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Containment of emerging VOC pollutants by biochar

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ABSTRACT

Air pollutants are known to be responsible for up to 8.9 million premature deaths per year across the world. Among the pollutions are, emerging organic pollutants such as volatile organic compounds (VOC) that pose significant global risk to human health and the environment. Contaminated lands by crude oil and petrochemical products are major source for the emission of VOCs in the world. Long-term solutions for remediation of VOC contaminations in soil and water are expensive and require advanced technologies. The challenge of access to affordable and practical solutions is particularly highlighted in the case of vast contaminated lands. Hence, the provision of a simple, affordable, easy-to-localise and environmentally sustainable solution is critical to contain the emission of harmful gases or contamination of the groundwater resources. This paper presents the results of a series of experimental investigations on efficiency and sustainability of biochar-based containment systems for VOC contaminated lands. A bespoke experimental setup was developed to study the kinetics of VOC sorption in biochar manufactured from a range of feedstock and pyrolysis temperatures. Sorption behaviour of pure and mixed VOC gases in biochar was investigated, and the effects of various parameters on the sorption capacity including material characteristics and environmental conditions were evaluated and dominant sorption mechanisms were identified. The results show that the uptake of VOC by biochar is mainly controlled by factors such as porous structure, surface chemistry and pore size distribution of adsorbents along with molecular properties of adsorbates.

Keywords: Biochar, VOC, Volatile Organic Compounds, Emerging Contaminants.

1 INTRODUCTION

Lands contaminated by the spillage of crude oil or other petrochemical products are a major source for the emission of volatile organic compounds (VOCs) in various regions and countries in the world. The VOCs can be transferred for several miles and have profound adverse effects on human health and the environment. In Niger Delta, Nigeria, for instance, untreated oil spills have severely affected the health of local communities so that the children born within 10km of oil spills are reported to be twice as likely to die in their first month. This has been directly linked to the exposure of pregnant women to harmful VOC emissions (*e.g.,* benzene and toluene) from crude oil contaminated soils (Elum et al., 2016).

Conventional methods for the remediation of contaminated soils are usually expensive and require advanced technologies (e.g., in-situ bioremediation). Such solutions are not affordable to local authorities and not practical in the case of large areas of contaminated lands such as those in Niger Delta. In such circumstances, the provision of a simple, affordable, easy-to-localise and environmentally sustainable containment solution is critical (and most likely the only solution) to protect the local communities against the emission of harmful gases or contamination of the groundwater resources. Carbonaceous by-product of controlled pyrolysis such as biochar, which is usually produced from locally available biomass/biowaste, offer a sustainable solution to the problem. The carbon elemental materials have features of highly adsorbent properties to the VOCs and can potentially be utilised as capping systems for short/long terms VOC containment until permanent treatment is in place.

Biochar is well-known for its effective sorption properties and has been used in several application including syngas cleaning and used as catalyst in production of biodiesel (Ahmad et al., 2014). Compared to other engineered adsorbents, and in addition to its favourable characteristics including

high surface area, pore size/volume and surface chemistry, biochar production is relatively simple and cost-effective, and its raw material can be sourced from locally available biowaste which makes it one of the most sustainable solutions when it comes to applications in large quantities, e.g., remediation of vast contaminated lands. However, most studies have focused on the application of biochar for removal of single species of contaminant and current understanding of its efficiency for removal of VOCs under competitive conditions (mixed gas) is limited.

This paper presents the summary results of a series of experiments on the sorption characteristics of single and multicomponent VOC systems on biochar (Rajabi et al, 2021a & b). Different types of biochar from various agricultural wastes were sourced and used as sorbents in this study. The VOC species of toluene, p-xylene, hexane, and acetone were selected and used in this study due to their aromatic and non-aromatic characteristics and their detection frequency near petroleum polluted sites, as reported by the CVEs (Rajabi et al., 2020). It should be mentioned that based on the outcomes of initial investigation on sorption capacity of biochar and due to time constrains, it was decided to perform single- and multi-component sorption experiments on two types of biochar only, i.e., bagasse and wheat straw. Physical and chemical properties of the samples were investigated using elemental analysis, Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and Brunauer–Emmett–Teller (BET) surface area analysis. A bespoke lab facility including a GC-FID was used to investigate the kinetics of both pure and mixed gas adsorption on biochar.

