



Interaction mechanisms of organic contaminants with burned straw ash charcoal

Wenhai Huang, Baoliang Chen*

Department of Environmental Science, Zhejiang University, Hangzhou 310028, China. E-mail: harmless87830375@yahoo.com.cn

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Abstract

Black carbons (e.g., charcoal) have a great impact on the transport of organic contaminants in soil and water because of its strong affinity and ubiquity in the environment. To further elucidate their interaction mechanism, sorption of polar (*p*-nitrotoluene, *m*-dinitrobenzene and nitrobenzene) and nonpolar (naphthalene) aromatic contaminants to burned straw ash charcoal under different de-ashed treatments were investigated. The sorption isotherms fitted well with Freundlich equation, and the Freundlich *N* values were all around 0.31–0.38, being independent of the sorbate properties and sorbent types. After sequential removal of ashes by acid treatments (HCl and HCl-HF), both adsorption and partition were enhanced due to the enrichment of charcoal component. The separated contribution of adsorption and partition to total sorption were quantified. The effective carbon content in ash charcoal functioned as adsorption sites, partition phases, and hybrid regions with adsorption and partition were conceptualized and calculated. The hybrid regions increased obviously after de-ashed treatment. The linear relationships of Freundlich *N* values with the charring-temperature of charcoal or biochar (the charred byproduct in biomass pyrolysis) were observed based on the current study and the cited publications which included 15 different temperatures (100–850°C), 10 kinds of precursors of charcoal/biochar, and 10 organic sorbates.

Key words: ash charcoal; organic pollutant; adsorption; partition; effective carbon

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Introduction

Black carbons (BCs), mainly soot and charcoal, are produced in natural and anthropogenic combustion processes (Forbes, 2006; Nowack and Bucheli, 2007). Its widespread occurrence in soil, sediment and aerosols, and its indispensable role in soil organic matter have aroused a considerable attention. In developing countries, the burning of vegetations and crops is used as an economical way to provide energy and the burning residues are often used as fertilizers for farmland. This contributes as the primary source of chars in soils (Yang and Sheng, 2003). In China, for example, the yearly outcome of straw is about 0.65 billion tons, and the number is expected to ascend to 0.76 billion by 2010 (Yu, 2008). In all these straws, about 20%–40% are directly burned serving as the main source of black carbon in agricultural soils and act as an efficient organic matter in enriching the farmland. However, with the irrigation of these farmlands, great amounts of black carbon are floating away with irrigation water. Black carbon has been regarded as a potential adsorbent to organic contaminants (Mitra et al., 2002; Cornelissen et al., 2005), which can enhance the soil contaminants loading capacity and eventually results in the sequestration of organic contaminants (Yang et al., 2006;

Lehmann et al., 2006; Lehmann, 2007; Renner, 2007; Xu et al., 2008). Therefore, sorption behavior of straw-generated black carbon is needed for precisely determining the fate of organic pollutants.

The sorption capacity of black carbon and its mechanisms have been well investigated (Allen-King et al., 2002; Jonker and Koelmans, 2002; Yang and Sheng, 2003; Sheng et al., 2005; Zhu and Pignatello, 2005; Yang et al., 2006; Nguyen et al., 2007; Chen et al., 2008a, 2008b; Chen and Chen, 2009). However, few research works have concentrated on sorption linking between charcoal and biochar. Charcoal is the remnants of incomplete combustion (Cornelissen et al., 2005), while biochar is produced by pyrolyzing certain biomasses under controlled oxygen-limited conditions. Biochar, the charred byproduct of biomass pyrolysis in bioenergy production, has been receiving substantive attentions due to its potential agricultural and environmental applications to sequester carbon, improve soil nutrient, and enhance crop productivity. Previous studies on sorption properties of charcoal and biochar have some similarities in the sorption mechanisms and characteristics (Allen-King et al., 2002; Jonker and Koelmans, 2002; Yang and Sheng, 2003; Yang et al., 2006; Sheng et al., 2005; Zhu and Pignatello, 2005; Nguyen et al., 2007; Chen et al., 2008a, 2008b). For example, charcoal and biochar are normally not fully carbonized and

* Corresponding author. E-mail: blchen@zju.edu.cn

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contain some non-carbonized matters (e.g., original organic residues). Resultantly, black carbon is deemed as the carbonized organic matter (COM), accounting mainly for the sorptive nonlinearity; and the non-carbonized organic matter (NOM) is related to partitioning mechanisms (Chen et al., 2008a). Sorption of organic contaminants to biochar is known to be affected by the structural properties, such as surface area, pore size distribution, surface functionality (Zhu et al., 2005). The structural properties are highly related to the pyrolytic temperatures at which the biochar is formed (Chun et al., 2004a, 2004b; James et al., 2005; Chen et al., 2008a, 2008b). But for ash charcoal produced under uncontrolled conditions, the burning temperatures of charcoal were seldom mentioned in previous reports.

The main objective of the current study was to further elucidate the interaction mechanism of organic contaminant with ash charcoal, and to examine whether the charcoals produced in field condition shares similar sorption characteristics with biochars made under controlled conditions. The ash charcoal samples were analyzed via elemental analysis, BET-N₂ surface area and scanning electron microscope (SEM). Sorption isotherms of polar (*p*-nitrotoluene, *m*-dinitrobenzene and nitrobenzene) and nonpolar (naphthalene) organic contaminants to the charcoal samples were compared. An adsorption-partition method was introduced to quantify different mechanisms of charcoal under different pretreatments.

