Sorption behaviour of xylene isomers on biochar from a range of feedstock

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Sorption behaviour of xylene isomers on biochar from a range of feedstock

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Graphical Abstract

Sorption Column

Outlet Flow
Glass Beads
Cotton Filter
Biochar Layer
Cotton Filter
Glass Beads
Inlet VOC Flow

Biochar Porous Structure

Non-Carbonised Mass
Mesopore
Micropore
Carbonised Mass

Sorption Capacity (mg/g)

- \( \alpha \)-Xylene
- \( p \)-Xylene
- \( m \)-Xylene

OHW500  WS300  WS400  WS500  CS300  CS400  CS500  RS300  RPS500

Functional Groups
\(-\pi-\pi\) stacking
Electrostatic Attraction
Partitioning in Non-carbonised Mass

Sorption Mechanisms
Highlights:

- The used biochar were found to be reasonably effective in removing xylene isomers.
- Access to surface functionality via biochar porous structure governs xylene sorption.
- Simpler shape and smaller kinetic diameter give p-xylene more access to active sites.
- π-π stacking, electrostatic and hydrogen bonding are main adsorption mechanisms.
Abstract

Inland oil spillage is one of the widespread sources of crude oil volatile organic compound emissions (CVEs) for which the long-term remedial solutions are often complex and expensive. This paper investigates the potential of a low-cost containment solution for contaminated solids by volatile organic compounds (VOCs) using biochar. The results of an extensive experimental investigation are presented on the sorption kinetics of xylene isomers (one type of the most frequently detected CVEs) on commercial biochar produced by prevalent feedstocks (wheat, corn, rice and rape straw as well as hardwood) at affordable temperatures (300-500°C). Chemical and physical properties of biochar were analysed in terms of elemental composition, scanning electron microscopy, specific surface area, ATR-FTIR spectra and Raman spectrometry. We show that for high-temperature biochar with similar surface chemistry, the sorption efficiency is mainly controlled by porous structure and pore size distribution. Biochar samples with higher specific surface area and higher volume of mesopores showed the highest sorption capacity (45.37-50.88 mg/g) since the sorbate molecules have more access to active sites under a greater intra-particle diffusion and elevated pore-filling. P-xylene showed a slightly higher sorption affinity to biochar compared to other isomers, especially in mesoporous biochar, which can be related to its lower kinetic diameter and simpler molecular shape. The sorption capacity of biochar produced at higher pyrolysis temperatures was found to be more sensitive to changes in ambient temperature due to dominant physical adsorption. Elovich kinetic model was found to be the best model to describe xylenes’ sorption on biochar which indirectly indicates π–π stacking and hydrogen bonding as the main mechanism of xylene sorption on these types of biochar.

Keywords: VOCs; Biochar; Crude oil contaminated soil; Adsorption; Partitioning; Xylene isomers.
**Nomenclature**

74 $\alpha$ the initial adsorption rate for Elovich model (mg.(g.min)$^{-1}$)

75 $\beta$ the Elovich parameter related to the number of available adsorption sites (g/mg)

76 $C$ carbon content (wt.%)

77 $C_{ti}$ the outlet concentration of the $i^{th}$ chemical at the any given time $t$

78 $C_{0i}$ the inlet concentration of the $i^{th}$ chemical at $t = 0$

79 $c$ the intra-particle diffusion constant (mg/g)

80 $H$ hydrogen content (wt.%)

81 $k_{PFOM}$ the rate constant for pseudo-first order model (min$^{-1}$)

82 $k_{PSOM}$ the rate constant for pseudo-second order model (g.(mg.min)$^{-1}$)

83 $k_{IPDM}$ the intra-particle diffusion rate constant (mg/(g.min$^{1/2}$))

84 $N$ nitrogen content (wt.%)

85 $n$ the number of data points

86 $O$ oxygen content (wt.%)

87 $\rho_i$ the density of the $i^{th}$ chemical (kg/m$^3$)

88 $Q_{eqij}$ the total sorbed amount of the $i^{th}$ chemical at equilibrium per unit weight of the $j^{th}$ sorbent (mg/g)

89 $Q_{Exp}$ the equilibrium sorbed mass obtained from experimental sorption (mg/g)

90 $Q_{model}$ the equilibrium sorbed mass estimated by sorption models (mg/g)

91 $Q_t$ the mass of sorbed chemicals per unit weight of the sorbent at time $t$ (mg/g)

92 $q_i$ the injection rate of the $i^{th}$ chemical (ml/min)

93 $R^2$ the coefficient of determination

94 $S$ sulphur content (wt.%)

95 $S_{BET}$ BET surface area (m$^2$.g$^{-1}$)

96 $SSE$ the sum of the squared errors

97 $t$ the sorption time (min)

98 $V_{total-BET}$ BET total pore volume (cm$^3$.g$^{-1}$)

99 $w_j$ the mass of the $j^{th}$ sorbent (g)
1. Introduction

Airborne volatile organic compounds (VOCs) are known to pose adverse effects on human health and contribute to the tropospheric ozone with regard to both Indoor Air Quality and ambient (outdoor) air pollution (Chaichan et al., 2018). Significant quantity of VOCs (142 tgc.year\(^{-1}\)) with anthropogenic origins are annually released into the atmosphere from oil and gas industries, factories, landfill, agriculture sites, biomass combustion and transport (Zhang et al., 2017a). The crude oil processing from extraction-to-refinery is recognised as one of the major sources of global human-made VOC emissions. Crude oil VOC emissions (CVEs) can either directly affect human health via occupational exposure (during all stages of crude oil processing) or indirectly influence the communities living near major crude oil industries (via atmospheric pollution). The effects of continuous inhalation of VOCs on the human respiratory system, liver and kidney function, skin, eye and the neurological network may lead to serious health problems (cancerous and non-cancerous) which have been well-documented (Rajabi et al., 2020). Petroleum contaminated soils are also recognised as a “hidden killer” to those people living near significant oil spills due to the high rate of infant mortality and serious health disorders as the result of exposure to the VOCs emitted (Hegarty, 2017).

