



Phenanthrene sorption to Chinese coal: Importance of coal's geochemical properties

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ABSTRACT

Phenanthrene (Phen) was chosen as the probe compound for determining the sorption of PAHs to a series of different coal samples from China. Based on elemental analysis and nuclear magnetic resonance (NMR) spectra analysis, coal samples were characterized with different metamorphic evolutionary degrees. The experimental sorption data were fitted well by the Freundlich model, suggesting enhanced sorption capacity and strong nonlinearity of coal samples. The combined partition and adsorption model yielded a better fit than the Freundlich isotherm, indicating that adsorption dominated the sorption at low aqueous concentrations. Correlations between coal properties and sorption capacity values indicated that C%, H/C and O/C atomic ratios were the key factors controlling the sorption behavior. Compared to total carbon, BC might play more important role in the sorption of Phen to coal samples. Moreover, there existed nonlinear relationships between combined carbon, aromatic and aliphatic carbon contents and $\log K_{Fr}$ and n values, respectively, indicating the significance of aromatic and aliphatic carbon in the coal sorption behavior.

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1. Introduction

The fate and bioavailability of hydrophobic organic compounds (HOCs) in the environment are largely governed by their sorption to solid phases [1]. It is widely believed that HOCs sorption to soils/sediments mainly followed linear characteristic [2,3]. However, recently, extensive and nonlinear sorption was observed for several condensed and aromatic sorbent material, including coal, kerogen, coke, cenosphere, soot and charcoal [4–9]. These types of material were suggested to make up the primary sorbents with high sorption enthalpies, nonlinear sorption behavior, competitive sorption, slow kinetics, and possible sorption–desorption hysteresis [9–12].

Coal is a major component of the geopolymers in the environment [13]. Having undergone different degrees of geochemical alterations with different temperature, pressure, source materials and duration, etc., different coals tend to show chemically and structurally much more heterogeneous characteristics with different sorption behavior. Yang et al. [14] simulated diagenetic alterations with a low-grade lignite at different temperatures, and

found that the sorption nonlinearity correlated well with rigidity and aromaticity of the organic matrix. A study on an isolated kerogen [15] indicated that variable micropore size distribution exhibited different sorption behavior for different molecular-size HOCs. In addition, sorption study on carbonaceous geosorbents showed that sorption capacities were probably correlated with surface areas of the sorbents [16–18]. Nevertheless, due to the different degrees of geochemical alterations, different origins and heterogeneous properties of coal, there is still a lack of information on the generic sorption mechanism. In this study, phenanthrene (Phen) was chosen as the probe compound to investigate the unique HOC sorption behavior with different coal samples from China. The aim was to elucidate the mechanisms for the sorption of Phen by coal, by establishing intercorrelations between sorption equilibrium, degree of coal geochemical alterations and different coal properties.

2. Materials and methods

2.1. Sample collection

Different coal samples were collected from various locations in China including: Chifeng (CF), Fuxin (FX), Yaojie (YJ), Yanghe (YH), Pingshuo (PS), Shenfu (SF), Jiahe (JH), Xinzhi (XZ), Jiexiu (JX), Changzhi (CZ) and Taixi (TX). More information, such as their origin and rank was listed in Table 1. Coal samples were pulverized to achieve particle sizes well below 63 μm and stored in glass bottles.

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Table 1

The origin, ranks and physicochemical properties of coal samples used in this study.