1 Materials and methods

1.1 Ash charcoal samples

The raw materials of charcoal-containing ash were obtained from burned straw ashes in a typical farm house in Zhejiang Province, China. Principally, dry straws were collected (mainly rice straws) and burned in the kitchen stove for energy provision, and no other means were introduced to control the whole burning process. The remains (straw ashes) of the burned straws were then collected and brought to laboratory for further treatment. The ashes were air-dried for two days and were sieved to obtain particles less than 165 μm . The treated ashes are referred to as original ash (termed as Ash-o). Then a certain amount of Ash-o (160 g) was incubated in a solution of HCl (1.0 mol/L) and stirred for 2 hr with a magnetic stirrer. The treated ashes were separated from water by vacuum filtration. These procedures were repeated thrice to wipe out all soluble salts. The prepared ashes were washed by distilled water till the solution became neutral afterwards. The residues were then oven-dried at 60°C, and mechanically ground with mortar and pestle to less than 165 μm (Ash-1). Further, a certain amount of Ash-1 (15 g) were treated with the same procedures using a mixture of 0.5 mol/L HF and 0.5 mol/L HCl to remove silicon contained in Ash-1. The treated material was named Ash-2. An amount of Ash-o was heated at 800°C for 4 hr to removal all organic carbon, and the residue ash (Ash-800) was used as the representative of ash including metallic element and silicon.

1.2 Characterization of samples

Elemental (C, H, N) analyses were conducted using an EA 112 CHN elemental analyzer (Thermo Finnigan, USA). The H/C ratios were calculated to evaluate the aromaticity. Ash content was measured by heating the samples at 800°C for 4 hr. The surface areas were measured with N₂ (0.162 nm²) adsorption at liquid nitrogen temperature (77 K) determined by a NOVA-2000E surface area analyzer (Quantachrome, USA). Four data points, with relative pressures ranged from 0.05 to 0.3, were used to construct the monolayer adsorption capacity. A JSM-6390 scanning electron microscope (JEOL, Japan) were used to determine the shape and the surface properties of the samples. The samples were adhered to the sample support for SEM observation under the device voltage of 20 kV.

1.3 Batch sorption experiment

Organic chemicals, *p*-nitrotoluene (*p*-NT), *m*-dinitrobenzene (*m*-DNB), nitrobenzene (NB), and naphthalene (NAPH), were chosen as model sorbates due to their different molecular polarities and dimensions (Table 1). They were obtained from Shanghai Reagent Company (China), and used as received without further purification. All sorption isotherms were obtained using 0.01 mol/L CaCl₂ to simulate the background electrolyte of environmental water, with 200 mg/L NaN₃ being added to inhibit the degradation by incidental bacteria. Relative initial concentrations (C_i/C_s) ranged from 0.01 to 0.86 for *p*-NT, 0.01–0.88 for *m*-DNB, 0.01–0.83 for NB, and 0.01–0.94 for NAPH to saturate potential adsorption (C_s refers to the solubility of organic contaminants as shown in Table 1). A given amount of sorbent (*p*-NT: 150, 50, and 30 mg for Ash-o, Ash-1, and Ash-2 samples, respectively; *m*-DNB: 1000, 100, and 60 mg for Ash-o, Ash-1, and Ash-2 samples; NB: 1500, 400 and 100 mg for Ash-o, Ash-1, and Ash-2 samples; NAPH: 50, 20, 5 and 300 mg for Ash-o, Ash-1, Ash-2, and Ash-800 samples) were mixed with 8 mL solution. Isotherms consisted of ten concentration points; each point, including the blank, was run in duplicates. The vials were sealed using Teflon-lined screw caps. The vials were placed on a rotating shaker and agitated in the dark at 20 r/min for 3 days. Preliminary tests indicated that apparent equilibrium was achieved in less than 48 hr. The solution was separated from solids by centrifugation at 4000 r/min for 15 min. The

Table 1 Selected properties of *p*-nitrotoluene (*p*-NT), *m*-dinitrobenzene (*m*-DNB), nitrobenzene (NB), and naphthalene (NAPH) and their dimensions based on van der Waals radii

Organic compounds	MW (g/mol)	<i>S</i> ($\mu\text{g/mL}$)	K_{ow}	MA (nm ²)	MV (nm ³)
<i>p</i> -NT	137	350	234	0.678	0.233
<i>m</i> -DNB	168	574.9	31	0.839	0.289
NB	123	1936	71	0.620	0.213
NAPH	128	32.05	1950	0.732	0.252

MW: molecular weight; *S*: aqueous solubility at room temperature; K_{ow} : octanol-water partition coefficient; MA: molecular area; MV: molecular volume.

equilibrium concentrations were measured using a UV-2550 spectrophotometer (Shimadzu, Japan) at wavelength of 275 nm (NAPH), 268 nm (NB), 284 nm (*p*-NT), and 260 nm (*m*-DNB), respectively with the detection limit of 0.1 mg/L ($S/N = 3$) (Chen et al., 2008a, 2008b). Because sorption by the sample vials was minimal and no biodegradation or photo-decomposition was detected through the experiment, the sorbed-amount of sorbate was calculated by mass difference.

