BTEX removals have also been demonstrated by activated carbons (Zhang et al. 2013; Konggidinata et al. 2017). Although biochar is not equivalent to activated carbon and air is not the same fluid as water, these studies still suggest a potential of using corncob-based biochar to obtain BTEX removals, including other trace organic contaminants (TorC), from the aqueous environment like many other black carbon materials (Mohan et al. 2014).

To this end, the current study explored the feasibility of using corncob-made biochar (hereafter referred to as biochar) to intercept BTEX from storm runoffs. Adsorption isotherms, adsorption kinetics, adsorption thermodynamics, and dynamic transport experiments were conducted to characterize the BTEX adsorption process onto the biochar. The Monte Carlo method was also used to explore the need for uncertainty management in applying this biochar material in stormwater filtration systems.

**MATERIALS AND METHODS**

**Biochar preparation and characterization**

The corncob was milled, washed, and air-dried at 80 °C before pyrolysis. Pyrolysis was conducted in a tube furnace under N2 flow at 600 °C for 2 hours. After chilling, the products were ground and sieved to a uniform size fraction of 0.9–1.2 mm. After that, the products were rinsed with deionized water to remove impurities and then dried again at 80 °C before further physical and chemical analysis and adsorption experiments.

The specific surface area (BET) of the biochar was examined by a surface area analyzer (TriStar II 3020). The surface morphology of the biochar was observed using a scanning electron microscopy (SEM) (JEM-6700F, Hitachi Limited, Japan). The elements concentration of the biochar was analyzed using a CHN elemental analyzer (Vario EL III, Elmentar, Germany). The saturation hydraulic conductivity of the biochar was also laboratory measured (ku-pF MP10).

**Batch experiment**

The BTEX adsorption experiments were carried out using 40 mL of different initial concentrations of BTEX/H2O solutions with 10 mg biochar under different temperatures. The mixed samples were placed in an incubator shaker for 48 hours and agitated at 275 rpm for 48 hours to reach equilibrium. Solutions were then filtered using a 0.45 um syringe filter, and the equilibrium BTEX concentrations of the solutions were measured by a GC-PID (Agilent GC, 7890A).

Langmuir and Freundlich isotherm models (Equations (1) and (2)) were used to fit the equilibrium adsorption experimental results.

\[
\text{Langmuir} \quad q_e = \frac{K_L q_{\text{max}} C_e}{1 + K_L C_e} \quad (1)
\]

\[
\text{Freundlich} \quad q_e = K_F C_e^{1/n} \quad (2)
\]

where \(q_e\) is the concentration of each BTEX compound per unit of mass of biochar (g kg\(^{-1}\)); \(C_e\) is the concentration of each BTEX compound in the solution (mg L\(^{-1}\)); \(q_{\text{max}}\) is the maximum adsorption capacity of the biochar (g kg\(^{-1}\)); \(K_L\) is a Langmuir equilibrium constant (L mg\(^{-1}\)); \(K_F\) is a constant related to the adsorption capacity (g L\(^{1/n}\) mg\(^{-1/n}\) kg\(^{-1}\)); \(n\) is a constant related to the intensity of adsorption and the heterogeneity of the binding sites.

The BTEX adsorption kinetics were investigated from 0 to 48 hours in a 40 ml solution that contained 10 mg biochar under different initial BTEX concentrations. The Pseudo-First-Order model (Equation (3)), Pseudo-Second-Order model (Equation (4)), the Elovich model (Equation (5)), and the Intra-Particle Diffusion model (Equation (6)) were
used to fit the dynamic BTEX adsorption process.

Pseudo-first order: \( q_t = q_e(1 - e^{-kt}) \) (3)

Pseudo-second order: \( q_t = k_2q_e^2t/(1 + k_2q_t) \) (4)

Elovich model: \( dq_t/dt = \alpha \exp(-\beta q_t) \) (5)

Intra-Particle Diffusion model: \( q_t = K_I t^{1/2} + I \) (6)

where \( q_e \) (mg g\(^{-1}\)) and \( q_t \) (mg g\(^{-1}\)) are the amounts of BTEX adsorbed at equilibrium and at time \( t \). \( k_1 \) is the pseudo-first-order rate constant (h\(^{-1}\)) and \( k_2 \) is the pseudo-second-order rate constant (g mg\(^{-1}\) h\(^{-1}\)). \( \alpha \) is the initial BTEX sorption (mg g\(^{-1}\) h\(^{-1}\)), and \( \beta \) is the desorption constant (g mg\(^{-1}\)). \( K_I \) is the intra-particle diffusion rate constant (mg g\(^{-1}\) h\(^{-1/2}\)) and \( I \) is a constant that indicates the thickness of the boundary layer.