Various methods have been proposed for remediation of oil contaminated soils but there are four common methods in practice which include (i) biological treatment (bioremediation and phytoremediation), (ii) chemical methods (oxidation and electro-kinetic remediation), (iii) thermal techniques (incineration, thermal desorption, microwave heating) and (vi) physical-chemical solutions (solvent extraction, soil vapour extraction, flotation and ultrasonication). The remediation techniques are long-term solutions to the problem; some low-cost/time-consuming (e.g. biological treatment), some expensive/fast (e.g. thermal techniques) or some
environmentally-unfriendly (chemical methods that consume large amounts of solvents) (Lim et al., 2016). In addition, hydrocarbons are firmly adsorbed to the organic matter within the heterogeneous structure of soil, and the complete removal of these compounds from the soil is not often feasible and rapidly achievable (Rajabi and Sharifipour, 2017, 2018a, b, 2019). These treatment technologies are also case-specific since their efficiencies are highly depended on the severity of crude oil contamination. The high permeability of the host soil and moderate ambient temperature can facilitate the remediation process, particularly for chemical-physical techniques (Zhang et al., 2020a). Containment is a temporary remedial solution which is faster and more importantly affordable to control emissions from crude oil contaminated soils particularly for those low-income communities living near vast crude oil contaminated lands (e.g. Niger delta). Containment through adsorption is a well-established technique to control hazardous emissions even at very low concentrations. Organic (e.g., activated carbon) and inorganic (e.g., silica gels, zeolites and alumina) materials have been analysed as sorbents within landfill capping structures to control the emission of gas species from buried wastes (Xie et al., 2017; Xie et al., 2018; Anjum et al., 2019; Wang et al., 2019). Engineered carbon-based sorbents (activated carbon, activated carbon fibre, graphene materials, carbon-silica composites, ordered mesoporous carbons (OMCs) and carbon nanotubes) have demonstrated extensive capacity for the removal of VOCs from atmospheric and aquatic streams (Zhu et al., 2020). However, their cost and high-tech production make them unfeasible and less attractive for controlling CVEs. Biochar, on the other hand, is an affordable by-product of biomass combustion under limited oxygen which has recently received widespread attention for applications in energy production, carbon sequestration, decontamination and separation science particularly when affordability and abandonment factors are of importance (Ahmad et al., 2014; Zhang et al., 2017a). The porous structure and surface chemistry of biochar
provide characteristics to the material to adsorb a wide range of organic and inorganic pollutants ranging from water purification to gas cleaning technologies, with comparable efficiency to other engineered carbon-based sorbents (Do Minh et al., 2020). Low-cost mass production of biochar using local bio-waste materials can demonstrate its suitability for CVE’s control and the treatment of petroleum contaminated soils.

This paper, for the first time, presents a set of comprehensive experimental analysis of the efficiency of biochar from a range of feedstock as an adsorbent to capture all xylene isomers. A recent review on global inventories of CVEs has highlighted that xylene isomers are among the most frequently- or highly-detected VOCs in regional emission inventories of crude oil exploitation and have detrimental effects on human health (Rajabi et al., 2020). Studies reported on the sorption of xylenes on biochar are limited to a single isomer of xylene and biochar samples from a limited range of feedstock, e.g. m-xylene on birch/pine biochar (Baltrėnas et al., 2015), p-xylene on peat moss-derived biochar (Kim et al., 2017), m-xylene on wood-chip biochar (Bushnaf et al., 2011; Meynet et al., 2014; Bushnaf et al., 2017), m-xylene on municipal solid waste (Jayawardhana et al., 2019) and xylenes on corn stalk (Zhang et al., 2020b). In this study, all three xylene isomers were studied to represent CVEs, and commercially available biochar produced at low costs from prevalent agriculture biowaste (rice, corn, rape and hardwood) at moderate pyrolytic temperatures (≤500 °C) were selected to nominate affordable sorbents suitable for vast VOC contaminated lands. A bespoke experimental setup equipped by an in-line GC-FID was utilised to study the kinetics of the sorption process. Comprehensive characterisation including elemental composition, BET surface area, ATR-FTIR, Raman spectrometry and scanning electron microscopy were carried out to obtain physical and chemical properties of sorbents. The effects of
biochar pore properties and surface chemistry on sorption are discussed along with other important parameters such as temperature conditions and the molecular shape and size of xylene isomers.