All the data were processed by the logarithmic form of Freundlich equation (Eq. (1)):

$$\log Q = \log K_f + N \log C_e \quad (1)$$

where, Q (mg/kg) is the amount sorbed per unit weight of sorbent; C_e (mg/L) is the equilibrium concentration; K_f ((mg/kg)/(mg/L) ^{N}) is the Freundlich capacity coefficient; and N (dimensionless) describes the isotherm curvature.

2 Results and discussion

2.1 Structural characteristics of the burned straw ash charcoal

The elemental compositions, BET-N₂ specific surface area, and ash contents of the original ash (Ash-o) and the treated ash (Ash-1, Ash-2, and Ash-800) are listed in Table 2. Previous studies on straw ash charcoal suggested that the inorganic carbon content was very low compared with organic carbon (6%–9% of the total carbon) (Yang and Sheng, 2003), therefore, the elemental carbon content were generally deemed organic carbon content afterwards. As shown in Table 2, some impurities were eliminated from ashes by acid treatment, which raised the content of carbon (from 2.80% to 7.28%), enhanced the aromaticity (H/C from 1.54 to 0.79) and magnified the surface area (SA) of samples (from 13.0 to 35.34 m²/g). The SEM photos of the tested ashes are shown in Fig. 1.

2.2 Sorption of organic contaminants by ash charcoal

Selected sorption isotherms of organic pollutants onto the treated ashes in aqueous solutions are presented in Fig. 2. The isotherms fit Freundlich equation well, and the regression parameters are listed in Table 3. From Fig. 2, the sorption capacities of sorbents followed the order of Ash-2 > Ash-1 > Ash-o for given sorbates. No evident sorption of *p*-NT and NAPH onto Ash-800 were observed (data not shown), indicating that sorption of straw ash samples are dominated by the charcoal component. The isotherms for Ash-o, Ash-1 and Ash-2 at low equilibrium concentrations ($C_e/C_s < 0.1$) were all of a concave-downward curvature,

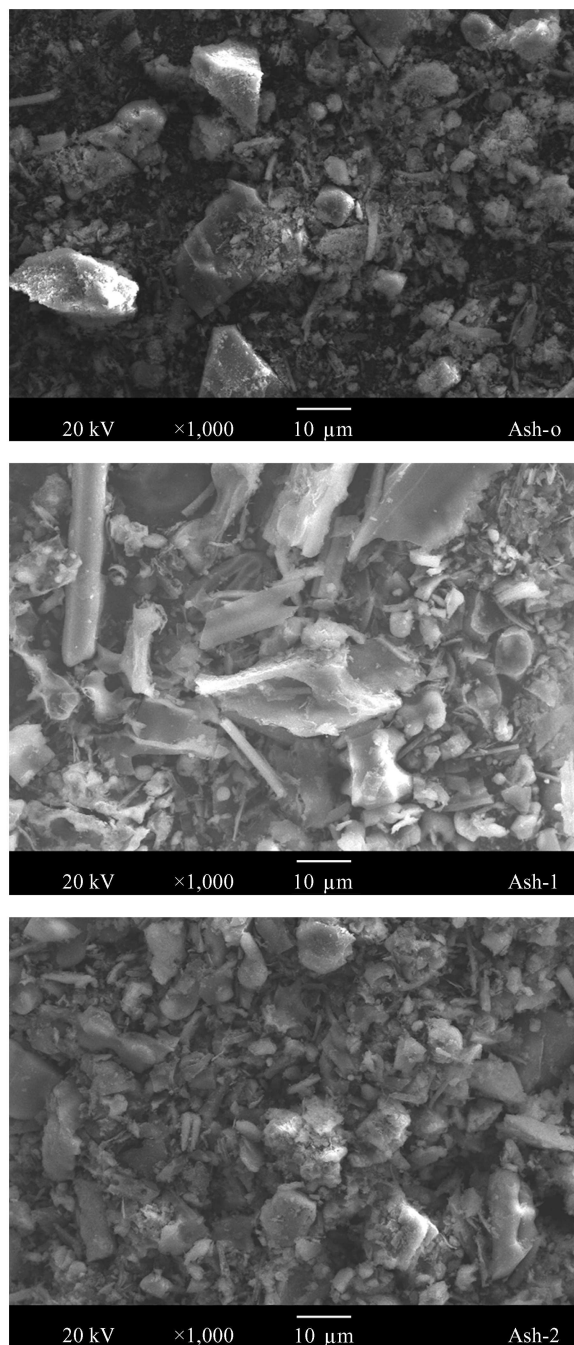


Fig. 1 SEM photos of ash samples of Ash-o, Ash-1 and Ash-2.

while at higher equilibrium concentrations (C_e/C_s : 0.1–0.6) the isotherms became linear. Similar results were