The adsorption thermodynamics of BTEX onto the biochar were calculated by Equations (7)–(10).

\[ \Delta G = -RT \ln k \] (7)
\[ k = q_e/C_e \] (8)
\[ \Delta G = \Delta H - T\Delta S \] (9)
\[ \ln k = \Delta S/R - \Delta H/(RT) \] (10)

where \( \Delta H \) is enthalpy, \( \Delta G \) is Gibbs free energy, \( \Delta S \) is entropy, \( T \) and \( k \) are the absolute temperature (K) and thermodynamic equilibrium constant, respectively.

**Dynamic transport experiment**

Glass chromatography columns of 20.0 cm length and 2.5 cm inside diameter were wet-packed with the biochar to minimize air bubbles. The columns were operated in an up-flow orientation with a peristaltic pump. The columns were first pumped with deionized water at a flow rate of 1 mL min\(^{-1}\) for at least 20 pore volumes (PVs) to minimize preferential flows and bubble accumulation inside the columns.

A tracer experiment was carried to obtain the column longitudinal dispersivity and pore water velocity using a KBr solution. BTEX breakthrough experiments were carried out under different flow rates, and the obtained BTEX breakthrough curves were used to fit the Pseudo-first order adsorption coefficient (\( k \)) of the one kinetic site adsorption model (Equations (11) and (12)) using the inverse procedure of HYDRUS-1D (PC-Progress, Inc.) (Šimůnek et al. 2008).

Control experiments were also carried to account for the adsorption effect from vessels and columns. The openings of the vessels and columns were sealed with parafin films to minimize the loss of BTEX to volatilization. For each BTEX solution, syringe filters were pre-filtered with the solution to minimize the loss of BTEX to filter adsorption.

**Uncertainty analysis**

The uncertainties of the hydraulic conductivity (\( K_s \), cm h\(^{-1}\)), longitudinal dispersivity (\( \alpha_L \), cm), and \( k \) (distributed around their laboratory measured values with 10% deviation) were evaluated for their influence on BTEX breakthroughs of a simulated 1-m long biochar filter. The adsorption retarded BTEX transport in this 1-m long biochar filter was simulated in HYDRUS 1D by coupling a standard convective-dispersive equation (CDE) (Equation (11)) with a first-order kinetic adsorption process (Equation (12)).

\[ \frac{\partial C}{\partial t} + \rho_b \frac{\partial S}{\partial t} = \frac{\partial}{\partial x} \left( \theta D \frac{\partial C}{\partial x} \right) - \frac{\partial qC}{\partial x} \] (11)

\[ \frac{\partial S}{\partial t} = k(S_e - S) \] (12)

where \( \theta \) is the volumetric water content (-), \( C \) is the BTEX concentration in the aqueous phase (M L\(^{-3}\)), \( t \) is the time (T), \( \rho_b \) is the bulk density of the porous matrix (M L\(^{-3}\)), where \( x \) is the longitudinal spatial coordinate (L), \( D \) is the hydrodynamic dispersion coefficient (L\(^2\) T\(^{-1}\)), \( \theta \) is the Darcy velocity (L T\(^{-1}\)), \( S_e \) is sorbed BTEX concentration that would be reached at equilibrium with the liquid phase concentration (M L\(^{-3}\)), \( S \) is the adsorbed BTEX concentration at the kinetic sorption sites (M M\(^{-1}\)), and \( k \) is the first-order adsorption coefficient.

