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Sorption of α-, β-, γ- and δ-hexachlorocyclohexane isomers to three widely different biochars: sorption mechanisms and application

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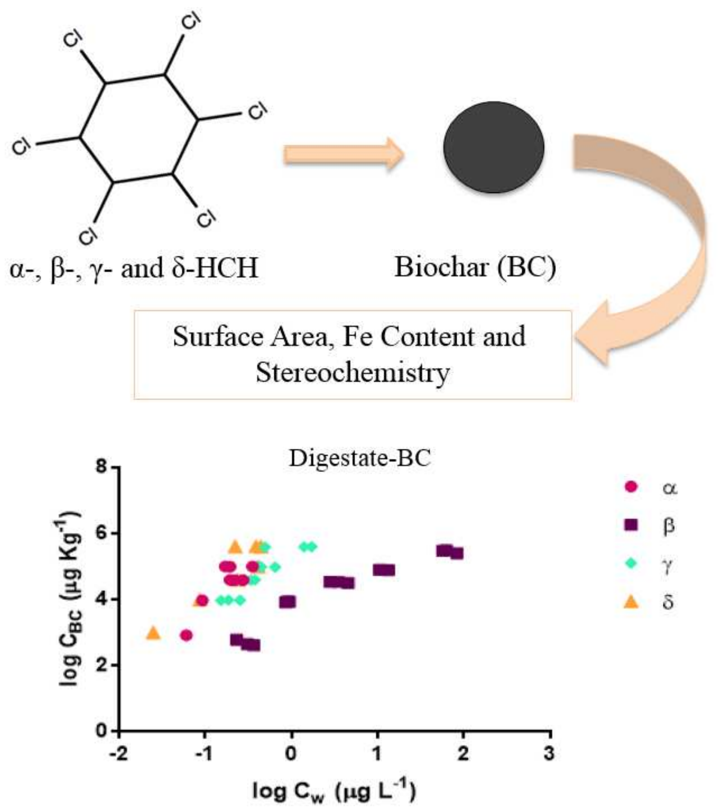
Keywords

Biochar, sorption, remediation, chlorinated pesticide

Graphical abstract



Abstract

Within this study different biochars (BC) with widely varying characteristics have been tested as materials for the adsorption of hexachlorocyclohexane's (HCH) isomers (α, β, γ and δ) from water. Three BCs produced from digestate (700 ºC), greenhouse tomato waste (550 ºC) and durian shell (400 ºC) were tested. The BCs demonstrated variable physico-chemical characteristics, especially with respect to surface area, with CO$_2$-surface area ranging from 5.4 to 328.6 m^2 g^{-1} and iron content ranging from 0.0733 to 11.17 g kg^{-1}. Isotherm tests were carried out to understand which mechanisms drive HCH uptake to BC, to assess whether stereochemistry affects adsorption and to assess whether competitive sorption occurs. Log K$_F$ values ranged from 3.7 to 5.8 (μg kg^{-1}) (μg L^{-1})$^{-n}$ for the various isomers on the three biochars. No competition (t-test, $P < 0.0001$) was observed between α-, β-, γ- and δ-HCH. Freundlich adsorption constants of α-, γ- and δ-HCH followed the order: BC digestate > BC greenhouse tomato waste > BC durian shell, in contrast to β-HCH which followed the order: BC durian shell > BC greenhouse tomato waste > BC digestate. In addition to stereochemistry, sorption

coefficients were affected most strongly by BC surface area and iron content, in addition to specific HCH BC matrix interactions. In this study the iron content of a carbonaceous material has been investigated, for the first time, as a factor that can affect the sorption of HCHs.

1. Introduction

Hexachlorocyclohexanes (HCH) are halogenated compounds classified as persistent organic pollutants (POP)[1] and are of worldwide concern due to toxic effects they can exert on the ecosystem[2]. There are four HCH isomers, α-, β-, γ- and δ-HCH, with different stereochemistry[3] (Fig. S1 in supporting information (SI)), and as a result they partition between environmental compartments in different manners[3]. HCHs are persistent in water and also have a long residence time in soil[2,4]. For example the half-life of α-HCH is around 3 months in soil (20 ºC) and 120-900 days in water (at 20 ºC, $7 < pH < 8.21$) [5].

HCHs have been used globally as insecticides from 1940[2,4,6,7], most commonly being sold in technical grade (mixture of isomers) or as lindane (γ-HCH), the only isomer with insecticidal properties[2,4]. The production of lindane is very inefficient and generates 8 to 12 tons of residues per ton of lindane[8]. Over the period in which lindane was used, an average of 4-7 million tons of wastes and residues (mainly α-HCH and β-HCH) were produced and this has resulted in widespread ecosystem contamination[2,4,6,8]. The presence of HCH-isomers in the environment represents a global problem and strategies to remediate contaminated sites are thus required.

Sorbent amendment is one relatively novel remediation strategy that allows metals[9,10] and organic contaminants[11-15] to be sequestered and rendered immobile[16] for uptake in biota or transport to groundwater. Carbonaceous materials are often used for this purpose and they are amended in small doses to contaminated soils and sediments[12,17-19]. Biochar (BC) is a carbonaceous material obtained by the pyrolysis of plant and animal based biomass in an oxygen free or oxygen limited environment[9,20,21]. BC is potentially a key technology for combating climate change as it is one of few Negative Emission Technologies (NET)[22]. Co-benefits of BC amendment include pollutant emission mitigation, soil quality improvement, waste management and energy production[12,23-28]. BC has similar physicochemical properties to activated carbon, the most commonly used carbonaceous material for the environmental application of organic pollutant immobilization, but it can be produced at much lower cost. BC surface area (SA), porosity and surface characteristics usually depend on the biomass feedstock, the pyrolysis method, time and temperature[26,29]. However, these parameters can be designed in order to obtain a material with desired characteristics which often entails a high SA and high porosity[11,30]. The amendment of BC to water[10,13,21,28], soil[14,21] and sediment[31] for the remediation of metals and organic contaminants has been demonstrated.