Sample	Sampling location	Rank	Element composition (%)					H/C	O/C	BC (%)	Alkyl C (%)	O-alkyl C (%)	Aromatic C (%)	Carbonyl C (%)
			C	O	H	N	S							
CF	Nei Monggol	Lignite	33.53	23.63	4.25	0.87	0.52	1.52	0.53	2.700	86.58	4.81	8.61	0.00
FX	Liaoning	Lignite	53.94	26.30	4.52	0.76	1.01	1.01	0.37	1.564	13.83	40.74	35.95	9.48
YJ	Gansu	Bituminous coal	32.35	11.75	3.20	0.59	0.32	1.19	0.27	0.199	29.26	1.01	53.82	15.45
YH	Henan	Bituminous coal	34.86	7.74	2.43	0.50	0.38	0.84	0.17	4.375	4.00	10.99	69.03	15.97
PS	Shanxi	Bituminous coal	60.45	15.59	4.39	1.09	0.60	0.87	0.19	1.497	0.00	7.59	73.72	18.69
SF	Nei Monggol	Bituminous coal	65.54	19.07	4.48	0.73	0.93	0.82	0.22	2.397	30.85	6.28	52.60	10.27
JH	Jiangsu	Bituminous coal	74.99	9.86	4.92	1.36	0.49	0.79	0.10	1.077	40.76	1.47	45.93	11.84
XZ	Shanxi	Bituminous coal	77.00	6.00	4.66	1.36	0.54	0.73	0.06	1.607	31.48	3.25	54.46	10.82
JX	Shanxi	Bituminous coal	77.80	4.82	4.36	1.54	1.15	0.67	0.05	3.111	19.47	9.09	57.92	13.52
CZ	Shanxi	Bituminous coal	80.13	4.21	4.00	1.07	0.41	0.60	0.04	7.323	18.52	8.84	56.22	16.42
TX	Ningxia	Anthracite	87.31	4.00	3.82	0.58	0.27	0.53	0.03	36.445	8.18	9.05	61.78	20.99

2.2. Coal characterization

Elemental contents (C, H, N, O and S) of coal samples were determined using an elemental analyzer (Elementar Vario EL3, Germany). Black carbon (BC) was determined using “CTO-375” method described by Cornelissen et al. [19]. The solid-state ^{13}C NMR spectra were obtained using cross-polarization (CP) and magic angle spinning (MAS) techniques. The NMR spectrometer was a Bruker DSX 400 MHz instrument, operating with CP (1 ms contact time) and MAS (5 kHz spinning rate) and a WB probe, at 75 MHz frequency for ^{13}C , with pulse width of 5 μs , and 27 ms acquisition time. The rotor was of 4 mm in diameter. Within the 150–350 ppm chemical shift range, C atoms were assigned to alkyl C (0–50 ppm), O-alkyl C (50–107 ppm), aromatic C (107–165 ppm), carboxyl C (165–190 ppm), and carbonyl C (190–220 ppm) [20,21]. The spinning sidebands were not corrected because their contributions were small and would cause only minor differences in the overall integrated intensities for these coal samples.

2.3. Sorption experiments

All batch experiments were conducted in triplicate. Concentrated Phen stock solutions were prepared with methanol and diluted with Milli-Q water as needed. Methanol concentrations in aqueous solutions were less than 0.5%, a level at which methanol has no measurable effect on sorption [22]. Because of differences in sorption capacity of the samples, the different solid-to-water ratios were chosen (30–80% reductions in aqueous-phase solute concentrations during sorption were achieved). NaN_3 (200 mg/L) was added to all samples to minimize biological activity. All batch experiments were conducted in 20 mL crimp-top glass reaction vials sealed with PTFE-lined butyl rubber septa (Alltech). The vials contained 0.005–0.02 g of the pulverized samples and were filled with the spiked aqueous solutions leaving a minimum headspace. All vials were shaken on the shaker for 7 days and centrifuged. Immediately after centrifugation, the supernatant was analyzed for Phen by HPLC equipped with a fluorescence detector (separation column, OSD, 150 mm \times 2.1 mm, 5 μm C18 silica; mobile phase, 10% water, 90% acetonitrile; emission/extinction wavelengths for Phen at 249/345 nm). Solute/system loss due to adsorption onto the glass surface and vial seals, or partitioning into the headspace was assessed by running the control experiments with reference vials containing no solids. The total mass was corrected for the system loss (<10%).

3. Results and discussion

3.1. Properties of coal samples

Element compositions of the eleven coals were summarized in Table 1. The carbon content ranged from 32.53 to 87.31% with the

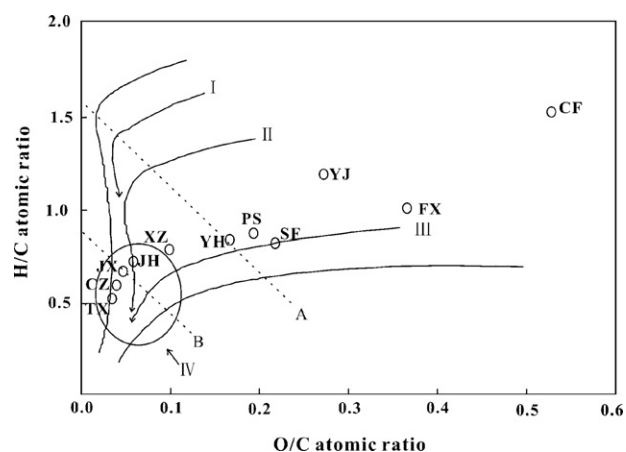


Fig. 1. Van Krevelen plot for different Chinese coal samples.