The Monte Carlo method is implemented in MATLAB (Mathworks, USA) by modifying the target parameter values (500 random values assigned for each parameter) in the input files (selector.in) for HYDRUS, and then executing the HYDRUS code in batch mode. It should be noted that HYDRUS currently does not offer a flexible choice of sorption models such as the Intra-Particle Diffusion model, and therefore this study did not compare the difference between different kinetic models in terms of uncertainty analysis.
RESULTS AND DISCUSSION

Characterization of corn cob biochar

The biochar was found to be comprised of 78.32% carbon, 3.934% hydrogen, and 0.483% nitrogen. The BET analysis (Table 1) indicated that the biochar is highly porous which is also verified by the well-developed pore structure observed by SEM (Figure 1). The laboratory-measured saturated hydraulic conductivity of the biochar was 10.79 cm h⁻¹, which falls between sand and clay, as normally reported for biochar materials (Barnes et al. 2014).

Adsorption performance

The kinetic adsorption trends of BTEX onto the biochar are demonstrated in Figure 2 for the Pseudo-First-Order and Pseudo-Second-Order models, and Figure 3 for the Elovich model and Intra-Particle Diffusion model. The fitted parameters are listed in Table 2 for the Pseudo-First-Order and Pseudo-Second-Order models, and in Table 3 for the Elovich model and the Intra-Particle Diffusion model. The kinetic adsorption trends demonstrate that the initial adsorption is a linear process but then gradually levels off as it approaches equilibrium. However, there is no fundamental difference between the fitting qualities of the Pseudo-First-Order and Pseudo-Second-Order models, and the fitting qualities of the Elovich model and Intra-Particle Diffusion model are less than those of the Pseudo-First-Order and Pseudo-Second-Order models. This outcome does not conform to the normally observed better performance of the Intra-Particle Diffusion model in predicting adsorption of trace organic contaminants (Ulrich et al. 2015; Inyang et al. 2016). It is alleged that the Pseudo-Second-Order model will perform better than the Pseudo-First-Order model if the contact time between adsorbent and adsorbate lasts longer than 30 minutes (Inyang et al. 2016). In a study that used smaller biochar particles (<0.25 mm) for stormwater treatment (Ulrich et al. 2015), a diffusion-limited kinetic transport model was also found to be best in describing the adsorption process of trace organic contaminants.

Table 1 | Specific surface area and pore structure of the biochar

<table>
<thead>
<tr>
<th>BET special surface area (m²/g)</th>
<th>Microporous special surface area (m²/g)</th>
<th>Micropore volume (cm³/g)</th>
<th>Average pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>127.3</td>
<td>20.4</td>
<td>0.21</td>
<td>32.4</td>
</tr>
</tbody>
</table>

Figure 1 | The SEM image of the biochar.

Figure 2 | Adsorption kinetic trends of BTEX onto the biochar: (a) Pseudo-First-Order; (b) Pseudo-Second-Order (T = 25 °C, initial BTEX concentration = 10 mg/L, biochar dosage = 0.01 g).
contaminants to biochar in column experiments. The disagreement between this experiment and other similar studies is probably caused by the insufficient contact time used in this study, which indicates that the contact time between the adsorbent and adsorbate should be considered when it comes to system design, especially when using prediction models. However, since the Pseudo-First-Order and Pseudo-Second-Order models are not mechanistic while the Intra-particle Diffusion model is mechanistic (Richard 1996), the Pseudo-First-Order and Pseudo-Second-Order models are useful for describing a process for which the mechanisms are not fully understood, which is the case for this study.

The adsorption thermodynamic parameters are listed in Table 4. It is observed that the $\Delta G$ is negative, indicating that the BTEX adsorption process is spontaneous thermodynamically. The $\Delta G$ value increases with temperature increase, indicating that the adsorption of BTEX is favorable at higher temperatures, which corroborates to the increased adsorption capacities at higher temperatures. The positive $\Delta H$ values also indicate that the sorption of BTEX by this biochar is endothermic, and the positive $\Delta S$ values indicate an increase in the degree of freedom of the adsorbed BTEX.