The remediation of HCH contaminated soil is most often accomplished via selective, reductive dechlorination and/or bioremediation. Zero valent iron (ZVI) is commonly used for the selective, reductive dechlorination of HCH, and the kinetics and extent of degradation seem to be affected by the axial/equatorial position of the chlorines[32]. In addition, it is well known that several microbial strains/consortia, such as *Pseudomona*s and *Flavobacterium*, are able to degrade HCHs[33]. The white-rot fungus *Bjerkandera adusta* degraded of 95% of γ-HCH in a soil slurry[34]. *Penicillium griseofulvum,* isolated from soil, effectively degraded β-HCH (starting concentration 1 mg L^{-1}) in nutrient stressed conditions to a residual concentration between 18.6 and 58.2% depending on the sucrose (carbon source) concentration in the medium (from 5 to 0 g L^{-1})[2]. Currently there is only one study that has investigated the use of BC to biotically remediate HCH polluted soil. Gregory et al.[35] added willow (*Salix sp.*) BC (pyrolysis at 350 and 550°C) to soil at dosages of 30 and 60 t ha^{-1}. They reported a 10- and 4- fold reduction in soil concentration of α- and γ-HCH, for both temperatures and dosages over a six month trial. The reduction was associated with an increase of soil dehydrogenase activity, which has been related to microbial activity, indeed the use of BC can increase the growth of Chryseobacterium, Flavobacterium, Dyadobacter and Pseudomonadaceae, which are common hydrocarbon bioremediators[35].

A few other studies have reported the use of activated carbon amendment, either alone or in combination with ZVI as a sorbent that can potentially assist in the abiotic removal of HCHs from water[7,36]. The ZVI, provides a media for degradation of HCHs, while the activated carbon provides sorption sites for the degradation products.

In the present study three different reference BCs[26,29] were tested as sorbent materials for the abiotic removal of HCHs' isomers from aqueous solutions by multipoint sorption isotherms. The goals of the study were to investigate i) whether BC can be used as a sorbent for HCH removal, ii) whether the stereochemistry of the HCH isomers has any effect on adsorption onto the BC surface, and iii) which mechanisms drive adsorption. The BCs tested had very variable physico-chemical characteristics, with respect to iron content, SA and the relationship was studied between these properties and sorption strength. This study adds to the limited knowledge that exists related to the use of BC as a sorbent material for HCHs, and the way in which BC physicochemical properties affect HCH sorption.

2. Materials and methods

2.1. Materials and Chemicals

Single compound spikes of α-HCH, β-HCH, γ-HCH, and δ-HCH were purchased from Sigma Aldrich. Spiking solutions were prepared in methanol (MeOH) at 1000 mg L^{-1}. The surrogate standard α-HCH-d_6, was used to check compound recovery and was considered acceptable if it was between 70 % and 130 %; data with recovery outside this range was rejected. The average recovery of all data was 90%. 3,3′,4,4′-Tetrachlorobiphenyl (PCB77) from Sigma Aldrich was used as internal standard and added to GCMS vials prior to analysis. In all experiments, Millipore water was used from a Direct-$Q_3^{®}$ Millipore system (18.2 Ω cm^{-1}, 25 ºC). Sodium azide (0.1 g) was added to the water batch tests in order to avoid HCH degradation during the experiments and before analysis. Polyethylene (PE) was used as a passive sampler in order to determine aqueous concentrations of HCH isomers; other information about the passive samplers can be found in 2.2. PE plastic sheets (26 μm thick, 0.30 ± 0.01 g) were purchased from VWR International Ltd. (Leicestershire, UK). PE was precleaned with hexane, methanol and pure water, as described by Hale et al. [37].

Three different BCs (powder) produced from digestate (700ºC, highest heating temperature (HHT)), tomato waste (550 ºC, HHT) and durian shell (400ºC, HHT) were used. The BCs have been extensively characterized and can be considered as reference materials[29]. The BCs are referred to as follows: BC 10 from digestate, BC 18 from tomato waste, BC 19 from durian shell, using the same acronyms as Singh et al.[29]. Biochars were chosen based on their different physicochemical properties, such as pyrolysis temperature, feedstock, iron content, surface area, etc in order to assess which parameter affected sorption of HCHs to the largest degree. pH was not considered a parameter that would affect sorption. All physicochemical characteristics of the BCs are given in Table 1 and further information about the materials can be found in the literature[29] and in SI.

2.2. Sorption isotherms

Batch tests (triplicates) were carried out in amber glass vials to which 40 mL of deionised water, a given HCH concentration spike, 0.05 g of BC, 0.15 g of PE and 0.1 g of sodium azide were added. Single- and multicomponent adsorption tests were carried out in order to investigate the uptake of each single isomer and to assess if any competition occurred between the isomers.

The concentration of HCHs spiked to the water ranged between 1 and 500 µg L^{-1} in the single component tests and between 4 and 2000 µg L^{-1} in the multicomponent (isomers mixture) tests and was considered representative of environmental conditions. The amount of co-solvent was ≤ 0.125% of the total water volume and co-solvent effects were considered to be negligible[38]. Batch tests were shaken for 28 days at 100 rpm on a horizontal shaking table at room temperature (25 ºC) and this was considered a sufficient time for the PE to reach equilibrium[39]. The PE was removed after 28 days, extracted and analysed, as explained below, and in order to assess the water concentration (C_w). C_w (µg L^{-1}) of the selected contaminants, equation 1 was used:

$$C_w = \frac{C_{PE}}{K_{PE-water}} \quad \text{eq (1)}$$

Where C_{PE} (µg kg^{-1}PE) is the selected contaminant concentration in the PE, and $K_{PE\text{-}water}$ (µg kg^{-1}PE) (µg L^{-1}water)$^{-1}$ is the PE-water partitioning coefficient. The $K_{PE\text{-}water}$ values were taken from Hale and coworkers[37].