lowest in YJ sample (32.35%) and the highest in TX sample (87.31%). The oxygen content varied greatly. Lignite coals (CF and FX) had the higher oxygen content (>20%). In contrast, TX anthracite with the highest coalification degree had the lowest oxygen content (<5%). The hydrogen content in coals was in the range of 2.43–4.92%. The content of nitrogen and sulfur was less than 2%. Therefore, carbon, oxygen and hydrogen were the primary elements in those coal samples. There existed a strong correlation between H/C and O/C ratios ($R^2 = 0.940$, $p < 0.0001$) and both of them declined with the increased carbon content.

The atomic ratios of H/C and O/C were plotted on the Van Krevelen diagram (Fig. 1). It showed the evolution pathways of four types of coal as a function of geochemical alterations [13,14,23]. Fig. 1 revealed that CF, YJ and XZ coals were mature type-II coals (with relatively high ratios of both H/C and O/C), while FX, YH, PS and SF coals were mature type III coals (with higher O/C), and JH, JX, CZ and TX coals were more matured as type IV coals when temperature was sufficiently high [13]. Moreover, CF and FX coals had the lowest metamorphic degrees in diagenesis, followed by YJ, SF, PS and YH coals. Meanwhile, JX, CZ and TX coals were in the region of the late metagenesis; JH and XZ coals were located in the region of catagenesis. The trend is consistent with the rank of the coals, i.e. lignite coal metamorphoses lightly from diagenetic stage, while anthracite coal metamorphoses deeply from metagenetic stage.

The CP/MAS ^{13}C NMR spectra of Chinese coals revealed a large contribution from alkyl C, aromatic C and carbonyl C (Table 1), but a small contribution from carboxyl C (Fig. 2). The aliphatic carbon (0–107 ppm) and aromatic carbon (107–165 ppm) ranged from 7.59% to 91.39% and from 8.61% to 73.72%, respectively. The carbonyl carbon contents were significantly related to the aromatic

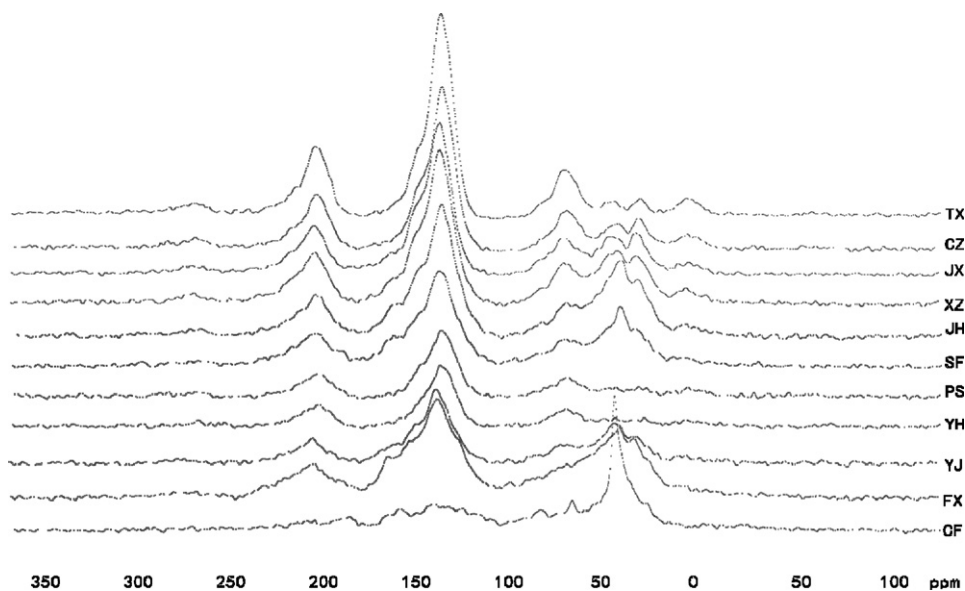


Fig. 2. CP/MAS ^{13}C NMR spectra of the eleven samples.

carbon contents ($R^2 = 0.902$, $p < 0.0001$). For CF and FX lignite, the ^{13}C NMR spectra showed a large contribution from the aliphatic carbon while for other high rank coals the aromatic carbon was abundant i.e. the low rank coal contained more aliphatic carbon, while the high rank coal contained more aromatic carbon and carbonyl carbon.