2 CHARACTERISATION OF BIOCHAR

Several types of commercial and non-commercial biochar were sourced from a range of feedstocks (wheat straw, corn straw, and bagasse) and pyrolysis temperatures (300, 400 and 500℃). The samples were ground and sieved to a uniform particle size of 0.5-1 mm. Efforts were made to prepare all samples (used in single and competitive sorption tests) with uniform particle size to ensure consistent intraparticle diffusion rate and to enable more accurate comparisons of the results. The samples were then washed using deionised water to remove impurities. The samples were then oven-dried at 85℃ for 24h. Higher temperatures were avoided to ensure no further alteration of the biochar composition due to increased temperatures. The dried samples were then kept in sealed containers prior to the adsorption kinetic tests. The sorption mechanism of volatile compounds onto carbon-based materials such as biochar is recognised to be a complicated process mainly governed by elemental composition, morphology, specific surface area, pore volume and surface functional groups of the adsorbent (Dai et al., 2019). In this section the results of elemental, FTIR, and pore structure analyses of selected biochar are briefly discussed.

2.1 The elemental analysis

The elemental composition of biochar samples was evaluated using a CHNS elemental analyser (Thermo Scientific™ FLASH 2000). Biochar samples (50-100 mg) were combusted in a furnace at 1200°C, and the oxides of carbon (C), hydrogen (H), and sulphur (S) were released along with nitrogen (N). A Micromeritics Surface Area Analyser was employed to analyse the porous structure of biochar samples via Brunauer, Emmett & Teller (BET). 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). Table 1 provides the results of elemental analysis and porous structure of selected biochar for this study.

Table 1. *Elemental analysis and porous characteristics of the used biochar*

Biochar	Feedstock	Pyrolysis Temp.(℃)	O/C	H/C	(O+N)/C	S_{BET} ($m^2.g^{-1}$)	$V_{Total-BET}$ ($cm^3.g^{-1}$)
BG500	Bagasse (BG)	500	0.289	0.024	0.293	78.15	0.1448
WS500	Wheat Straw (WS)	500	0.443	0.040	0.458	58.38	0.0786
CS500	Corn Straw (CS)	500	0.552	0.030	0.585	15.67	0.0298

Elemental analysis showed that the BG500 has the highest carbon content (76wt.%) and the lowest ratios of aromaticity (H/C). BG500 and WS500 were found to be rich in carbon with 67% and 76% carbonised mass, respectively. However, the ratios of aromaticity (H/C), hydrophilicity (O/C) and polarity (O+N)/C) for WS500 are two times larger than BG500. The lower polarity of BG500 can be related to its

higher carbon content in comparison with WS500 with higher polar compounds (e.g., cellulose, fatty acids, and lignin) and aromaticity which enhances its polarity too (Cao et al., 2019).

2.2 FTIR Analysis

Surface functional groups of biochar are important factors in adsorption of VOCs as well as partitioning effect and electrostatic attractions between polar and non-polar VOC molecules and biochar surface (Ahmad et al., 2014). The FTIR analysis show that BG500 with a peak at 1118 cm-1 (as the results of OH association and C–O deformation) is rich in surface oxygen- and hydrogen-containing groups, providing active sites charged by carbonyl and carboxyl groups to readily adsorb xylene isomers. The functional groups are rich in electrons which explains the reasons for attracting hydrophobic VOCs (Kim et al., 2017). A range of oxygen- and hydrogen-containing functional groups on biochar surface were identified by the FTIR spectra of biochar samples. We did not observe certain peaks in BG500 (i.e., 1314-1378 cm-1) which can related to the absence of polar compounds such as lignin, cellulose, and hemicelluloses in this biochar. The hydrophilic surface of Bagasse was found to be low (compared to othes) and there are fewer polar groups which was confirmed by its lower ratio of O/C (hydrophilicity) and (O+N)/C (polarity).

2.3 Pore structure analysis

The feedstock of biochar is important in shaping the pore structure and specific surface area (SSA) of biochar; controlled by the contents of lignin, hemicellulose, and cellulose in biochar (Zhang et al., 2017). BG500 showed the highest SSA and PV (78.1 m2.g-1 and 0.145 cm3.g-1) followed by WS500 (SSA: 58.4 m2.g-1 and PV:0.079 cm3.g-1). Figure 1 shows the SEM images of biochar samples used in this study.

Further investigations into the results of pore size distribution (PSD) analysis highlighted that biochars manufactured at similar pyrolysis temperatures (i.e., BG500, WS500, and CS500), have high SSA that is due to the higher ratios of mesopores within biochar matrix. Mesoporous biochar with high SSA/PV contain narrow channels with increased active sites or surface functional groups (Gao et al., 2018), that enhance the sorption capacity of biochar via effective pore-filling and intra-particle diffusion processes.