2. Material characterisations

2.1. Chemicals and biochar

Analytical grade (extra pure +99%) p-xylene, m-xylene and o-xylene in liquid form were purchased from Acros Organics (Table S1 in Supplementary Materials). Five types of commercial biochar sourcing from a range of feedstock have been used. These include Oxford hardwood (OHW), wheat straw (WS), corn straw (CS), rice straw (RS) and rape straw (RPS) produced at a range of pyrolytic temperatures (300, 400 and 500°C). Apart from the OHW which was procured from Oxford Charcoal Company (UK), the rest of biochar’s were obtained from Nanjing Zhironglian Technology (China). All samples were firstly ground using mortar and pestle, and sieved to a uniform particle size of 0.5-1 mm (Zhang et al., 2017b; Zhang et al., 2020c). The powder samples obtained were then washed using deionised (DI) water to remove impurities. The samples were oven-dried at 85°C for 24h to avoid any alteration of the biochar composition at higher temperatures. The completion of the drying process was confirmed based on stabilisation of the sample weight over 24h for all cases. The dried samples were kept in sealed containers prior to the adsorption kinetic tests.

2.2. Characterisation of biochar

The sorption mechanism of aromatic compounds onto carbon-based materials is a complicated process mainly governed by elemental composition, morphology, specific surface area, pore volume and surface functional groups of the sorbent (Dai et al., 2019). This section summarises
the detailed analyses carried out on biochar samples. The elemental compositions of biochar samples were determined using a CHNS elemental analyser (Thermo Scientific™ FLASH 2000). A Micromeritics Surface Area Analyser was employed to analyse the porous structure of biochar samples via Brunauer, Emmett & Teller (BET), and pore size distribution (PSD) was indirectly calculated based on N$_2$ adsorption-desorption isotherms, according to the Nonlocal Density Functional Theory (NL-DFT) (Kim et al., 2019). Scanning Electron Microscopy (Quanta 650 FEG SEM, FEI Company, USA), Fourier-Transform Infrared spectroscopy (Spotlight 400 FTIR Microscopy, Perkin Elmer, USA) and Raman microspore (XploRA™ PLUS, Horiba, Japan) were also employed to examine the physical properties and surface chemistry of the biochar samples.

2.2.1. Biochar Elemental analysis

The results of biochar CHNSO elemental analysis are presented in Table 1. The oxygen content was measured by the deduction of CHNS mass from the total mass of each sample according to Chen et al. (Chen et al., 2008). Based on the elemental analysis, OHW500 has the highest carbon content (72.70 wt.%) and the lowest ratios of aromaticity (H/C). The analysis also confirms that the carbon content has increased with an increase in pyrolytic temperature, whereas the oxygen content has decreased. Similarly, aromaticity (H/C) and polarity (O/C & (O+N)/C) have decreased at elevated pyrolytic temperatures. Similar observations have been reported for biochar manufactured from corn straw (Chang et al., 2018) and wheat straw (Cao et al., 2019a). The variations of both aromatic ratios (O/C & (O+N)/C) with temperature also indicates an increase in hydrophobicity of biochar as the result of decrease in polar functional groups (Zhang et al., 2017b). The low polarity index (H/C) in high-temperature biochar refers to high carbon contents and
enhanced aromatic structures, whereas a high-polar biochar has an organic-rich structure which usually contains fatty acids, lignin and polar compounds (e.g., cellulose) (Cao et al., 2019b).

Table 1. Physical, chemical and porous characteristics of biochar used in this study.

<table>
<thead>
<tr>
<th>Biochar</th>
<th>Feedstock</th>
<th>Pyrolysis Temperature (°C)</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
<th>S (%)</th>
<th>O (%)</th>
<th>O/C</th>
<th>H/C</th>
<th>(O+N)/C</th>
<th>S_{BET} (m^2.g^{-1})</th>
<th>V_{Total-BET} (cm^3.g^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>OHW500</td>
<td>Hardwood</td>
<td>500</td>
<td>72.7</td>
<td>3.01</td>
<td>0.56</td>
<td>NF</td>
<td>23.73</td>
<td>0.326</td>
<td>0.041</td>
<td>0.334</td>
<td>19.92</td>
<td>0.0468</td>
</tr>
<tr>
<td>WS300</td>
<td>Wheat straw</td>
<td>300</td>
<td>61.91</td>
<td>4.35</td>
<td>0.94</td>
<td>&lt;0.3</td>
<td>32.55</td>
<td>0.526</td>
<td>0.070</td>
<td>0.541</td>
<td>1.67</td>
<td>0.0128</td>
</tr>
<tr>
<td>WS400</td>
<td>Wheat straw</td>
<td>400</td>
<td>64.28</td>
<td>3.66</td>
<td>1.57</td>
<td>&lt;0.3</td>
<td>30.39</td>
<td>0.473</td>
<td>0.057</td>
<td>0.497</td>
<td>18.37</td>
<td>0.0361</td>
</tr>
<tr>
<td>WS500</td>
<td>Wheat straw</td>
<td>500</td>
<td>66.57</td>
<td>2.66</td>
<td>0.98</td>
<td>&lt;0.3</td>
<td>29.49</td>
<td>0.443</td>
<td>0.040</td>
<td>0.458</td>
<td>38.38</td>
<td>0.0586</td>
</tr>
<tr>
<td>CS300</td>
<td>Corn straw</td>
<td>300</td>
<td>47.05</td>
<td>4.14</td>
<td>3.02</td>
<td>&lt;0.3</td>
<td>45.69</td>
<td>0.971</td>
<td>0.088</td>
<td>1.035</td>
<td>1.23</td>
<td>0.0075</td>
</tr>
<tr>
<td>CS400</td>
<td>Corn straw</td>
<td>400</td>
<td>49.92</td>
<td>3.07</td>
<td>2.55</td>
<td>&lt;0.3</td>
<td>44.26</td>
<td>0.887</td>
<td>0.061</td>
<td>0.938</td>
<td>8.74</td>
<td>0.0155</td>
</tr>
<tr>
<td>CS500</td>
<td>Corn straw</td>
<td>500</td>
<td>61.82</td>
<td>1.87</td>
<td>2.02</td>
<td>&lt;0.3</td>
<td>34.14</td>
<td>0.552</td>
<td>0.030</td>
<td>0.585</td>
<td>15.67</td>
<td>0.0298</td>
</tr>
<tr>
<td>RS300</td>
<td>Rice straw</td>
<td>300</td>
<td>47.36</td>
<td>3.74</td>
<td>1.43</td>
<td>&lt;0.3</td>
<td>47.27</td>
<td>0.998</td>
<td>0.079</td>
<td>1.028</td>
<td>2.96</td>
<td>0.0095</td>
</tr>
<tr>
<td>RPS500</td>
<td>Rape straw</td>
<td>500</td>
<td>68.92</td>
<td>2.77</td>
<td>1.18</td>
<td>0.46</td>
<td>26.67</td>
<td>0.387</td>
<td>0.040</td>
<td>0.404</td>
<td>12.56</td>
<td>0.0225</td>
</tr>
</tbody>
</table>