3.2. Application of Freundlich isotherm

The sorption data were fitted with the Freundlich equation:

$$C_s = K_{Fr} C_w^n \quad (1)$$

where C_s is the concentration of Phen in coal (mg/kg), C_w is the aqueous concentration (mg/L), K_{Fr} is the Freundlich distribution ratio [(mg/kg)/(mg/L) n] and n denotes the Freundlich exponent.

Freundlich isotherm parameters were presented in Table 2 and isotherms of the samples were shown in Fig. 3. The Freundlich model fitted all the data well with high R^2 and low MWSE values. The sorption capacities varied with $\log K_{Fr}$ values from 4.43 to 6.01 with the highest in anthracite and lowest in lignite coal. $\log K_{Fr}$ values in this study were comparable with the literature values. Kleineidam et al. [5] obtained $\log K_{Fr}$ values from 4.15 to 4.70 in three coal samples. Relatively high $\log K_{Fr}$ values (5.54–6.5) were obtained for five higher rank coal samples [24]. In addition,

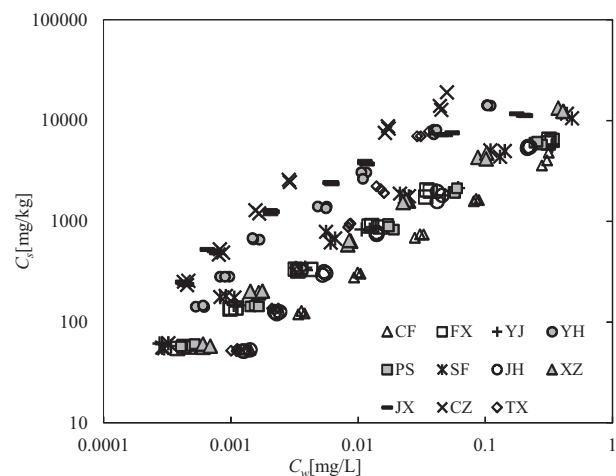


Fig. 3. Phen sorption isotherms of different Chinese coal samples.

a good correlation was found between $\log K_{Fr}$ values and n values ($R^2 = 0.808$, $p < 0.005$). Sorption isotherms showed nonlinearity with n values ≤ 0.9 except for sample TX. Table 2 showed the organic carbon normalized sorption coefficient (K_{oc}) at aqueous concentra-

Table 2
Freundlich model parameters for different coal samples.

Sample	N^a	$\log K_{Fr}$	n	MWSE ^b	R^2	$\log K_{oc}$	
						$1 \mu\text{g L}^{-1}$	1mg L^{-1}
CF	18	4.06	0.81	0.01	0.998	5.12	4.53
FX	18	4.24	0.71	0.03	0.990	5.37	4.50
YJ	18	4.11	0.65	0.01	0.996	5.64	4.60
YH	18	5.12	0.85	0.06	0.986	5.96	5.52
PS	18	4.21	0.72	0.01	0.995	5.26	4.43
SF	17	4.34	0.71	0.04	0.990	5.40	4.52
JH	18	4.42	0.90	0.06	0.982	4.88	4.54
XZ	18	4.46	0.81	0.03	0.992	5.14	4.57
JX	21	4.65	0.62	0.10	0.956	5.91	4.76
CZ	16	5.44	0.88	0.06	0.975	5.91	5.53
TX	18	5.95	1.43	0.02	0.993	4.73	6.01

^a N = number of observations

^b MWSE is the mean weighted square error = $1/(N-2) \sum [(C_s \text{ measured} - C_s \text{ model})^2 / C_s \text{ measured}^2]$