The Freundlich isotherm (equation 2) was used to model sorption as has been carried out previously[11,13,14,28,30,40].

$$C_{BC} = K_F\, C^{n}{}_{w} \qquad \text{eq (2)}$$

$$M_{tot} = C_{BC}\, m_{BC} + C_w V_w + C_{PE}\, m_{PE} \qquad \text{eq (3)}$$

Where C_{BC} is the HCH concentration in the BC expressed in µg kg^{-1} calculated from the mass balance in equation 3, K_F is the Freundlich adsorption constant (µg kg^{-1}) (µg L^{-1})$^{-n}$, n is the Freundlich exponent (unitless), while M_{tot} is the initial spiked mass of HCHs (µg), m_{BC} is the mass of BC added (kg), V_w is the volume of water used (L) and m_{PE} is the mass of PE added (kg). Blank replicates without HCH spikes, with and without BC, PE and water respectively were also set up. No interfering peaks were detected in any of the systems.

2.3 HCHs extraction and quantification

After the sorption tests the HCHs were extracted from the PE as described in literature[13,37]. Briefly, PE was rinsed until clean, gently dried with a paper wipe and extracted with 20 mL of heptane/acetone (80:20 v/v) for 4 days. The extract was reduced using a vacuum-concentrator-centrifuge Christ RVC 2-25 and solvent switched to toluene. PCB77 was spiked at 0.1 mg L^{-1} to all GCMS vials before carrying out analysis.

HCHs were analyzed using an Agilent Technologies 6850 Network GC system with a 5973 mass selective detector (Agilent Technologies, USA) using the method described by Ceci et al.[2] with a few modifications; further details can be find in SI.

2.4 Statistic analysis and principal component analysis (PCA)

Linear regression analysis was carried out using GraphPad Prism 7 (©2017 GraphPad Software, Inc.). The linear regression analysis allowed an investigation of whether i) the single isomer isotherms were the same as the multicomponent isotherms and ii) there were statistically significant differences between the sorption of the different HCH isomers.

Multivariate analysis of the variables reported in Table 1 was carried out via principle component analysis (PCA) using Sirius v. 8.1 1997-2009 by PRS, Norway to interpret the data. The PCA was used as tool to transforms the (possibly) correlated variables into a (smaller) number of uncorrelated variables called principal components.

3. Results and discussion

3.1 Single- and multicomponent isotherms

Single- and multicomponent equilibrium tests were carried out in order to i) investigate the sorption mechanism of HCHs to these BCs and ii) assess if any sorption competition occurred. Single component isotherms for α-, β-, γ- and δ-HCH for BC 10, 18 and 19 are shown in Fig. S2 in SI. Fig 1a-c shows a selection of both the single and multicomponent isotherms for γ-HCH, δ-HCH and α-HCH on BC 10, 18 and 19 respectively. The sorption isotherms for all of the other isomers and BC combinations can be found in Fig. S3-5 in SI.

Statistical analysis (linear regression) showed that the isotherms determined for the single compounds and the mixture for the same isomer (single- and multicomponent), for all tested BCs were not significantly different ($P < 0.0001$) from each other. This finding suggests that there was no competition between isomers for sorption sites on these BCs at the compound concentrations tested. A complete lack of competition between such similar compounds is unlikely, the effect seen here is most likely due to the low concentrations at which the batch tests were carried out, and the abundance of available sorption sites at these low concentrations.

Variable results have been presented in the literature related to competitive sorption of organic compounds on BCs and other similar sorbents. Xing and coworkers[41] investigated competition between s-triazine analogs, a substituted benzene analog and trichloroethene (TCE) (a dissimilar compound) onto glassy and rubbery polymers, a mineral soil, a peat soil and soil humic acid particles. They observed no competition for the rubbery polymer, a significant competition between analogs for all other sorbents and weak/no competition between s-triazine and trichloroethene for all sorbents. Zheng et al.[40] investigated the sorption of atrazine and simazine (dissimilar compounds) on BC and reported the occurrence of competition at solute concentrations up to 10 mg L^{-1} (up to 5 times higher than those used here). The authors concluded that atrazine and simazine may compete for the same sorption sites on the BC surface. Schreiter and coworkers[42] investigated the sorption (single- and bi-component) of TCE and tetrachloroethylene (PCE) onto BCs (450 ºC) produced from different feedstocks (cattle manure, grain husk, and wood chips). They observed the TCE sorption onto BCs was affected by the presence of PCE (reduction of the sorption); in contrast, the sorption of PCE was much less strongly affected by the presence of TCE.

It appears that competition is dependent upon the interaction between the sorbate and sorbent surface, as well as the concentration of the sorbate used. The structure of the HCHs, and the surface functional groups of these BCs are different to those used in previous studies, and sorption behavior, sites and mechanism may be different.

3.2 Freundlich adsorption constants

Since the linear regression analysis showed no significant difference between the single- and multicompound isotherms, Freundlich adsorption constants K_F (Table 2) were calculated using all data (single- and multicompound). A comparison between the $K_{F\ \mathrm{singlecomponenent}}$ and $K_{F\ \mathrm{multicomponenent}}$ can be found in the SI in Table S1. The sorption of HCHs to BC was found to be well described by the Freundlich model and the square of the coefficients of correlation (r^2) (Table 2) ranged between 0.73 and 0.98 for all the isomers.