2.2.2. ATR-FTIR analysis

Surface functional groups of biochar play an important role in VOC sorption along with the partitioning effect and electrostatic attractions between polar and non-polar VOC molecules and biochar surface (Ahmad et al., 2014). ATR-FTIR spectra of biochar samples are presented in Fig. 1. Spectra of the biochar samples indicate similar peaks assigned to C-H bending except for OHW500. For CS and WS biochar, the peaks are reduced at elevated pyrolysis temperatures except for C-H bending at 748-879 cm^{-1}. The trend on which peaks emerge for RS300 is generally similar to CS and WS biochar. The spectra of RPS500 and OHW500 are more or less similar with strong peaks at 874 and 1412 cm^{-1} and moderate peaks at 1410-1412 cm^{-1} associated with C–O asymmetric stretching and O–H deformation of carboxyl groups. RPS500 is the only biochar that showed an obvious peak at 1118 cm^{-1} related to OH association and C–O deformation. It can be concluded that the biochar used are rich in surface oxygen- and hydrogen-containing groups which...
provide active sites equipped by carbonyl and carboxyl groups to adsorb xylene isomers as also
observed by (Jiang et al., 2019) since these functional groups are rich in electrons and able to
attract hydrophobic VOCs (Kim et al., 2017).

![ATR-FTIR spectra of all biochar samples.](image)

**Fig. 1.** ATR-FTIR spectra of all biochar samples.

**2.2.3. Pore structure analysis**

Gas adsorption onto carbon-based materials is highly influenced by the adsorbent’s porous
structure and surface area (Dai et al., 2019). Table 1 also summarises the specific surface area
(SSA) and pore volume (PV) of biochar samples based on the results of BET method and
calculated based on N\textsubscript{2} adsorption-desorption isotherms. The samples were degassed at 105°C for approximately 12h prior to analysis (Kim et al., 2012). From 300°C to 400°C, aromatic C=C stretching and C=O stretching of conjugated ketones and quinones left the outer surface of biochar structure and resulted in obvious jumps in SSA for WS400 and CS400. With elevated pyrolysis temperature to 500°C, the removal of C–O stretching vibration in ester and aliphatic ether as well as aromatic skeleton vibration and C–H vibration in plane (lignin) led to further enhancement in SSAs, as also observed by (Lee et al., 2013; Zhao et al., 2013). RS300 has a higher SSA (2.96 m\textsuperscript{2}.g\textsuperscript{-1}) compared with WS300 and CS300 since 1,3-disubstituted C-H bending (cellulose) and C=C ring stretching vibrations of lignin did not emerge in RS300 spectra. Overall, the small SSA in biochar with low-temperature pyrolysis may be attributed to pore blockages due to the agglomeration of amorphous carbon in pores and channels (Cao et al., 2015), whereas pyrolysis under higher temperatures cease pore obstructions and generates new pores into intact channels (Sun et al., 2014). The feedstock of biochar is another important factor affecting the porous structure of biochar and SSA (Qin et al., 2020) due to differences in lignin, hemicellulose and cellulose contents (Zhang et al., 2017b). This would explain the variations of SSA observed among the high-temperature biochar samples of this study.