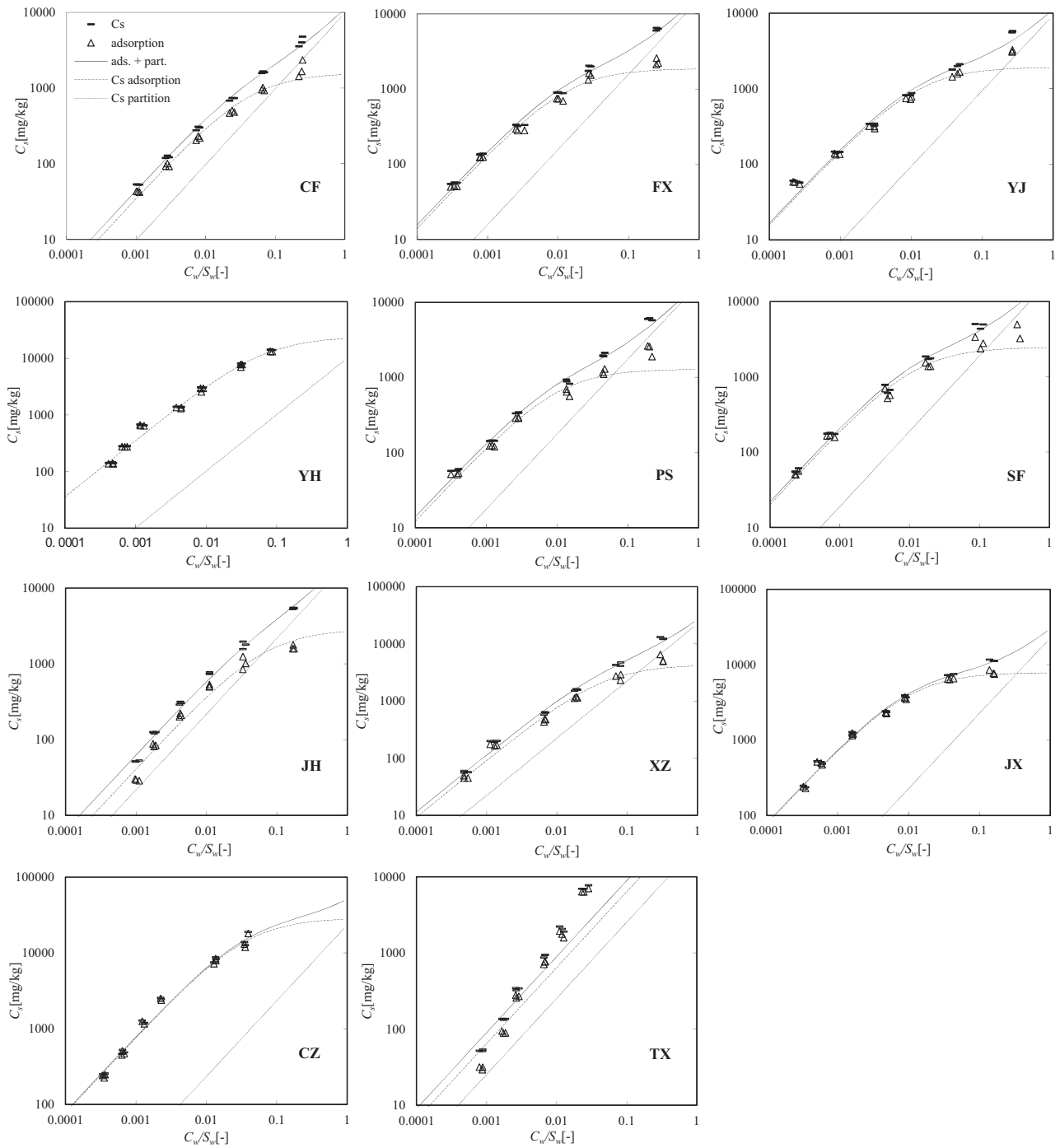


Fig. 4. Dual sorption isotherm for Phen (solid line: combined isotherm; dashed line: Langmuir adsorption part; dotted line: partitioning part.).

tions of 1 $\mu\text{g/L}$ and 1 mg/L , respectively. The $\log K_{oc}$ values were in the range of 4.73–5.96 at C_w of 1 $\mu\text{g/L}$ and 4.43–6.01 at C_w of 1 mg/L . These coal samples, except TX, act as much stronger sorbents for Phen at lower concentrations, than at higher concentration, e.g., at 1 mg/L . Moreover, the K_{oc} values were variable at lower aqueous concentrations while became similar at higher concentration.