The average of all the single- and multicomponent n values was 1.2 ± 0.4; however most values (excluding n for α-, γ- and δ-HCH for BC 10) deviated less than 13% from unit. The average n value greater than one is skewed by the values for α-, γ- and δ-HCH for BC 10 which were substantially larger than 1. Freundlich exponents greater than 1 imply an increase of the sorbent-surface sorption strength with increasing sorbate equilibrium concentration[43]. This behavior has previously been reported for the sorption of organic compounds onto carbonaceous materials. For example Hale et al.[11] reported n value 1.43 for pyrene sorption onto and onto aged activated carbon (chemically aging at 60

˚C); while Kupryianchyk and coworkers[13] obtained n of 1.38 for phenanthrene sorption onto coconut activated carbon. Freundlich exponents of 1.77 and 1.98, have been reported for toluene adsorption onto multi walled carbon nanotubes in deionized and synthetic sea water[43].

3.3 Effect of HCH stereochemistry on sorption to BC

Fig 2 (a-c) shows isotherms (single- and multicomponent) for α-, β-, γ- and δ-HCH for BC 10, 18 and 19 (a, b and c respectively). A linear regression analysis of the K_F for each isomer and BC (Table 2) was used in order to investigate whether there were statistically significant differences between the sorption of each of the isomers to each of the BCs. The results revealed statistically significant differences ($P < 0.0001$) between K_F values for isomers and BCs, and the discussion below is based on these differences. Log K_F values for the four isomers on BC 10, 18 and 19 ranged from 3.7 to 5.8 ($\mu g\ kg^{-1}$) $(\mu g\ L^{-1})^{-n}$. The values for each isomers and BC are listed in Table 2.

The effect of the size of the HCH isomers has been assessed; the correlation between the volumes for the isomers α, β, γ and δ (263.4, 266.6, 263.2, 264.7 $Å^3$ respectively) and log K_F is shown in Fig. S6, other information can be found in SI. There was no correlation between the Freundlich coefficients and the volume of the isomers ($y = - 0.17 x + 50.3$; $r^2 = 0.12$), probably because of the small variation in the volumes (around 1%). No effect of the molecular size has been observed in this study. This issue may be due to the fact that the isomers' size differences are not sufficient to imply differences in the sorption.

The effect of the molecular size on the adsorption is a well known issue. Pignatello and coworkers[45] studied the effect of soil humic on the organic compounds of wood charcoal, which was suspended in a humic solution. They found that the adsorption of small organic compounds that would not experience any size exclusion decreased in proportion to their molecular size, benzene < naphthalene < phenanthrene. Schreiter et al.[42] investigated the sorption of different BCs reporting a higher log K_F for the smaller sorbates. For example the log K_F for manure-derived BC is 5.1 and 4.8 for TCE and PCE, respectively, explained by the size exclusion of larger sorbates in narrow-pored BCs.

While there was no difference in the order of the HCH isomers' adsorption strength to BC10 and 18 (followed: δ > α > γ > β), the absolute K_F values differed, with those of BC10 being on average one order of magnitude higher than those of BC18 (Table 2) for α, γ and δ isomers. For BC 19, the order of adsorption strength was δ ~ β > γ > α (Table 2). BC 10 had the strongest sorption of α, γ and δ-HCH (log K_F-values for α, γ and δ were 5.7, 5.5 and 5.8 for BC 10 compared to 4.4, 4.2 and 5.0 for BC 18 and 4.1, 4.2 and 4.4 for BC 19).

Variation in the partitioning of the HCH isomers has been previously reported for other materials. Goss and coworkers[3] reported differences between the various HCH isomers with regard to partitioning over water, quartz surface and humic acid (HA) phases. For example, the HA-air and quartz-air sorption coefficients of β-HCH were observed to be higher of those of α- and γ-HCH ($Ki_{,\mathrm{quartz,air}}/\mathrm{m}^3\cdot\mathrm{m}^{-2}$ at 35 ˚C was 1.36×10^{-2}, 11.1×10^{-2} and 1.37×10^{-2} for α, β and γ, respectively). Hale et al.[37] reported differences in the sorption of the HCHs to the rubbery polymer polyethylene, with log $K_{PE\text{-}water}$ values following the order α > γ > β > δ. They reported log $K_{PE\text{-}water}$ (PE thickness 26 µm) 2.80, 2.24, 2.62 and 2.20 respectively for α-, β-, δ- and γ-HCH. The authors also used hexadecane as a proxy for polyethylene and found that estimated partitioning coefficients followed the order: α > γ > δ > β, with log $K_{hexadecane\text{-}water}$ of 3.05, 2.12, 2.84 and 2.21 L kg^{-1} for α-, β-, δ- and γ-HCH, respectively. Thus isomer stereochemistry can clearly play a role in the environmental behaviour of HCHs isomers based on HCH stereochemistry and HCH interactions with the selected matrix.

3.3 Effect of BC type on sorption of HCHs

In order to investigate which sorbent properties affect HCH sorption onto BC, sorption coefficients (Log K_F) were correlated with selected BC physicochemical characteristics from Table 1. Freundlich sorption constants were also normalized to the Fe content ($K_{F,Fe}$) and the CO_2-SA ($K_{F,SA}$) of the BCs, being the parameters advocated to affect the most the adsorption organic contaminants[26,29].