The PSD analysis of biochar samples is presented in Fig. S1. The PDS was calculated using NL-DFT method and based on N\textsubscript{2} adsorption-desorption isotherms (Kim et al., 2019). Although the biochar samples with high SSA (WS500, WS400, OHW500 and CS500) demonstrate a meso-level PSD at 5-40 nm, OHW500 provides a wider PSD extended to macro level. The PSD of low-SSA samples has several peaks at various pore levels which shows a complex structure with interconnected channels at macroscopic level (160-200nm). The results of PSD analysis confirm that for the biochar samples manufactured at similar pyrolysis temperature (i.e. WS500, CS500,
and OHW500), the high SSA observed for WS500 can be attributed to the higher number of mesopores available within its structure. A mesoporous biochar with high SSA/PV can provide narrow channels with more active sites (surface functional groups) which also elevates the sorption capacity via a better pore-filling and intra-particle diffusion (Gao et al., 2018). Fig. 2 shows SEM images of RPS500 which shows a different porous structure with a high SSA but very low mesopore volume in comparison to WS500, WS400 and OHW500, which can be attributed to their differences in their feedstock type.

Fig. 2. SEM images of RPS500 with various magnifications (a) 100x, (b) 500x, (c) 1000x, (d) 2000x.
3. Sorption experiments

3.1. Experimental setup

A bespoke testing system was designed for conducting the dynamic sorption experiments and analyse the biochar performance for removing volatile organic compounds (Fig. S2). In this system, the VOCs in liquid phase are first converted into gas phase using a stripping method. Pure nitrogen (99%) is used as the carrier gas with a constant flow of 0.2L/min which is regulated by a FR2000 Series Variable Area Flow Meter (accuracy: 0.1L/min). Chemically resistant and non-contaminating tubing (Tygon® SE-200) was used to ensure isolated and leak-free connection is established throughout the testing system. A gas-tight microsyringe (Hamilton-1725 TLL; 250μl) driven by a dual-syringe infusion pump (Cole-Parmer, USA) was employed to slowly inject the liquid chemicals (0.01-0.04 ml/h) through a metal needle into the flow of carrier gas. On average, 4 to 5 hours are required to produce a stable gas stream of desired VOC concentrations (100-400 ppmv). The stabilisation of the VOC concentration in the gas stream is noted when the differences in the VOC concentrations between the four successive readings by the gas analyser are less than 5%. An in-line non-sorptive bead-pack was used to ensure homogeneity of the inflow gas before injecting that into the sample column. To avoid condensation, the bead-pack was placed in a water bath with a constant temperature.

The sorption column (No. 11 in Fig. S2) consists of a gas-tight solvent-resistant Plexiglass cell and two valves to regulate inlet/outlet flows. Two layers of glass bead (thickness ≈ 3cm) were used to introduce well-mixed gases to sorbent layer (2±0.1g) and prevent layer perforation which was separated from sorbent layer by a filter paper (Whatman™, grade 1, retention>11μm) and non-adsorbent cotton. A GC-FID (GC 866, Chromatotec, France) was utilised for continuous measurement of the outflow gas composition. After achieving a stable influent concentration, the
flow was introduced to the sorption column using valves, and the effluent concentrations of VOCs are analysed at 15-minute intervals by the GC-FID unit until a steady gas composition is observed in the effluent gas which indicates completion of sample saturation. It is noted that the control tests (i.e. without sorbent layer) were also carried out to ensure there is no leakage in the system and therefore reductions in gas concentrations can be reliably attributed to sorption process. Each sorption test was repeated three times for assessing the repeatability of the results and the mean value was used.

3.2. Data analysis

The dynamic sorption of VOCs onto biochar was estimated based on the fundamental of mass conservation equations (Gangupomu et al., 2016):

\[
Q_{eqij} = \frac{1}{w_j} \left[ \sum_{t=0}^{t=t} q_i \times \rho_i \times \left( \frac{C_{ti} - C_{0i}}{C_{ti}} \right) \times t \right]
\]

where, \(Q_{eqi}\) is the total sorbed amount of the \(i^{th}\) chemical at equilibrium per unit weight of the \(j^{th}\) sorbent (mg/g); \(w_j\) is the mass of the \(j^{th}\) sorbent (g); \(q_i\) is the injection rate of the \(i^{th}\) chemical (ml/min); \(\rho_i\) is the density of the \(i^{th}\) chemical (mg/ml); \(C_{ti}\) is the outlet concentration of the \(i^{th}\) chemical at the any given time \(t\) (min); \(C_{0i}\) is the inlet concentration of the \(i^{th}\) chemical at \(t = 0\) and \(t\) is the sorption time (min).

3.3. Effect of gas concentration on biochar sorption behaviour

In order to assess the uncertainties of sorption experiments, all sorption tests were repeated three times with strong repeatability limited to a variation of <4.96%. The mean values are reported and
used to estimate the final capacity of each biochar. The influence of initial concentration on the sorption capacity was investigated for three xylene isomers on biochar WS500. A range of gas concentrations (i.e. 100, 200, 300 and 400 ppmv) were injected into 2g of biochar at 25±1°C, and the quantity of sorbed gas was calculated for each concentration. The results are shown in Fig. S3. From the results, it can be observed that by increasing the initial gas concentration, the equilibrium time ($t_e$) is reduced. The reduction in $t_e$ is more evident for p-xylene (by about 86% in $C_0$=400 ppmv, 50% in 300 ppmv and 15% in 200 ppmv) which may be attributed to variations in kinetic diameter of xylene molecules at different concentrations. At lower concentrations, it seems that active sites on biochar are occupied slowly which leads to higher $t_e$. By increasing the initial concentration, the interactions between xylene molecules and active sites of biochar intensify which facilitates sorption mechanism via higher intra-particle diffusion and reduces the equilibrium time (Zhang et al., 2017a). This may explain the longer equilibrium time observed for o-xylene and m-xylene, which have larger kinetic diameters compared to p-xylene molecules (Table S1). For the case of o-xylene, the equilibrium time was slightly reduced at the highest gas concentration, whereas for m-xylene, similar sorption behaviour was observed for all gas concentrations.