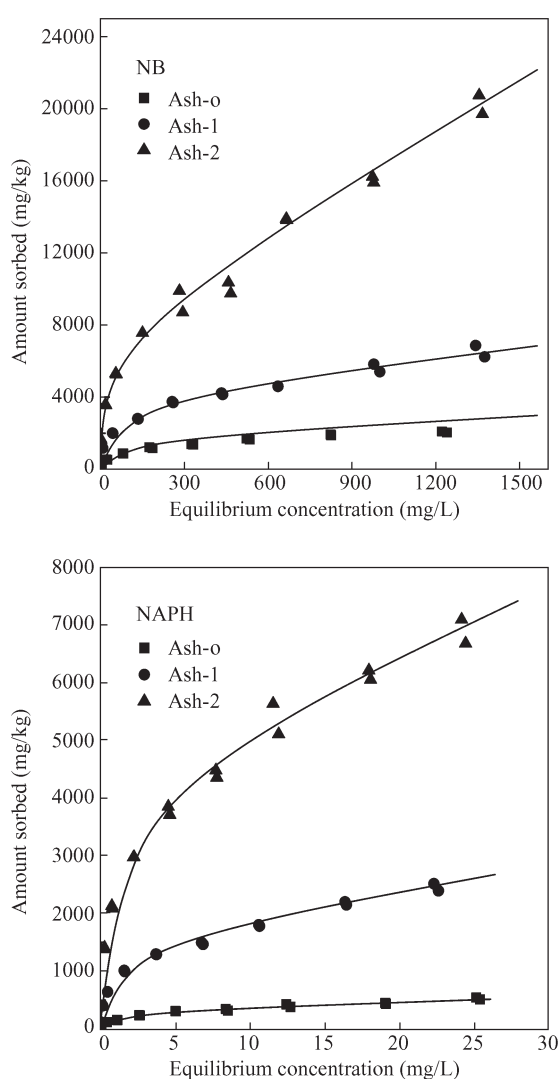
Table 2 Elemental compositions, ash contents, BET-N₂ specific surface area (SA) of original ash derived from crop residue and acid treated-ash samples*

Sample	C (%)	H (%)	N (%)	H/C	Ash (%)	SA (m ² /g)
Ash-o	2.80	0.36	0.04	1.54	83.8	13.0
Ash-1	4.09	0.56	0.24	1.64	88.4	27.2
Ash-2	7.28	0.48	0.41	0.79	86.1	35.3
Ash-800	0.16	0.059	0.00	4.39	100	12.2

* Elemental compositions, atomic ratios are on an ash basis. H/C: atomic ratio of hydrogen to carbon.

Table 3 Regression parameters of sorption isotherms of *p*-NT, *m*-DNB, NB, and NAPH to original ash, acid treated-ash samples in aqueous solutions

Sorbate	Sorbent	Freundlich regression			Linear parameters at high conc.	
		N	$\log K_f$	R^2	Linear equation	R^2
<i>p</i> -NT	Ash-o	0.318 ± 0.017	2.379 ± 0.029	0.956	$Q = 2.387C_e + 728.3$	0.838
	Ash-1	0.321 ± 0.013	2.913 ± 0.021	0.975	$Q = 8.609C_e + 2535$	0.908
	Ash-2	0.385 ± 0.017	3.202 ± 0.028	0.969	$Q = 24.72C_e + 6365$	0.933
<i>m</i> -DNB	Ash-o	0.342 ± 0.012	2.405 ± 0.023	0.987	$Q = 2.190C_e + 1074$	0.986
	Ash-1	0.369 ± 0.010	2.775 ± 0.019	0.988	$Q = 5.133C_e + 3109$	0.892
	Ash-2	0.334 ± 0.021	3.318 ± 0.039	0.942	$Q = 25.76C_e + 6552$	0.980
NB	Ash-o	0.348 ± 0.007	2.264 ± 0.017	0.994	$Q = 0.728C_e + 1222$	0.912
	Ash-1	0.334 ± 0.005	2.750 ± 0.013	0.996	$Q = 2.581C_e + 3042$	0.964
	Ash-2	0.358 ± 0.012	3.116 ± 0.029	0.981	$Q = 10.49C_e + 6045$	0.979
NAPH	Ash-o	0.378 ± 0.009	2.192 ± 0.009	0.991	$Q = 10.79C_e + 251.8$	0.943
	Ash-1	0.344 ± 0.005	2.915 ± 0.005	0.997	$Q = 68.20C_e + 1079$	0.978
	Ash-2	0.382 ± 0.008	3.325 ± 0.008	0.993	$Q = 155.6C_e + 3251$	0.953

**Fig. 2** Sorption isotherms of NB and NAPH to ash samples.

obtained in previous studies on biochars (Chen et al., 2008a, 2008b). The nonlinearity at low equilibrium concentrations was due to adsorption onto the surface of carbonaceous material. At higher equilibrium concentrations, however, the adsorptive sites are saturated, and the partition of solutes into the noncarbonized organic matter

(NOM) in ash charcoal predominates sorption (Chen et al., 2008a).