3.3.1 Freundlich coefficients normalized for BC iron content

The effect of iron content on the HCH sorption has been investigated to understand if any interaction, for example ion-dipole, between the Cl of the HCH and the iron in the BC surface functional groups would occur. The tested BCs had the following, highly variable, iron contents: 1.19, 11.7 and 0.0722 g kg^{-1} for BC 10, 18 and 19 respectively (Table 1). Normalizing to the iron content allows one to compare the adsorption of the HCHs to the different BCs like if they had the same iron content. This issue implicitly means that, if the BCs had the same iron content, this paremeter does not affect the calculated log $K_{F,Fe}$. The log $K_{F,Fe}$ values, thus allow to assess the parameters afftecting the HCHs sorption onto BCs excluding the Fe content. Following the normalization, the average log $K_{F,Fe}$ ranged between 2.94 and 5.76 (by comparison, log K_F ranged from 3.68 to 5.83). The calculated log $K_{F,Fe}$ were the higher for all isomers for BC 10 than for BCs 18 and 19. This implies that if the BCs had the same iron content, BC 10 would show stronger sorption of α, γ and δ-HCH than BCs 18 and 19. One possible reason for this observation is the high SA of BC10, which was, at 328.6 m2 g-1, one to two orders of magnitude higher than that of BC18 and BC19 (5.4 and 63.8 m^2, respectively). The SA is known to be one of the most important parameters driving the sorption of organic compounds onto sorbent surfaces. For BC 18 and 19, the opposite trend was observed, where the α-, γ- and δ-HCH were sorbed (Fe-normalization) more strongly to BC 19 than to BC 18, despite BC 18 having the highest SA. This finding implies that, in addition to SA and Fe, there are other properties that affect sorption[46]. In contrast to the other isomers, β-HCH had a completely different order of sorption strength: BC 19 > BC 10 > BC 18, showing the sorption for this compound does not follow SA and is likely also dependent on sorbent-sorbate interactions. β-HCH is a stronger H-acceptor and has significant H-donor properties, in contrast to the other isomers which are H-acceptors[3,47]. Xiao et al.[48] demonstrated this H-acceptor property as they observed β-HCH to have an air/water partitioning coefficient (log $K_{aw}/L_w\ L^{-1}{}_a$) of -4.82, much lower than that of α-, and γ-HCH (-3.58 and -3.96, respectively) because of the stronger H-bridge formation between water and β-HCH.

3.3.2 Freundlich coefficients normalized for BC SA

The role of the SA was evaluated to check its influence on the HCHs sorption. The effect of the pore size distribution has been related to the sorption to assess if the HCHs' stereochemistry leads to any different steric hindrance. The tested BCs exhibited the following CO_2-SAs (0.4-1.5 nm pores): 328.6, 5.4 and 63.8 m^2 g^{-1} for BC 10, 18 and 19[29] respectively (Table 1). Normalizing to the SA allows one to compare the adsorption of the HCHs to the different BCs at the same SA (CO_2-SA) and thus SA is excluded from the subsequent discussion. After normalization for BC SA, the $K_{F,SA}$ of α, γ and δ showed the following trend BC 18 > BC 10 > BC 19, with log $K_{F,SA}$ ranging from -1.84 and 1.25. One possible characteristic that may play a role is the BC iron content. HCH have variable H-acceptor/electron donor properties[3,47] and this implies that there are varying interactions between the Cl of the HCH and the iron in the BC surface functional groups. The presence of Fe^{+3} on the BC surface may increase the sorption of chlorinated compounds due to the occurrence of ion-dipole interactions. The surface of BC contains a great number of variable functional groups making ion exchange, proton interaction and electrostatic interactions with the π-electrons associated with C=C or C=O possible binding mechanisms with solutes[26].

Similar to the Fe-normalized K_F values, β-HCH demonstrated a trend different from that of the other isomers. For this isomer sorption followed: BC 18 > BC 19 > BC 10.

To the best of our knowledge this is the first study in which the iron content of a carbonaceous material has been investigated as a factor that can affect the sorption of HCHs, and the data indicate that Fe content could play a role. However, previous studies have investigated the interaction between chlorinated compounds and zero-valent iron (ZVI). Wu et al.[49] investigated the TCE dechlorination using ZVI incorporated into a polymeric membrane. They observed that TCE sorption in the membrane led to a preconcentration of TCE and resulted in a synergetic effect between TCE sorption and degradation. Chang et al.[36] investigated the sorption of γ-HCH onto nZVI/Cu bimetallic nanoparticles (Cu doping on the Fe surface) supported on activated carbon (AC-Fe^0-Cu). They reported the simultaneous degradation and adsorption of γ-HCH by respectively, the ZVI and the AC. For the BCs used here, the presence of ZVI on the BC surface is unlikely, as ZVI oxidizes to $Fe^{+2/+3}$ over a period of 60 days[50]; and the Fe is thus mainly expected to be present as iron oxides.

3.3.3 Other parameters affecting HCH sorption to BC

The measured Log $K_{F,BC}$ values are plotted correlated with log K_{ow} values (from Hale et al. 2010) for α-, β-, γ- and δ-HCH (log K_{ow} = 3.94, 3.92, 3.83, 3.19 respectively) in Fig. S7 in SI. No correlation between the Freundlich coefficients and the K_{ow} was observed ($y = -0.89x + 7.9$; $r^2 = 0.16$), thus HCHs isomers uptake onto BCs was not affected by compound hydrophobicity. Relationships with Freundlich sorption partitioning coefficients (K_F) were also tested for the BC physicochemical properties listed in Table 1 (Temperature, micropore volume, mean pore size, % C, % C aromatic, % N, % O, % H, O:C, H:C, CEC, C-C/C-H, C-O, C=O, COO, BPCA-carbon) as shown in Fig. S8 in SI. No clear relationships were observed between any of the BC properties and HCH sorption (r^2 ranged between 0.019 and 0.34). The effect of variable feedstock has not been assessed in this work. In order to properly assess how feedstock affected the sorption, different feedstocks should have been used to make BCs at the same temperature .

3.3.4 Multivariate analysis

Multivariate analysis, i.e. PCA, was carried out for the physicochemical characteristics of BC 10, 18 and 19 reported in Table 2. The resultant PCA shown in Fig. 3 allows an assessment to be made as to whether there is any correlation between the parameters (sorption to the BCs and the BC physicochemical properties). Results of the PCA showed that α-, γ- and δ-HCH behave similarly; the points $K_{F\alpha}$, $K_{F\gamma}$ and $K_{F\delta}$ plot very close to each other and this shows they are highly related. On the other hand, α, γ and δ have a vastly different behavior than β-HCH, supporting all previous observations and discussion. Variables arranged via a 90º angle are not related. Variables related to each other via a 180º angle are inversely related. The behavior of the tested BCs was dominated by various physicochemical properties. SA and Fe content were the parameters that affected the sorption of the HCHs to the greatest extent for BC 10 and BC 18, respectively, and this is the first study to show that Fe content is a BC property that can influence HCH sorption. Sorption onto BC 19 was affected to the greatest extent by the CEC, which is determined by negative surface charges and thus H-bridge formation and ion-dipole interaction possibilities. This may explain why this BC has the greatest sorption affinity for β-HCH; it could be due to the H-donor properties of this isomer. Overall the PCA confirmed the fact that sorption to these BCs is driven by various different physicochemical properties and that it is difficult to pick out one or more key property that clearly drives the sorption.