3.4. Effect of biochar feedstock on gas sorption behaviour

It is well demonstrated that the initial structural configuration of feedstock is an influential parameter on structural properties of the resultant biochar and its sorption capacity (Zhao et al., 2013). Fig. 3 presents dynamic sorption curves of xylene isomers on WS500, CS500, OHW500 and RPS500. From the results, it can be observed that WS500 and OHW500 offer the highest sorption capacities for the xylene isomers (36.82-50.87 mg/g), while CS500 demonstrated a
moderate sorption capacity (23.81-25.88 mg/g) and RPS500 showed the lowest capacity (6.54-
7.22 mg/g). Although these biochar are commercially available at relatively low costs, their
sorption capacity is comparable to engineered carbonaceous materials designed for removal of
xylene isomers, e.g. multi-walled carbon nanotubes with average sorption capacities of 15.27,
31.36, and 21.88 mg/g for p-xylene, m-xylene, and o-xylene, respectively (Yu et al., 2012), and
rice husk activated carbon with sorption capacity of 23.15 mg/g for p-xylene (Yakout, 2014). This
range of sorption capacity can be sufficient to demonstrate biochar applications to control VOC
emissions from contaminated soils, for example, according to real monitoring of volatile vapours
from hydrocarbon contaminated soils (Bocos-Bintintan et al., 2019). The concentrations of VOCs
emitted from crude oil contaminated lands highly depend on various factors controlled by the type
of host soil, crude oil composition, environmental conditions, and history of contamination (Tran
et al., 2018). Recent works on remediation of petroleum contaminated lands have reported the
range of initial concentrations of low-carbon hydrocarbons (such as xylenes) within the soil
structure to be about 12.2-16.1 mg/g (e.g., (Tran et al., 2018; Labianca et al., 2020)). On the other
hand, the adsorption capacity of proposed biochar-based capping system has been found to be
much higher (23.81-50.87 mg/g) which suggest the efficiency of proposed solution for
containment of VOC emissions from crude oil contaminated lands.

High xylene sorption capacities of WS500 and OHW500 can be attributed to their strong affinity
towards hydrophobic VOCs as the result of their low molarity and high aromaticity (Wang et al.,
2016). The OHW500 has a comparable carbon content (72.7 wt.%) to WS500 but shows lower
sorption capacity. This can be explained by its wider range of OHW500 PSD and higher O-
containing surface groups in OHW500. As the result the interactions between hydrophobic xylenes
and rich-in-π-electron sites of biochar being hindered by oxygen groups. In addition, CS500
showed a lower sorption capacity compared to WS500 and OHW500, probably due to its lower
volume of mesopores. RPS500, WS500 and OHW500 have similar carbon contents and SSA/PV,
however RPS500’s lower sorption capacity can be related to its pore structure and pore size
distribution, i.e. smaller volume of mesopores and wider range of macropores (Fig. 2a) have led
the xylene molecules to pass through larger channels in biochar without any interactions with its
active sites and pore-filling.

Fig. 3. Sorption of xylene isomers on biochar with various feedstocks at 25°C; (a) WS500, (b)
OHW500, (c) CS500 and (d) RPS500.
3.5. Effect of pyrolysis temperature on the sorption behaviour of biochar

The maximum sorption capacity of xylene isomers on WS and CS biochar with different pyrolytic temperatures (300, 400 and 500°C) are presented in Fig. 4. Sorption capacity of xylenes increased on both types of biochar as pyrolytic temperature increased. The effect of increasing pyrolytic temperature on sorption capacity was found to be stronger for WS biochar compared with CS. By considering a dual adsorption-partition mechanism for VOC sorption on carbonaceous materials (Xiang et al., 2020), the increase in sorption capacity observed at elevated pyrolysis temperatures for WS and CS biochar can be attributed to their increased carbon contents and confirms adsorption on carbonised mass as the dominant mechanism. This is particularly evident for CS biochar in which increasing pyrolysis temperature from 300 to 500°C has resulted in increased carbon contents from 47.05 to 61.82%. On the other hand, the carbon content in WS biochar does not increase considerably by temperature, and therefore the increase in sorption capacity of WS at higher pyrolysis temperature may be related to other factors such as the evolution of biochar porous structure (new pores generation and pore blockage mitigation) during the pyrolysis process which can be also confirmed by the improvement in SSA and PV of WS chars.
3.6. Effects of biochar SSA and surface chemistry on sorption capacity

Fig. S4 presents maximum sorption capacity of biochar samples for xylene isomers versus SSA. In general, increased SSA and PV would improve the accessibility of xylene molecules to the carbonised mass of biochar which highlights the importance of porous structure in sorption behaviour of biochar. For instance, WS500 (SSA: 38.38 & PV: 0.0586) and CS500 (SSA: 15.67 & PV: 0.0298) which have fairly similar carbon contents (C_{WS500}: 66.57% & C_{CS500}: 61.82%) have presented different sorption behaviour mainly due to their different porous structure. RPS500 is the only sample with low sorption capacity whilst possessing a relatively high SSA. This can likely be related to its wide range of macro-level pore sizes (Fig. 2) which provides open channels for the gas molecules to pass through without being adsorbed onto the active sites. Another influential factor to be taken into account when interpreting the possible correlations between the VOC sorption capacity of biochar and the SSA/PV is the total amount of oxygen- and hydrogen-containing functional groups on biochar surfaces. The ATR-FTIR spectra (Fig. 1) show that the
WS and CS biochar contain similar O- and H-containing functional groups, and the access to these functional groups is improved with increased SSA/PV.