It is interesting to note that Freundlich N values of all sorption isotherms were in the range of 0.318–0.382, independent of the type of ash sorbents and the sorbate. This was consistent with previous conclusion that Freundlich N values are related with H/C indices of the charcoal sorbents and charring temperature but had little relative to the used sorbates (Chen et al., 2008a). Therefore, when Freundlich N value is about 0.3, the H/C index of the charcoal sorbent can be estimated to be 0.5–0.75, which approaches the actual H/C index of Ash-2 (i.e., 0.792) in the present study (Table 2). Meanwhile, the charring temperature of the selected charcoal in the current study is estimated to be 300–400°C, which is approximate to the burning temperature of straw (200–370°C) (Wang et al., 2009). This suggests that even under actual condition, Freundlich N values can also be a good indicator of the charring temperature of charcoals. To further prove this finding, the Freundlich N values and the corresponding charring-temperature of a series of laboratory-produced chars were cited from literature (Chen et al., 2008a, 2008b; Chen and Chen, 2009; James et al., 2005; Bornemann et al., 2007; Sander and Pignatello, 2005; Sun and Zhou, 2008). In which 15 different temperatures (100–850°C), 10 kinds of precursors of charcoal/biochar, and 10 organic sorbates were included. The relationship of Freundlich N values and the charring-temperature are demonstrated in Fig. 3. For either polar chemicals or nonpolar chemicals, the N decreased linearly with increasing pyrolytic temperature, being independent of the precursors of charcoals and properties of solute, even though K_f (Freundlich affinity coefficient) varied greatly from 10 to 390,000 $\text{mg}^{(1-N)}\text{L}^N/\text{kg}$. Some aberrant points are also observed in Fig. 3, which might be attributed to that the charcoals used in those studies were not fully pyrolyzed or combusted, for the heating processes were not more than 1 hr (James et al., 2005; Bornemann et al., 2007). It was suggested that for charring temperature higher than 400°C, the duration time should be longer than 4 hr to stabilize some property of chars (Scott and Glasspool, 2005). At the same time, some N values of natural charcoals formed from pyroclastic flow, wildfires, and forest fires (Sawada et al., 2000) were also

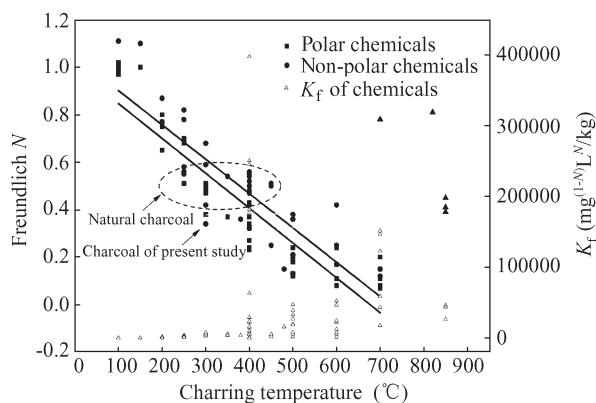


Fig. 3 Relationship between Freundlich N and the charring-temperature of charcoals/biochars from a series of cited references with the related K_f (empty triangle). The short axis of oval dash line represents the N range of natural charcoal (James et al., 2005) or charcoal of the current study; while the long axis represents the estimated range of charring temperatures. The solid triangle represents some aberrant N .

compared with the laboratory-produced chars. Based on sorption parameters, the estimated charring temperature were from 250 to 450°C, consistent with previous studies on pyroclastic deposit temperature (360–400°C, Sulpizio et al., 2008; 365–640°C, Scott and Glasspool, 2005). Similarly, temperature of moderately burned soil surface in forest fire were evaluated to be 300–400°C (Chandler et al., 1983).

2.3 Adsorption and partition contribution to ash charcoal

A mixed adsorption-partition system was introduced to describe the sorption of organic pollutant to ash charcoal. With the increase of solute concentration, partition effect dominated the whole sorption progressively, whereas the adsorptive sites were saturated easily at comparably lower concentrations. Thereby, an isotherm-separation method was applied to quantify respective contribution of adsorption and partition to total sorption of organic contaminants. This approach has been successfully employed to assess the contribution of black carbon to the sorption of soils, sediments and charcoals (Accardi-Dey and Gschwend, 2002; Allen-King et al., 2002; Chen et al., 2008a, 2008b; Chiou and Kile, 1998; Cornelissen and Gustafsson, 2004). The total sorbed amount of solute can be calculated as follows:

$$Q_T = Q_A + Q_P \quad (2)$$

where, Q_T (mg/kg) is the total amount of the solute sorbed onto the charcoal; Q_A (mg/kg) and Q_P (mg/kg) are the amounts contributed by adsorption and partition, respectively. At high solute concentration range, Eq. (2) can be transformed to:

$$Q_T = Q_A^{\max} + Q_P = Q_A^{\max} + K_P C_e \quad (3)$$

where, Q_A^{\max} is the saturated adsorption capacity of a charcoal estimated from the high concentration data; $K_P C_e$ is the partition contribution at high concentration with K_P being the partition coefficient; C_e is the solute equilibrium

concentration. Linear regression of sorption isotherms at high solute concentration range were conducted, and the regression parameters are presented in Table 3.