3.4 Correlation between sorption to BCs and other carbonaceous sorbents

In order to assess if there was any similarity between the sorption of the HCHs to the tested BCs and that to other carbonaceous sorbents, the currently measured K_F values were compared to partitioning coefficients (K_D in L Kg^{-1}), calculated using polyparameter linear free energy relationships (pp-LFER)[47] for peat[51], activated carbon[52], organic carbon[53], humic acid[54] and coal tar[55]. More information about how these values and the corresponding pp-LFERs were calculated, is given in the SI. The resulting correlations are shown in Fig. S9. Evidently there was a lack of correlation between the $K_{F,BC}$ determined here and the calculated K_D's. This implies that the currently studied BCs behave differently from the other carbonaceous sorbents. Carbonaceous materials are very diverse, heterogeneous materials and sorption to one is often not mirrored in sorption to another[56], although coal tar PP-LFERs were found to describe sorption to natural sediments extremely well[57].

4. Conclusion

This study demonstrated BC and aBC can represent cost effective sorbent to amend PFCs contaminated soils. Due to the higher surface area the aBC has higher performances than the BC. On the other hand the choose of the material should be connected to the perfomances required; furthermore, being the BC obtained from wood waste the increasing of the % of sorbent would not represent a problem for the cost point of view.

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Tables and figures

Table 1. Biochar characteristics. Properties of BC 10, 18 and 19 taken from Sing et al. [29].

	BC 10	BC 18	BC 19
feedstock	Digestate	Tomato waste	Durian shell
T (C)	700	550	400
CO_2–SA (m^2 g^{-1})*	328.6	5.4	63.8
N_2–SA (m^2 g^{-1})#	28.4	1.9	2.7
micropore volume (cm^3 g^{-1})*	186.6	5.1	36.6
mean pore size (Å)*	1.05	5.85	3.42
% C	59.1	30.7	65.5
% C aromatic	81	58	55
% N	1.16	2.54	2.15
% O	10.7	28	19.4
% H	0.97	1.23	3.4
O:C	0.14	0.68	0.22
H:C	0.2	0.48	0.62
CEC ($mmol_c$ kg^{-1})	71.1	96.5	106.9
Fe content (Average) (g kg^{-1})	1.19	11.7	0.0733
C-C/C-H (% of C 1s peak)	75.3	56.1	69.9
C-O (% of C 1s peak)	17.7	12.2	14.1
C=O (% of C 1s peak)	4.6	5	4.2
COO (% of C 1s peak)	3.1	5	3.3
BPCA-carbon (g kg-1)	105.2	47.7	99.7

*Specific SA and porosity measurements were carried out using CO_2 adsorption (0.4-1.5 nm pores) at 0ºC with Micromeritics ASAP2020 Gas Adsorption and Porosity System; other information can be found in literature[29].

N_2-SA (pores > 1.5 nm) was measured at the University of Florida, Gainesville, FL.

The parameters used for PCA analysis were: T, CO_2–SA (pores > 0.4 nm) micropore volume, mean pore size, % C, % C aromatic, % N, % O, % H, O:C, H:C, CEC, Fe content, C-C/C-H, C-O, C=O, COO, COO.

Table 2. List of log Freundlich adsorption constants (log K_F), log K_F normalized for the BC iron content (log $K_{F,Fe}$) and BC SA (log $K_{F,SA}$) for BC 10, 18 and 19 calculated based on all data points (single- and multicomponent isotherms) for each HCH.

BC type and HCH isomer	log K_F $(\mu g\ kg^{-1})\ (\mu g\ L^{-1})^{-n}$	log $K_{F,Fe}$ $(\mu g\ g_{Fe}^{-1})\ (\mu g\ L^{-1})^{-n}$	log $K_{F,SA}$ (CO_2-SA) $(\mu g\ m^{-2})\ (\mu g\ L^{-1})^{-n}$	n	r^2
BC 10 α	5.65 ± 0,178	5.57	0.137	1.82 ± 0.246	0.786
BC 10 β	3.68 ± 0.0722	3.60	-1.84	1.04 ± 0.0740	0.964
BC 10 γ	5.54 ± 0.0843	5.46	0.0183	1.96 ± 0.149	0.901
BC 10 δ	5.83 ± 0.238	5.76	0.318	1.81 ± 0.288	0.768
BC 18 α	4.39 ± 0.578	3.32	0.658	1.17 ± 0.110	0.858
BC 18 β	4.01 ± 0.0548	2.94	0.274	0.968 ± 0.0643	0.919
BC 18 γ	4.22 ± 0.102	3.15	0.491	0.987 ± 0.167	0.725
BC 18 δ	4.99 ± 0.0617	3.92	1.25	1.28 ±0.142	0.880
BC 19 α	4.13 ± 0.0270	5.27	-0.67	0.937± 0.0313	0.977
BC 19 β	4.42 ± 0.0280	5.55	-0.39	0.986 ± 0.0386	0.962
BC 19 γ	4.20 ± 0.0415	5.34	-0.602	0.853 ± 0.0481	0.943
BC 19 δ	4.44 ± 0.0660	5.58	-0.364	1.03 ± 0.107	0.865