In general, there are four main interactions among xylene isomers and biochar:

i. Surface functional groups (carbonyl and carboxyl) of biochar which can react with the hydrogen atoms of xylene methyl groups (mostly p-xylene due to higher polarity) via hydrogen bonding (Kim et al., 2017),

ii. Benzene rings of xylenes (mostly m- & o-xylene due to their relative non-polarity) that can generate strong hydrophobic bonds with aromatic compounds of biochar surface (lignin) via π-π stacking (Navarro Amador et al., 2018),

iii. Electrostatic attractions (Solanki and Boyer, 2019) and;

iv. Partitioning in non-carbonised mass (Chen et al., 2017).

3.7. Effects of xylene properties on the sorption capacity of biochar

The physical properties of sorbate molecules are effective on the sorption capacity of carbonaceous sorbents since intra-particle diffusion within porous media and affinity between sorbate and sorbent are affected by molecular characteristics of sorbate (Qian et al., 2015). As observed in Fig. 4, the sorption of p-xylene is slightly higher than m-xylene and o-xylene on most biochar samples. Although all xylenes have a fairly similar cross-sectional area about 0.375-0.380 nm² (Table S1), the kinetic diameter of p-xylene (5.8Å) is lower than that of m-xylene and o-xylene (6.8Å). This difference is derived from different position of methyl chains around the central benzene ring shaping a bigger lateral dimensions for m- and o-xylene (Gonzalez et al., 2018). A simpler
molecular shape gives p-xylene a priority to have access to active sites of sorbent via mesopores. Slightly larger molecules of m- and o-xylene prevents their access to all pores and canals, and the entrance to some pores may be even blocked by other similar molecules in competitive process of single-component sorption.

The Raman spectra of WS500 before and after sorption of xylene isomers are presented in Fig. S5. Raman spectrometry provides information about the vibrational modes of sample molecules (in this case, xylene isomers) which is widely used to characterise carbon-based sorbents (Shu et al., 2017). As shown in Fig. S5, the Raman spectra of WS500 before and after sorption has two major peaks at 1326 and 1577 cm\(^{-1}\) related to D and G bands which are typically observed in carbon-based sorbents (Alcaraz et al., 2018). D band confirms the presence of hexagonal graphitic sheets with symmetry breaking defects and lattice distortions in carbon materials, while G band points to in-plane stretching of hybridised carbon atom in the graphitic structure (Anjum et al., 2019). The Raman intensity ratio of I\(_D\)/I\(_G\) remained relatively unchanged (~0.978-0.985) which indicates that there were no alterations in the carbonaceous structure of biochar due to gas sorption process.

Moreover, the overall Raman intensities of biochar reduced due to sorption of xylene isomers which can be attributed to the vibrational modes of surface molecules in biochar being limited by attached xylene’s molecules. This reduction is higher for the case of p-xylene in comparison with m- and o-xylene which also verifies higher sorption of p-xylene on WS500 determined by experiments. The spectra of WS500 after sorption of m- and o-xylene are more or less similar which may be attributed to their comparable sorption capacities.

### 3.8. Effects of ambient temperature on sorption
In order to assess the effect of ambient temperature on VOC sorption behaviour of biochar, two types of biochar, WS500 and WS300, were selected which showed higher sorption capacities within their comparative groups. The sorption column was submerged in the water bath to provide constant temperatures throughout the tests. The dynamic sorption experiments were then carried out at 35 and 45°C to simulate the range of ambient temperatures reported for major crude oil contaminated sites (Das and Chandran, 2011), and the results are presented in Fig. 5.

Fig. 5. Effects of ambient temperature on sorption capacity of xylene isomers on (a) WS500 and (b) WS300.

As it can be observed, for both biochar types, increasing temperature reduces the sorption capacity, and WS500 shows much higher reduction in capacity (~80-91%) compared to WS300 (63-71%). This can be related to the different mechanisms of xylene sorption on biochar WS300 and WS500. As discussed in section 3.5, the physical adsorption is the dominant mechanism in biochar produced at high pyrolysis temperature, while partitioning governs sorption process in biochar produced at low pyrolysis temperature. Physically-induced sorption is more sensitive to temperature changes in comparison with partitioning-induced sorption, therefore, higher reduction in sorption capacity observed for WS500 at higher ambient temperatures can be related to its
dominant physical adsorption towards xylenes, while partitioning still takes place in both biochar samples (Zhang et al., 2017b).