The adsorption contributions in the isotherm of charcoals can be calculated using Eq. (4):

$$Q_A = Q_T - Q_P = Q_T - K_P C_e \quad (4)$$

Accordingly, the quantitative contribution of separated adsorption isotherms and partition isotherms are plotted in Fig. 4. The separated adsorption isotherms fit Langmuir

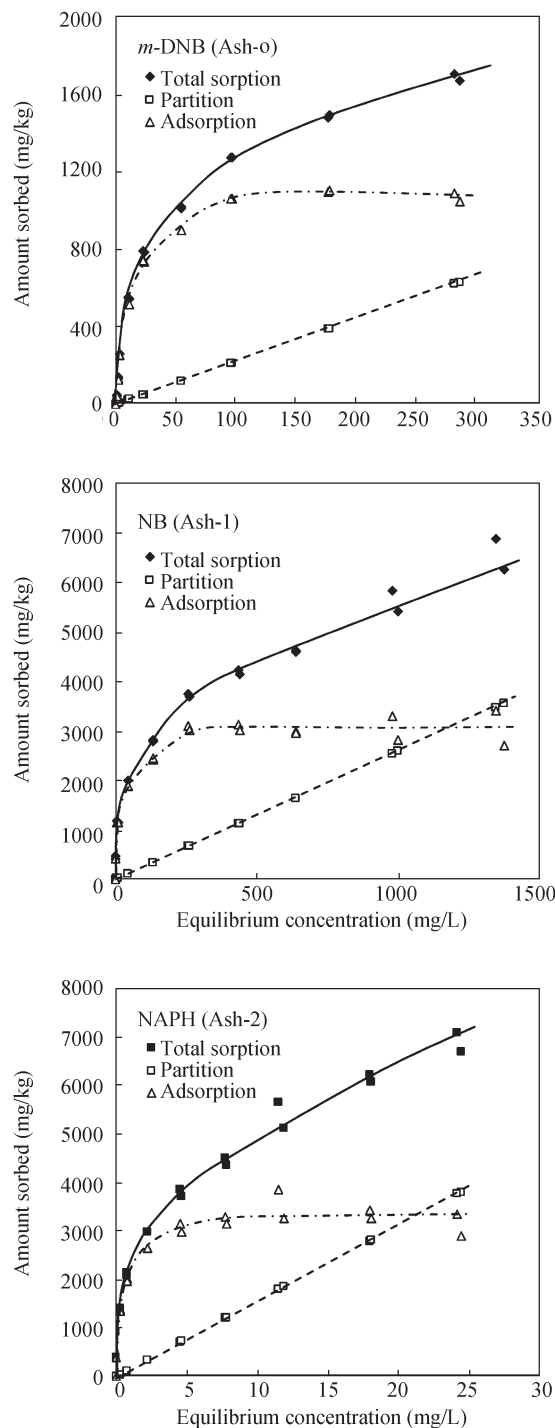


Fig. 4 Separated adsorption and partition isotherms from total sorption of chemicals to ash samples.

equation well (Fig. 4), suggesting that the introduced method for separating the adsorption and partition is reasonable. For a given sorbate, the contribution of maximum adsorption increased in the order of Ash-o < Ash-1 < Ash-2, which is in line with their specific surface areas; while partition coefficient K_P increased with the carbon content of sorbents. The relative contribution of adsorption and partition were calculated against the relative equilibrium concentration (C_e/C_s , C_s is the aqueous solubility) of solute (Fig. 5). The relative contributions of adsorption to total sorption of polar chemicals (i.e., NB) by Ash-o were higher than those of less polar solute (i.e., NAPH), which was attributed to the lower affinity of adsorptive sites of charcoal with less polar chemicals (Cornelissen et al., 2004; Xiao et al., 2004). In comparison with Ash-o, relative contribution of adsorption to total sorption of the tested chemical by Ash-2 decreased, suggesting that the acid treatment changed some properties and/or some structures of Ash-o, and could not be only considered as a condensation method (Chun et al., 2004b).

Principally, K_{oc} are calculated by normalizing the K_P by organic carbon content of sorbent. In the presumption all organic carbons in charcoal medium are involved into the partitioning processes. In the present study, the K_P values are plotted against the organic carbon content of ash samples (Fig. 6a). The linear relationship was obtained with an intercept on the X-axis. The intercept on the X-axis ($K_P = 0$) could be interpreted as the organic carbon content which had no contribution to the total partitioning of chemicals, hence the slope could be regarded as the effective carbon-normalized partition coefficient (K_{oc}^*).

The intercept on the X-axis were all about the same value for the four chemicals, which meant that the carbon making little contribution to the total partitioning were all of the same. Accordingly, for a given sorbent, the carbon content in partitioning effect (C_P , %) were of the same value for the four different sorbates (0.32%–0.48% for Ash-o; 1.15%–2.17% for Ash-1; and 4.68%–4.95% for Ash-2, Table 4). In addition, the calculated $\log K_{oc}^*$ increased with the decrease of $\log C_s$ of organic solute ($R^2 = 0.97$), which suggested that the calculating method of K_{oc}^* in the present study was reasonable.

Correspondingly, the Q_A^{\max} values are plotted against the organic carbon content of samples (Fig. 6b). The positive intercept on X-axis were deemed as the carbon content making no contribution to the total adsorption of chemicals. Contrarily with the observation of K_P , the effective content of organic carbon (C_A) relating to adsorption varied with different organic solutes (Table 4). For strongly polar chemicals (i.e., *m*-DNB and NB), the effective carbon contents for adsorption were larger than those of less polar chemicals (i.e., *p*-NT and NAPH). This was because that adsorptive sites are favorable to polar organic molecule over nonpolar one, which is in line with the conclusion that adsorptive sites of charcoal favored the adsorption of more polar chemicals.