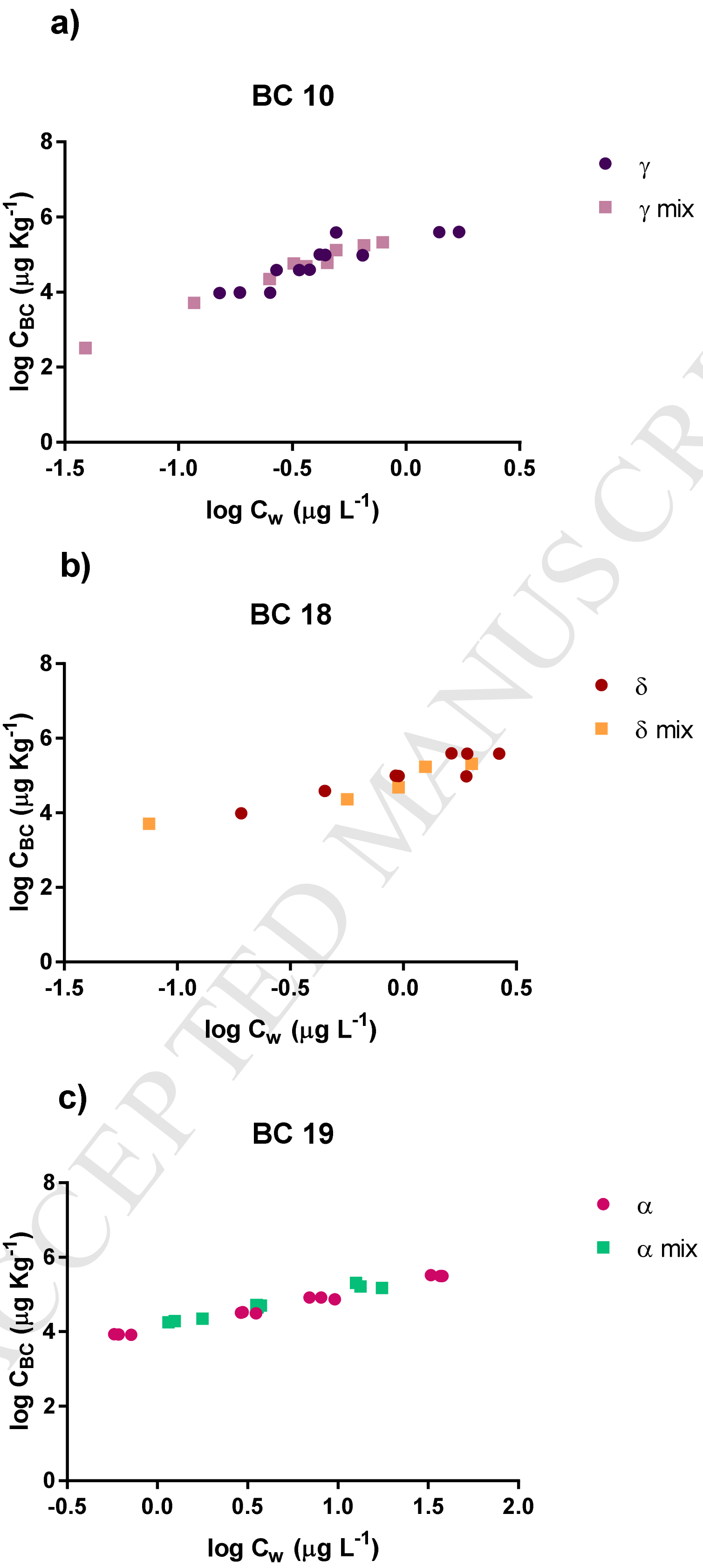

Figure 1 (a-c). Single- and multicomponent (mix) isotherms comparison. Comparison between γ, δ and α single- and multicomponent onto BC 10, 18 and 19 (a, b and c) respectively. All data are reported as single points.

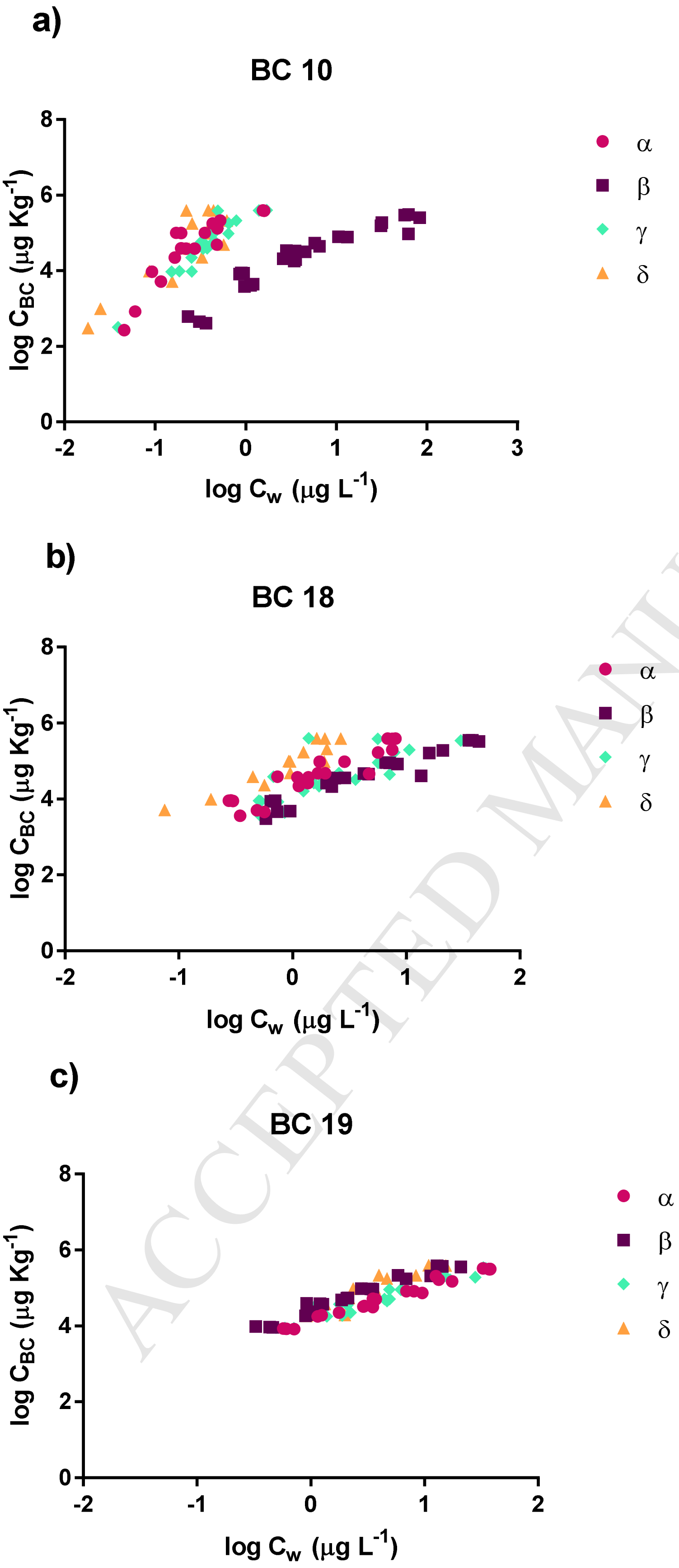
a)
BC 10
log C$_{BC}$ (μg Kg^{-1})
8
6
4
2
0
-2
-1
0
1
2
3
log C$_{w}$ (μg L^{-1})
α
β
γ
δ
b)
BC 18
log C$_{BC}$ (μg Kg^{-1})
8
6
4
2
0
-2
-1
0
1
2
log C$_{w}$ (μg L^{-1})
α
β
γ
δ
c)
BC 19
log C$_{BC}$ (μg Kg^{-1})
8
6
4
2
0
-2
-1
0
1
2
log C$_{w}$ (μg L^{-1})
α
β
γ
δ