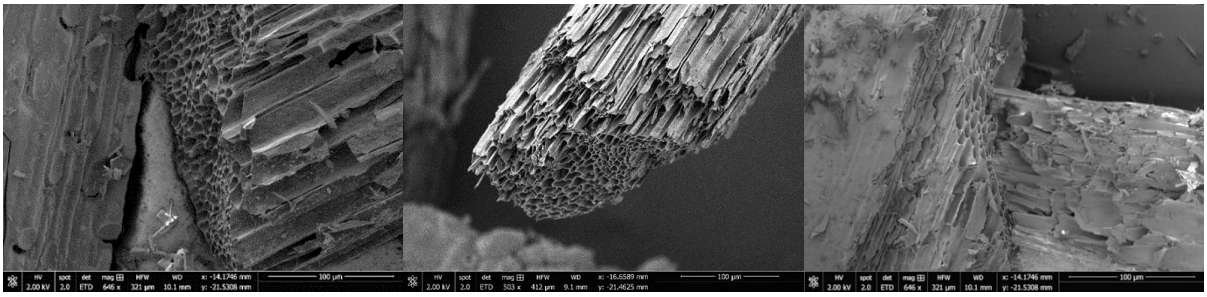


Figure 1. *SEM images and pore structure of WS500 (left), BG500 (middle) and CS500 (right).*

3 SINGLE-COMPONENT VOC SORPTION BEHAVIOUR IN BIOCHAR

Figure 2, presents the results of single-component adsorption tests (kinetics) on BG500 and WS500 biochar. BG500 exhibited the highest adsorbed mass for acetone, followed by p-xylene, toluene, and hexane. Differences in sorption capacities can be related to the kinetic diameters of VOC molecules as well as differences in surface chemistry and porous structure of biochar. Acetone interacts with carbonised mass via carboxylic groups (Yu et al., 2018), and with a low kinetic diameter (3.8 Å), it penetrates smaller pores. Therefore, the small gas molecules have access to more active sites which may not be available to larger gas molecules (Zhang et al., 2017). The maximum adsorption of acetone on BG500 (110 mg/g) is two times higher than that of WS500 (45 mg/g) which is due to the higher SSA/PV of BG500. Higher SS and PV would increase the pore-filling and access to active sites. Hexane, on the other hand, showed the lowest sorption capacity on both biochar types which can be related to its molecular arrangements limiting its success rate in being adsorbed onto the surface of biochar. Hexane molecules (C6H14) can interact with carbon molecules via CH-π bonding, whereas other aromatic chemicals such as xylene and toluene can also interact via π-π stacking (Thongsai et al., 2019). Hexane showed higher affinity to BG500 (37 mg/g) in comparison with WS500 (20 mg/g), possibly due to its higher inclination towards hydrophobic carbon surfaces in BG500 with fewer oxygenated groups and greater porosity (Hernández-Monje et al., 2018). The results showed that toluene and p-xylene are adsorbed onto carbon surface of biochar via π-π stacking (Solanki and Boyer,

2019), electrostatic attraction (Kim et al., 2017), functional groups (Chen et al., 2017) and partitioning into non-carbonised mass (Rajabi et al., 2021b).

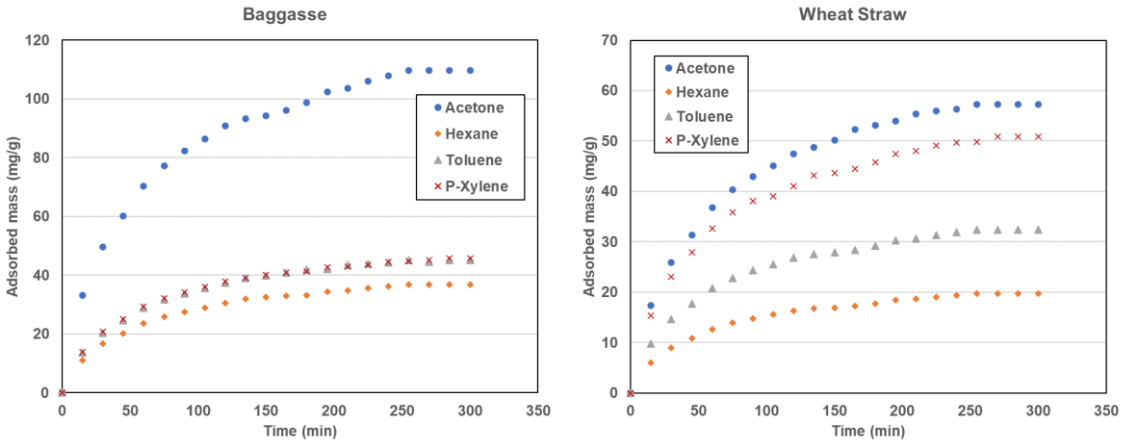


Figure 2. *Kinetics of sorption of single VOCs on Bagasse (left) and Wheat Straw (right) biochar.*