For a specific sorbate-sorbent system, the sum of C_P and C_A was not always equal to the determined carbon content of the sample (C_T). According to Table 4, the sum of ($C_P + C_A$) larger than C_T was observed for Ash-2, which could be attributed to that some organic carbon might simultaneously contribute to adsorption and

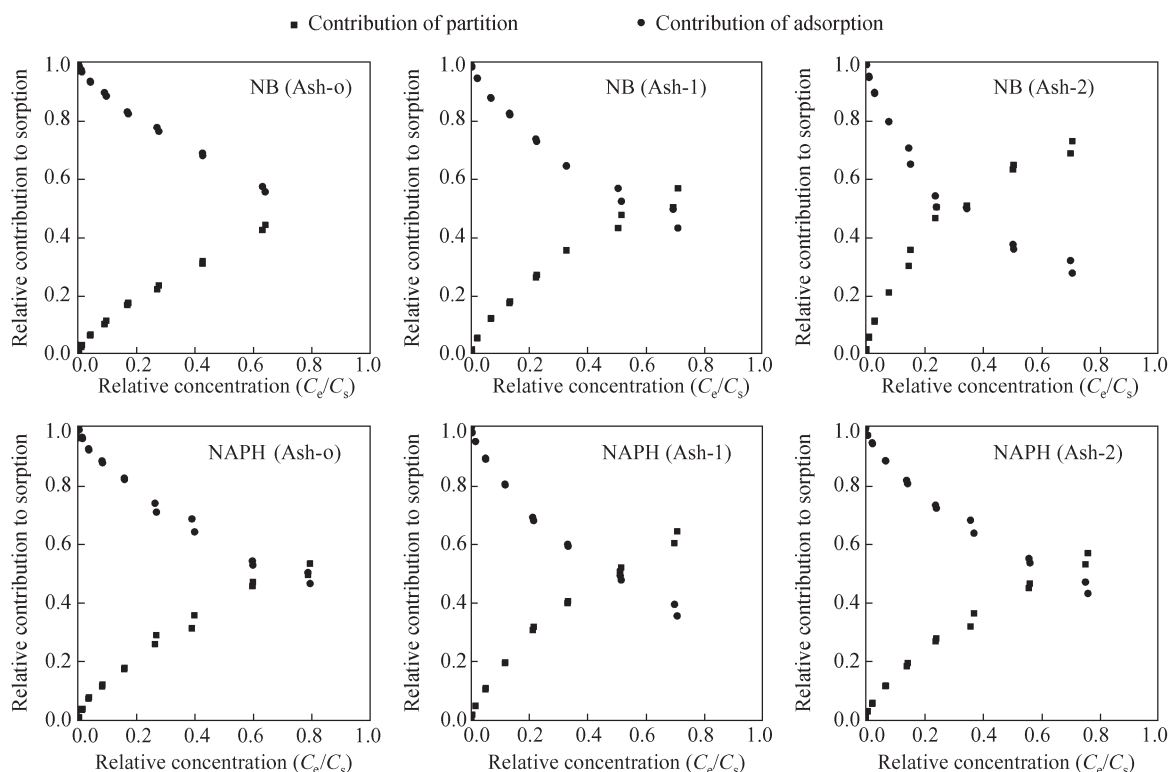


Fig. 5 Relative contribution of adsorption and partition to total sorption of chemicals to ash samples.

Table 4 Regression parameters of isotherms of *p*-nitrotoluene (*p*-NT), *m*-dinitrobenzene (*m*-DNB), nitrobenzene (NB), and naphthalene (NAPH) to original ash, and treated-ashes in aqueous solutions