Figure 2 a-c. α, β, γ and δ (single- and multicomponent) isotherms for BC 10, 18 and 19 (a, b and c) respectively. All data are reported as single points.

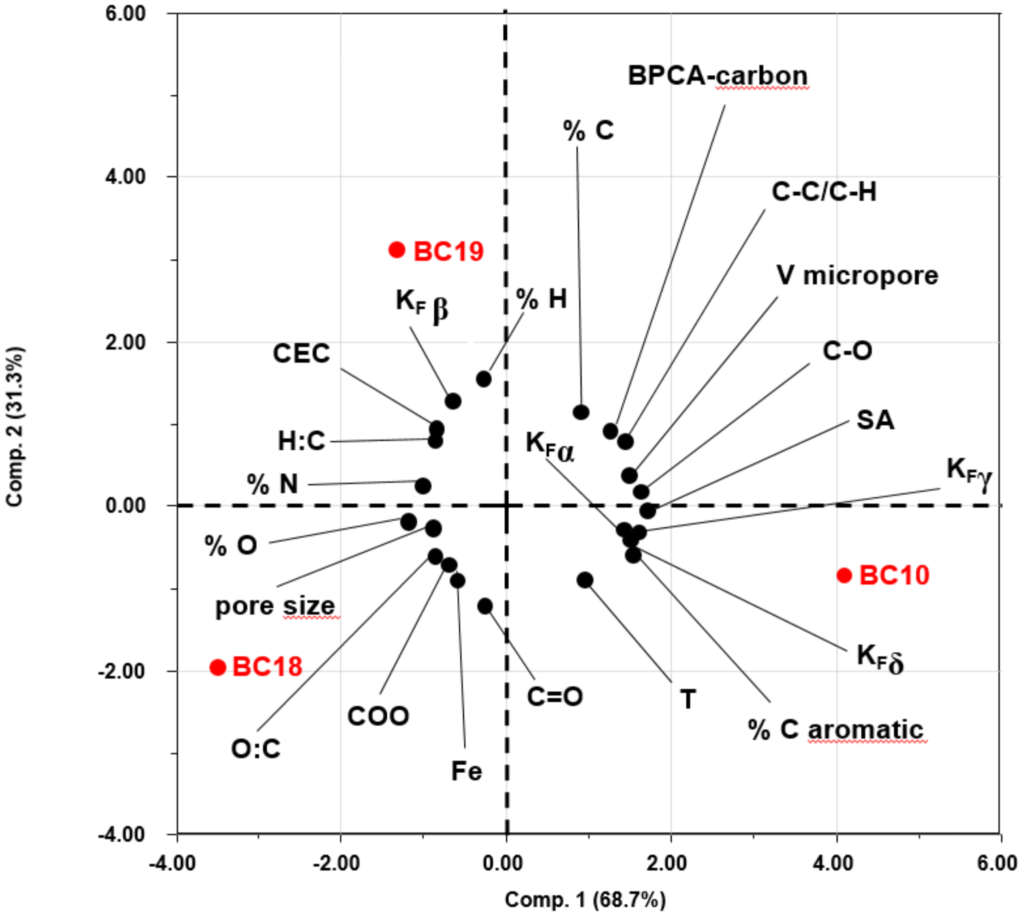

Figure 3. Principle component analysis (PCA). Multivariate analysis carried out for all the parameters reported in Table 1 for BC 10, 18 and 19.

1) Biochars were used for the sorption of α-, β-, γ- and δ-hexachlorocyclohexane.
2) Isotherms were carried out in single- and multi-component (isomers mixture).
3) No competition was observed in water batch tests between α-, β-, γ- and δ-HCH.
4) LogK_F ranged from 3.7 to 5.8 (µg kg^{-1})(µg L^{-1})$^{-n}$ for all the isomers on biochars.
5) Sorption is affected by BC surface area, iron content and HCH/BC interactions.