The adsorption isotherms of BTEX onto the biochar are illustrated in Figure 4, and the fitted parameters are listed in Table 5. The fitting quality indicates no fundamental difference between the Langmuir and Freundlich-type isotherm models. However, it should be noted that the adsorption test was carried out for only 48 hours, but actually it might take time much longer to reach a ‘true’ equilibrium (Ulrich et al. 2015). Therefore, despite that they are reported as isotherm parameters in this study, these fitted parameters of adsorption isotherms are better considered as partition coefficients for 48-hour adsorption. The adsorption capacity for BTEX follows the order of Xylenes > Ethylbenzene > Toluene > Benzene, which was also similarly observed by using ordered mesoporous carbon (Konggidinata et al. 2017) and zeolite (Vidal et al. 2012) for BTEX adsorption. The Langmuir and Freundlich type isotherms are often used to reveal the adsorption mechanisms between adsorbate and adsorption sites. However, there is no fundamental difference between the fitting qualities of these two isotherm models for this biochar material. This outcome is probably caused by the well-developed pore structure of the biochar, which eliminated the heterogeneity effect of adsorption sites, or that the 48 hours reaction time is insufficient to reach the ‘true’ equilibrium of BTEX adsorption onto the biochar.

### Table 2 | The kinetic model parameters of BTEX adsorption on the biochar

<table>
<thead>
<tr>
<th>BTEX</th>
<th>$q_e$ (mg g$^{-1}$)</th>
<th>$k_1$ (h$^{-1}$)</th>
<th>$R^2$</th>
<th>$q_e$ (mg g$^{-1}$)</th>
<th>$k_2$ (g mg$^{-1}$ h$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>4.867</td>
<td>0.047</td>
<td>0.9998</td>
<td>7.095</td>
<td>0.005</td>
<td>0.9991</td>
</tr>
<tr>
<td>Toluene</td>
<td>9.65</td>
<td>0.290</td>
<td>0.9966</td>
<td>10.88</td>
<td>0.037</td>
<td>0.9774</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>15.94</td>
<td>0.263</td>
<td>0.9967</td>
<td>18.09</td>
<td>0.019</td>
<td>0.9808</td>
</tr>
<tr>
<td>Xylene</td>
<td>19.79</td>
<td>0.352</td>
<td>0.9965</td>
<td>22.07</td>
<td>0.023</td>
<td>0.9694</td>
</tr>
</tbody>
</table>

$T = 25 ^\circ C$, initial BTEX concentration = 10 mg/L, biochar dosage = 0.01 g.
(Pseudo-First-Order and Pseudo-Second-Order).
The column dispersivity and pore water velocity were calculated as 3.20 cm and 0.47 cm min\(^{-1}\), respectively, by fitting nonreactive tracer breakthrough curves to a one-dimensional form of the advective-dispersive equation (ADE) with CXTFIT code. The breakthrough curves of BTEX showed that a higher flow rate can lead to quicker BTEX breakthroughs of the 20-cm column (Figure 5). Due to the different adsorption capacities for each BTEX compound, the breakthrough time also follows the order of Xylene > Ethylbenzene > Toluene > Benzene. Normally, the service time of a biochar filter will be determined by the pollutant that breaks through the column quickest. In this column experiment, benzene is the easiest breakthrough compound among the BTEX suite.

Furthermore, the inversely estimated first-order kinetic adsorption rate coefficient \(k\) in Equation (12)) was found to decrease as the flow rate increases. Using benzene as an example, \(k\) were 0.0461 h\(^{-1}\) under 1 mL h\(^{-1}\), 0.0457 h\(^{-1}\) under 2 mL h\(^{-1}\), 0.0452 h\(^{-1}\) under 3 mL h\(^{-1}\), respectively. This phenomenon is not unexpected since theoretically a higher flow rate will lead to less contact time between adsorbate and adsorbent, which is less conducive for kinetic adsorption. Nevertheless, this outcome could be also partially caused by the fact that the diameter of the column used in this study is less than 50 times the particle diameter of the biochar. Under such a column setup, the boundary effect might have caused non-homogeneous flow conditions that influenced the adsorption kinetic process of the BTEX and the biochar material in the column.