It should be mentioned that VOC adsorption on carbonaceous materials is primarily dominated by physicochemical processes mainly controlled by physical attractions (i.e., pore-filling and van der Waals forces) as well as functional groups and stacking. The maximum adsorption of toluene on BG500 (45 mg/g) is slightly higher than that for WS500 (33 mg/g) which can be related to enhanced pore-filling within BG500 mass and its higher SSA. The gas molecules of p-xylene can be accumulated onto the low-SSA structure of WS500 due to higher polarity (WS has more polar groups compared to BG).

3.1 Effect of pyrolysis temperature on biochar sorption capacity

Figure 3 presents the results of maximum sorption capacity of xylene isomers on WS and CS biochar at different pyrolysis temperatures. The results, show that the sorption capacity of increased with increase in pyrolysis temperature. WS biochar showed stronger variations in sorption capacity by pyrolysis temperature. Increased sorption capacity of biochar at higher pyrolysis temperatures can be related to increased carbon contents (Xiang et al., 2020).

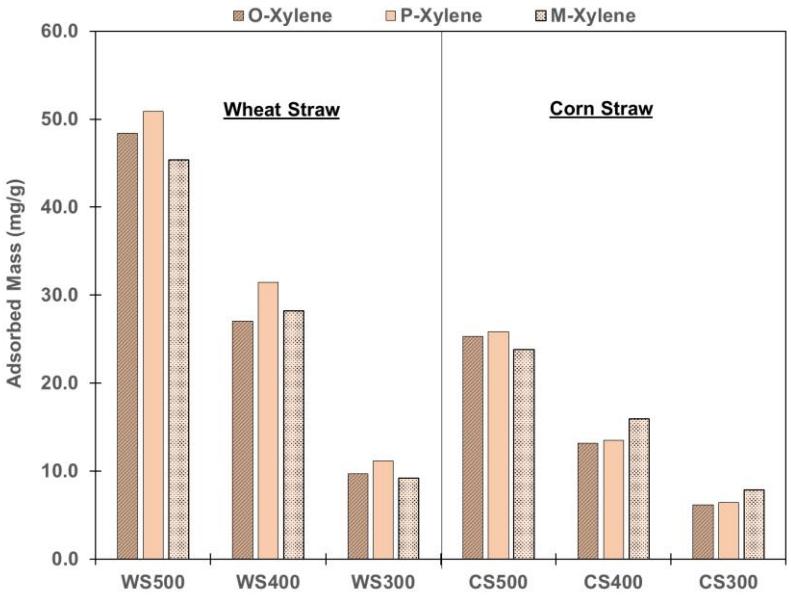


Figure 3. *Effects of pyrolysis temperature on xylene sorption capacity of WS and CS biochar*

Temperature of pyrolysis for CS biochar ranges between 300 and 500℃. Pyrolysis at such range can result in an increased carbon content (from 47 to 62%). However, it was found that the carbon content of the WS-based biochar, did not increase considerably by temperature. It is anticipated that the

increase of sorption capacity for the case WS at higher pyrolysis temperature is related to other factors such as porosity evolution which are also evident from increased SSA and PV for WS biochar produced at high temperature.

4 COMPETITIVE VOC SORPTION BEHAVIOUR IN BIOCHAR

Figure 4 presents the results of competitive adsorption experiments for mixed VOCs on Bagasse and Wheat Straw biochar. Overall, the higher SSA/PV of BG500 provided more accessible active sites to the mixed gas molecules leading to much higher adsorption capacity (109 mg/g) in comparison to that of WS500 (50 mg/g). The total adsorbed mass of individual VOCs in multi-compound experiments is noticeably lower (27-75%) than that of single gas experiments. This may be explained by the fact that the overall adsorption capacities of VOC gases were limited as the results of competitive inhibition, which led to lower adsorbed mass and faster saturation (Vikrant et al., 2020).