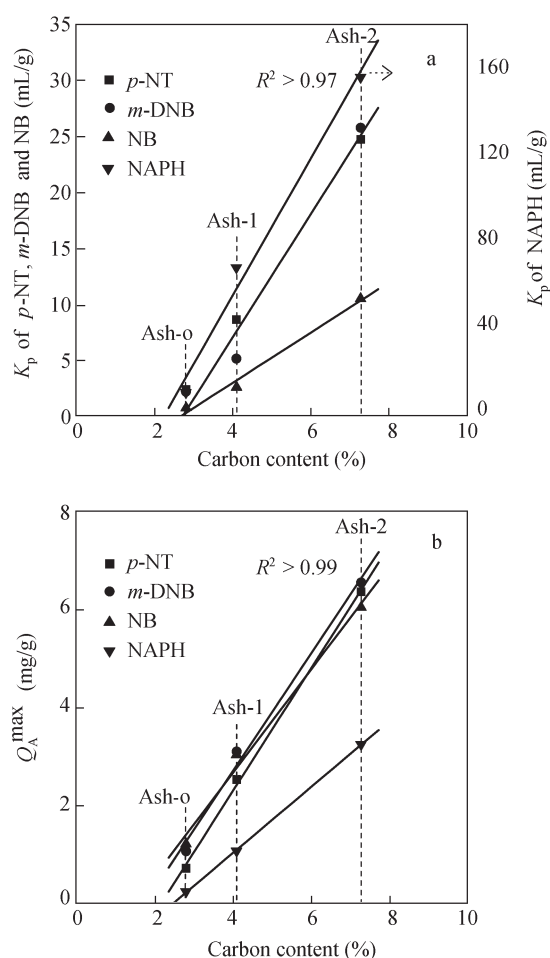
Sorbate	Sorbent	K_P (ml/g)	K_{oc}^*	C_P (%)	C_A (%)	$(C_P + C_A) - C_T$ (%)	Q_A^{max} (mg/g)	$Q_{A,SA}^{max}$ ($\mu\text{mol}/\text{m}^2$)	$Q_{A,SA}^{max*}$ ($\mu\text{mol}/\text{m}^2$)
<i>p</i> -NT (2.450) ^a	Ash-o	2.387	501.0	0.48	0.58	-1.74	0.728	0.410	1.85
	Ash-1	8.609		1.72	2.03	-0.34	2.535	0.679	1.12
	Ash-2	24.72		4.93	5.09	2.76	6.365	1.313	1.87
<i>m</i> -DNB (1.979)	Ash-o	2.19	550.3	0.40	0.90	-1.51	1.074	0.493	2.23
	Ash-1	8.633		1.57	2.59	0.07	3.109	0.679	1.12
	Ash-2	25.76		4.68	5.47	2.88	6.552	1.103	1.57
NB (2.677)	Ash-o	0.728	224.1	0.32	1.16	-1.32	1.222	0.766	3.47
	Ash-1	2.581		1.15	2.89	-0.05	3.042	0.907	1.50
	Ash-2	10.49		4.68	5.74	3.15	6.045	1.389	1.97
NAPH (2.269)	Ash-o	10.79	3147	0.34	0.37	-2.08	0.252	0.152	0.69
	Ash-1	68.2		2.17	1.60	-0.32	1.079	0.309	0.51
	Ash-2	155.6		4.95	4.83	2.50	3.251	0.718	1.02

The partition coefficient (K_P) and the maximum adsorption capacity (Q_A^{max}) were calculated from the slope and the Y -axis intercept of the linear equation over high relative concentration range (i.e., $C_e/C_s = 0.1:0.6$), respectively.

^a Numbers in the parentheses are the theoretical estimated value of maximal monolayer arrangement of the tested organic solutes ($Q_{A,mn}^{max}$).

K_{oc}^* is carbon-normalized partition coefficient, which is derived from the slope of the linear equation of K_P vs. f_{oc} .

C_P is the carbon content making contribution to partition; C_A is carbon content making contribution to adsorption; C_T is the total carbon content of the ash samples; Q_A^{max} is the SA-normalized Q_A^{max} , i.e., $Q_A^{max} = 1000 \times Q_{A,mn}^{max} / (SA \times M)$, where SA (m^2/g) is the specific surface area of sorbents; M (mg/mmol) is the molecular weight of solute; the number of 1000 is the unit conversion factor; $Q_{A,SA}^{max}$ is the Ash-800 normalized Q_A^{max} , i.e., $Q_{A,SA}^{max} = Q_A^{max} \times 1000 / ((SA - \text{Ash content} \times SA \text{ of Ash-800}) \times M)$.

**Fig. 6** Linear relationship between K_P and carbon content (a), and the relationship between Q_A^{max} and carbon content of ash samples (b).

partition. While for Ash-o, the sum of $(C_P + C_A)$ smaller than C_T might suggest that some of organic carbon fraction was ineffective neither in partitioning nor in adsorption.

The increased $(C_P + C_A) - C_T$ value from Ash-o to Ash-2 corresponded to the increase of SA of ash samples. As more adsorptive sites were exposed after acid treatment, organic carbon fractions initially functioned as partitioning phase could serve as adsorptive sites as well.

The theoretical estimated value of maximal monolayer arrangement of the tested organic solutes ($Q_{A,mn}^{max}$, $\mu\text{mol}/\text{m}^2$) were calculated and compared with the SA-normalized maximum adsorption quantities Q_A^{max} (Table 4). All Q_A^{max} were lower than the predicted $Q_{A,mn}^{max}$. This might be attributed to the inefficient sorption of silica (total ash) which was of high content in all ash samples ($> 80\%$) and appreciably contribute to the measured SA ($12.15 \text{ m}^2/\text{g}$). On the hypothesis that Ash-800 was independent part of all ash samples and contributed independently to the total SA of all samples, the SA-normalized adsorptive saturation capacity Q_A^{max} of charcoal was re-calculated to exclude the SA contribution of silica ash based on Ash-800 (Table 4). The re-calculated $Q_{A,SA}^{max}$ values were comparable to the theoretical monolayer capacity $Q_{A,mn}^{max}$. The larger gap between the $Q_{A,mn}^{max}$ and the Q_A^{max} for naphthalene was also observed.

3 Conclusions

There is no distinct difference in the sorption properties between charcoal and biochar. The relationship between Freundlich N values and the charring-temperature of black carbon is established. The organic carbon fractions with different functionalities of partitioning, adsorption, both or neither in charcoal is suggested. The calculated adsorption amount normalized by specific surface area excluding silica ash's SA which is comparable with the theoretical estimated value of maximal monolayer arrangement of the tested solute. These observations prove the importance of pyrolytic temperature in determining the properties of

charcoals, and then the availability of estimating pyrolytic temperature of charcoals through Freundlich N of sorption isotherm provides a link between charcoal and biochar.

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