Furthermore, under dynamic solute transport scenarios, it is commonly observed that a higher hydraulic loading rate (HLR) can facilitate the solute transport but discourage the adsorption of the solute (Šimůnek et al. 2008; Balkhair 2017). Therefore, the difference between the equilibrium batch experiment and the nonequilibrium dynamic experiment

### Table 3 | The kinetic model parameters of BTEX adsorption on the biochar

<table>
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<tr>
<th>BTEX</th>
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<th>Intra-Particle Diffusion model</th>
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<td>(\alpha) (mg g(^{-1}) h(^{-1}))</td>
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<tr>
<td>Benzene</td>
<td>0.526</td>
<td>1.152</td>
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### Table 4 | Thermodynamic parameters of BTEX adsorption onto the biochar

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<thead>
<tr>
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<th>283 K</th>
<th>298 K</th>
<th>318 K</th>
<th>(\Delta H) (kJ/mol)</th>
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<td>Benzene</td>
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Dynamic transport experiment

The column dispersivity and pore water velocity were calculated as 3.20 cm and 0.47 cm min\(^{-1}\), respectively, by fitting nonreactive tracer breakthrough curves to a one-dimensional form of the advective-dispersive equation (ADE) with CXTFIT code. The breakthrough curves of BTEX showed that a higher flow rate can lead to quicker BTEX breakthroughs of the 20-cm column (Figure 5). Due to the different adsorption capacities for each BTEX compound, the breakthrough time also follows the order of Xylene > Ethylbenzene > Toluene > Benzene. Normally, the service time of a biochar filter will be determined by the pollutant that breaks through the column quickest. In this column experiment, benzene is the easiest breakthrough compound among the BTEX suite.

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should be noted when it comes to biochar application in stormwater filtration systems.

**ENGINEERING IMPLICATIONS**

Uncertainty is a risk that needs to be understood and contained for system reliability and sustainability (William et al. 2019; Schaubroeck et al. 2020). In this study, the batch and dynamic experiments demonstrate that the contact time, ambient temperature, and initial BTEX concentrations can influence the BTEX adsorption process onto the biochar. Furthermore, the means of biochar production, such as pyrolysis temperature, surface treatment, and grain size, can also influence the adsorption capability of biochar materials in general (Inyang et al. 2016). For biochar application in stormwater treatment, uncertainties can come from various aspects such as the uncontrollable stochastic process of natural precipitation and controllable system operational settings. Therefore, it is necessary to

<table>
<thead>
<tr>
<th>BTEX</th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_L$ (L mg⁻¹)</td>
<td>$q_{max}$ (mg g⁻¹)</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.504</td>
<td>6.211</td>
</tr>
<tr>
<td>Toluene</td>
<td>1.526</td>
<td>10.99</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>0.774</td>
<td>21.00</td>
</tr>
<tr>
<td>Xylene</td>
<td>0.478</td>
<td>30.64</td>
</tr>
</tbody>
</table>

*T = 25 °C, biochar dosage = 0.01 g.

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**Table 5** | The Langmuir and Freundlich type isothermal model parameters of BTEX adsorption onto the biochar

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**Figure 5** | BTEX breakthrough curves of a 20-cm long and 2.5 cm diameter biochar column under different flow rates (Only selected experimental data points are illustrated for graphical clarity, and the data point intervals are: 10-min for B, 100-min for T, E, and X. The beginning of the breakthrough curves of T, E, and X are not illustrated in detail).
understand the impact on biochar performance from both controllable and uncontrollable uncertainties.

The Monte Carlo uncertainty analysis on hydraulic conductivity ($K_s$), materials dispersivity ($\alpha_L$), and first-order kinetic adsorption rate coefficient ($k$) are demonstrated in Figure 6. It is observed that lowering the hydraulic loading rate (HLR) or increasing the influent concentration can widen the impact of $\alpha_L$ uncertainties (Figure 6(a)). From the hydraulic perspective, a low $\alpha_L$ is highly desirable since it can enhance system reliability by maintaining a more uniform longitudinal flow and transport of water and solute. Therefore, the negative effect of $\alpha_L$ on solute transport can be restrained by high HLR or low influence concentration. In terms of uncertainty management, $\alpha_L$ is a mechanical feature of the biochar that can be controlled by enhancing the uniformity of the material grain size.

Although a proper $K_s$ is required to maintain system hydraulic efficiency, $K_s$ is normally negatively related to the contact time between adsorbate and adsorbent in dynamic transport scenarios. Nevertheless, the negative influence of high $K_s$ can be conveniently managed by lowering HLR. As shown by the uncertainty analysis, a lower HLR or influence concentration can lead to a longer service time despite the uncertainties from $K_s$ (Figure 6(b)).