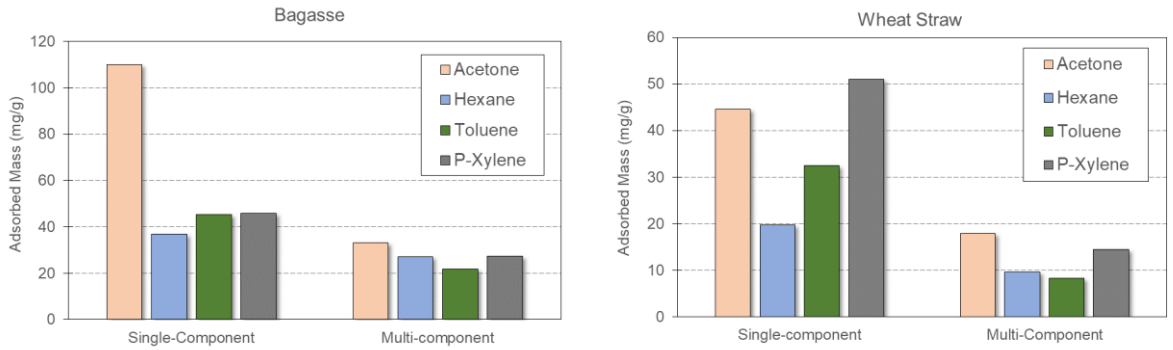


Figure 4. *Adsorption capacity of Bagasse (left) and Wheat straw (right) biochars observed in single- and multi-component adsorption tests.*

The reductions in the saturation time can be related to the higher molecular diffusion rate (Figure 5) under competitive sorption tests. According to Jahandar Lashaki et al. (2016), accumulation of adsorbate molecules in pores can occur due to: (i) superposition of wall effects in pores smaller than 7Å (in comparison to adsorbed species of 4.3-6.8Å); and/or (ii) limitations associated with the narrow micropores of the adsorbent. Lighter VOCs used in this study (e.g., acetone) showed stronger reduction in the adsorption capacity in mixed gas tests. Such observation was particularly highlighted in the results of adsorption in bagasse. This is likely to be related to van der Waal's interactions between carbon and heavier compounds (Samaddar et al., 2019). The larger adsorption of hexane by WS500 compared to toluene can be related to the differences in the molecular diffusivity of hexane in biochar. It is noted that toluene has the lowest sorption compared to other VOCs that is due to its larger kinetic diameter and less access to active sites.

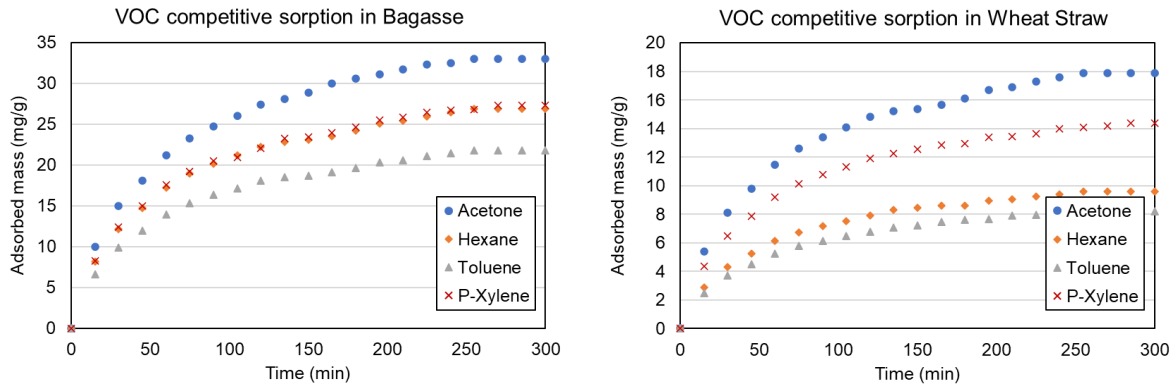


Figure 5. *kinetics of competitive sorption of acetone, hexane, toluene, and p-xylene on WS500 and BG500 biochar.*

5 CONCLUSIONS

This paper presented the results of an experimental study on sorption of aromatic and non-aromatic volatile organic compounds on various types of biochar. The biochar used were products of pyrolysis of commonly available agricultural wastes (wheat straw, corn straw and bagasse). All biochar used demonstrated similar total adsorption capacity for single (51-110 mg/g) and mixed gases (50-109 mg/g). Among those, the Bagasse biochar had the highest capacity for adsorbing both single and multi-component gases. This was found to be related to the larger specific surface area and pore volume. Amongst the gases studied, biochar had the highest tendency to adsorb acetone which has the smallest molecular diameter compared to the others used in this study. However, it was observed that its removal dropped to 65% in the presence of other gases in multi-component adsorption tests. This paper provided crucial insights into sorption mechanisms and overall adsorption capacity of biochar for both single and multicomponent VOCs. Based on the study conducted by Rajabi et al (2020), the ultimate sorption capacities of biochar studies in this work are sufficiently higher than total concentrations of VOCs frequently detected in oil contaminated sites, Therefore the results of this study provide further confidence in suitability of proposed method for the application of VOC containment and removal from crude oil contaminated sites using commercially available biochar.

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