3.9 Sorption modelling

Based on the experimental data generated in this work, we adopt the conventional kinetic models to develop an insight into the mechanisms involved in VOC sorption on biochar. A number of well-established kinetic models including the PFOM and PSOM (which are pseudo-first and second-order models, respectively), the Elovich model (ELM) and the Weber–Morris intra-particle diffusion model (IPDM) are adopted (Wu et al., 2009). The equations describing these adsorption kinetic models are as follows (Largitte and Pasquier, 2016):

PFOM: \[ Q_t = Q_{eq}[1 - \exp(-k_{PFOM}t)] \]  \( (2) \)

PSOM: \[ Q_t = (k_{PSOM}Q_{eq}^2t)/(1 + k_{PSOM}Q_{eq}t) \]  \( (3) \)

ELM: \[ Q_t = \frac{1}{\beta} \ln(1 + \alpha \beta t) \]  \( (4) \)

IPDM: \[ Q_t = k_{IPDM}t^{1/2} + c \]  \( (5) \)

where \( Q_t \) is the mass of sorbed chemicals per unit weight of the sorbent at time \( t \) (mg/g), \( k_{PFOM} \) is rate constant for pseudo-first order model (min\(^{-1}\)), \( k_{PSOM} \) is rate constant for pseudo-second order model (g.(mg.min\(^{-1}\))), \( \alpha \) is the initial adsorption rate for ELM model (mg.(g.min\(^{-1}\))), \( \beta \) is the Elovich parameter related to the number of available adsorption sites (g/mg); \( k_{IPDM} \), is the intra-particle diffusion rate constant (mg/(g.min\(^{1/2}\))) and \( c \) is the intra-particle diffusion constant (mg/g). The coefficient of determination \( (R^2) \) and the sum of the squared errors \( (SSE) \) are used to compare the best fit of the models with the experimental results of VOC sorption on biochar:
\[ SSE = \sum_{i=1}^{n} (Q_{Exp} - Q_{model})^2 \]  

where, \( Q_{Exp} \) is the equilibrium sorbed mass obtained from experimental sorption (mg/g); \( Q_{model} \) is the equilibrium sorbed mass from the sorption models (mg/g), and \( n \) is the number of data points.

Fig. 6 presents the experimental and modelled dynamic sorption for xylene isomers on selected biochar (WS500 and CS500). The obtained models’ parameters are provided in Table S2. The results show that the best fit by the PFOM and ELM models present strongest agreement with the experimental data based on both criteria of maximum \( R^2 \) and minimum \( SSE \). The best fits using PSOM and IPDM models present an acceptable fit based on \( R^2 \), but significantly higher values of \( SSE \) compared to the other two models. The amount of sorption near equilibrium is underestimated by the PSOM model by 12.7% and overestimated by the IPDM model by 18%. Although Langmuir PFOM and ELM have relatively similar assumptions (localised sites with no interactions among sorbed ions (Largitte and Pasquier, 2016)), ELM has noticeably lower \( SSE \) than the PFOM (\( SSE_{ELM}=3.0574 \ll SSE_{PFOM}=20.6452 \)) to estimate xylenes sorption on biochar materials as higher order models were also suggested to estimate sorption of most volatile compounds on biochar structures (Creamer et al., 2014). Adsorbates are usually interacted with biochar surface via chemical reactions (electrostatic interactions, \( \pi-\pi \) stacking and hydrogen bonding) as well as pore filling (Rajapaksha et al., 2019). Elovich is generally related to chemical adsorption (Mohammed et al., 2018), and the obtained data fitting again indicates \( \pi-\pi \) stacking and hydrogen bonding as the main interactions of xylene isomers and these types of biochar.

4. Conclusions
This study presents the sorption behaviour of xylene isomers on a number of commercially available biochar samples with a diverse range of feedstock and pyrolysis temperatures. WS-based biochar provided the highest sorption capacity which highlights the influence of feedstock on biochar removal of xylene isomers. Biochar porous structure governs xylenes sorption via pore-filling in mesopores as well as providing accessibility to surface functional groups. P-xylene showed slightly higher affinity to certain types of biochar which was correlated with the higher volume of mesopores in those biochar, smaller kinetic diameter and simpler molecular shape of p-xylene. High-temperature biochar indicated higher gas sorption sensitivity to changes in ambient temperature. It may be attributed to their physical sorption mechanisms, while partitioning is believed to be the main sorption mechanism of low-temperature ones. The most satisfactory match (by fitting) with the experimental results was provided by Elovich kinetic model which indirectly points to electrostatic attraction, π–π stacking and hydrogen bonding as main chemical interactions between xylenes and biochar. This study demonstrates extensive potential for biochar to be used as an engineered barrier and containment system to tackle the challenge of VOC contaminated lands. Biochar based capping systems can potentially provide an efficient and cost-effective containment solution for VOC emission from oil contaminated sites prior to implementation of long-term remediation of crude oil-contaminated lands.
Fig. 6. Experimental and modelled sorption dynamic curves for all xylene isomers on WS500 and CS500.
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References


Cao, Y., Xiao, W., Shen, G., Ji, G., Zhang, Y., Gao, C., Han, L., 2019b. Carbonization and ball milling on the enhancement of Pb(II) adsorption by wheat straw: Competitive effects of ion exchange and precipitation. Bioresource Technology 273, 70-76.


Rajabi, H., Sharifipour, M., 2018b. Influence of weathering process on small-strain shear modulus (Gmax) of hydrocarbon-contaminated sand. Soil Dynamics and Earthquake Engineering 107, 129-140.