$k$ is an inherent feature of biochar that is influenced by the adsorption driving force between adsorbent and adsorbate as well as ambient temperatures. Based on the experimental observations of this study, a lower HLR can also encourage adsorption by increasing the contact time between adsorbate and adsorbent. This uncertainty analysis also indicated that a low HLR can increase the service time of the biochar filter and thus lower the impact from $k$ uncertainties (Figure 6(c)).

Furthermore, compared to the influence of uncertainties from $K_s$, $\alpha_L$, and $k$, a lower HLR or influent BTEX concentration can be more conducive to extend the service time of a biochar filter, but the influence of the uncertainties from $K_s$, $\alpha_L$, and $k$ can be generally increased by lowering the HLR. From the numerical perspective, these are indicating that the system performance is a collective result of a set of highly inter-related parameters. It should be emphasized that it is not always feasible to minimize the uncertainties. Instead, it will be more practical to regulate the impact of those uncertainties based on proper understandings of uncertainties (Schaubroeck et al. 2020). Nevertheless, from the engineering perspective, HLR is more controllable, and adjusting HLR is an effective strategy to manage the negative impact of uncertainties on biochar applications (Ulrich et al. 2015).

Additionally, since urban storm runoffs are highly contaminated (Zeng et al. 2019), clogging is inevitable for the porous materials used in stormwater treatment facilities (de Matos et al. 2018; William et al. 2019). Therefore, it will be unwise to use expensively made biochar materials for suspended solids (TS) and major pollutant interceptions. Instead, biochar should be implemented as a polishing step in stormwater purification processes. In this way, the pollutant concentrations can be significantly reduced before reaching the biochar unit, and the service time of the biochar unit can be appropriately extended.
It should also be noted that the adsorption process is merely a translocation of the pollutant from one phase to another, while the ultimate pollutant elimination still relies on the biodegradation promoted by the labile carbon and microbial sanctuary offered by biochar (Ranieri et al. 2013). Therefore, biochar application should not only focus on the adsorption capability of biochar materials but also treat the biochar unit as a bioreactor for pollutant degradation in a longer time scale (Wu & Wu 2019). A proper way to exploit the adsorption capability of biochar is to retain the target pollutant long enough on biochar for biodegradation to take effect, and in some cases, organic carbon amendments can be intentionally added to potentially enhance the biological attenuation of the adsorbed pollutant within the treatment system (Ulrich et al. 2017).

Furthermore, there are other potentially negative aspects of applying biochar materials in stormwater filtration systems that deserve attention. For instance, the hydraulic conductivity and pollutant adsorption capacity of carbonaceous materials, naturally including biochars, will wear out over time and thus should also be considered in system sustainability assessment (Cameron & Schipper 2012). Also, nutrient release from biochar materials can be an issue if the biochar is made of agricultural waste of high nutrient content or with inappropriate production procedures (Mohanty et al. 2018). Therefore, despite the positive aspects of biochar application, those negative aspects should also be recognized and studied by both laboratory and field studies so that proper application strategies can be developed.

CONCLUSIONS

A corncob-made biochar was tested for its BTEX adsorption capability from the aspects of adsorption isotherms, adsorption kinetics, adsorption thermodynamics. The biochar demonstrated BTEX adsorption capabilities, and the BTEX adsorption is a thermodynamically spontaneous, and endothermic process. The adsorption capacity for BTEX follows the order of Xylene > Ethylbenzene > Toluene > Benzene. The BTEX adsorption kinetic experiment and adsorption retarded BTEX transport study indicated that the BTEX adsorption kinetics are positively related to the driving force between the BTEX concentrations and the active adsorption site as well as the contact time between the BTEX and the biochar.

In terms of the biochar application in stormwater filtration, the Monte Carlo uncertainty analysis indicated that the BTEX interception is sensitive to the hydraulic conductivity of the biochar filter and the adsorption kinetics of the biochar material. However, a conservative HLR can help to offset the negative influence of material uncertainties by increasing the service time of the biochar filter. Although this corncob-made biochar demonstrated effective BTEX adsorption/interception capabilities, it should be noted that from the perspective of sustainability the adsorption capability of biochar materials should be used to retain the adsorbed pollutant long enough for biodegradation to take effect, not merely to translocate the pollutant from water to biochar.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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