3.3. Application of the combined adsorption and partition model

Natural geosorbents could be divided into two principal sorption domains: (1) amorphous soft carbon domain (partitioning); and (2) more condensed hard carbon domain (adsorption) [10,25,26]. Among all the dual models, the Langmuir-type equation

had been commonly used to fit the nonlinear adsorption component [27]:

$$C_s = K_p C_w + \frac{Q_{\max} b C_w}{1 + b C_w} \quad (2)$$

where K_p is the partition coefficient for organic carbon (L/kg), Q_{\max} is the maximum site sorption capacity (mg/kg), and b is the Langmuir site sorption affinity (L/mg). The K_p value was estimated according to Eqs. (3) and (4) [28]:

$$\log K_{oc} = \log K_{ow} - 0.21 \quad (3)$$

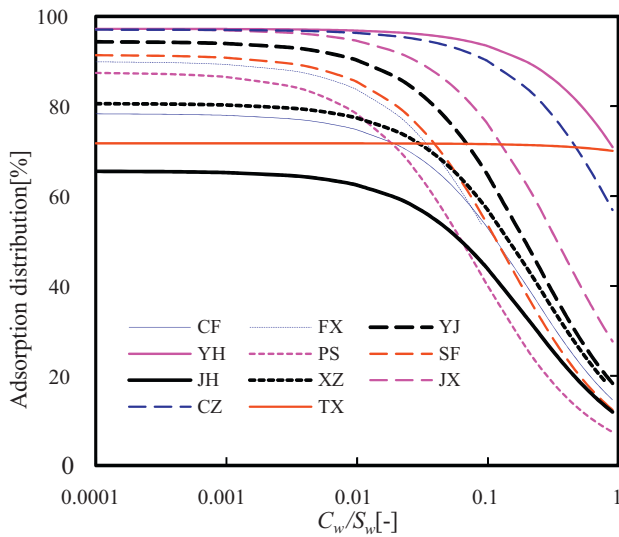


Fig. 5. Adsorption contributions to the total sorption.

and Eq. (3):

$$K_p = K_{oc} \times f_{oc} \tag{4}$$

The parameters of the Langmuir-type dual model were summarized in Table 3. On the log–log scale, the data-intense isotherms showed an inflection point which was concentration-dependent. In contrast to the Freundlich sorption isotherm, the combined partition and Langmuir model captured the inflection very well except for TX coal (Fig. 4). In general, the Langmuir-type dual model yielded better fit with $R^2 > 0.981$ and smaller MWSE values. The $\log Q_{max}$ values of the samples generally increased with the carbon content. Computed $\log Q_{max}$ values in the Langmuir-type adsorption component were in the range of 3.11–5.83 mg/kg, with the highest values in TX sample and the lowest in PS sample. Langmuir site sorption affinities (b) were in the range of 0.07–65.15 L/mg, with the highest in SF and the lowest in TX.

As shown in Fig. 4, computed linear partitioning curve was gradually close to the total fitting curve with increasing aqueous concentration except for sample TX. Similarly, the isotherm exhibited a concave-downward shape at low concentrations but a practically linear shape at high concentration have been reported in literature [29–31], which was attributed to the adsorption by high surface-area carbonaceous material (HSACM) at relatively low

Table 3
The dual model parameters of the Phen sorption isotherms.

Sample	N	$\log K_p$	$\log Q_{max}$	b	MWSE	R^2
CF	18	3.89	3.20	17.60	0.01	0.993
FX	18	4.09	3.27	59.23	0.02	0.998
YJ	18	3.87	3.28	64.86	0.04	0.994
YH	18	3.90	4.38	11.79	0.03	0.999
PS	18	4.14	3.11	75.21	0.02	0.995
SF	17	4.18	3.39	65.15	0.03	0.993
JH	18	4.23	3.46	11.40	0.02	0.998
XZ	18	4.25	3.64	16.98	0.03	0.995
JX	21	4.25	3.90	78.22	0.01	0.998
CZ	16	4.26	4.46	21.09	0.03	0.983
TX	18	4.30	5.83	0.07	0.21	0.981

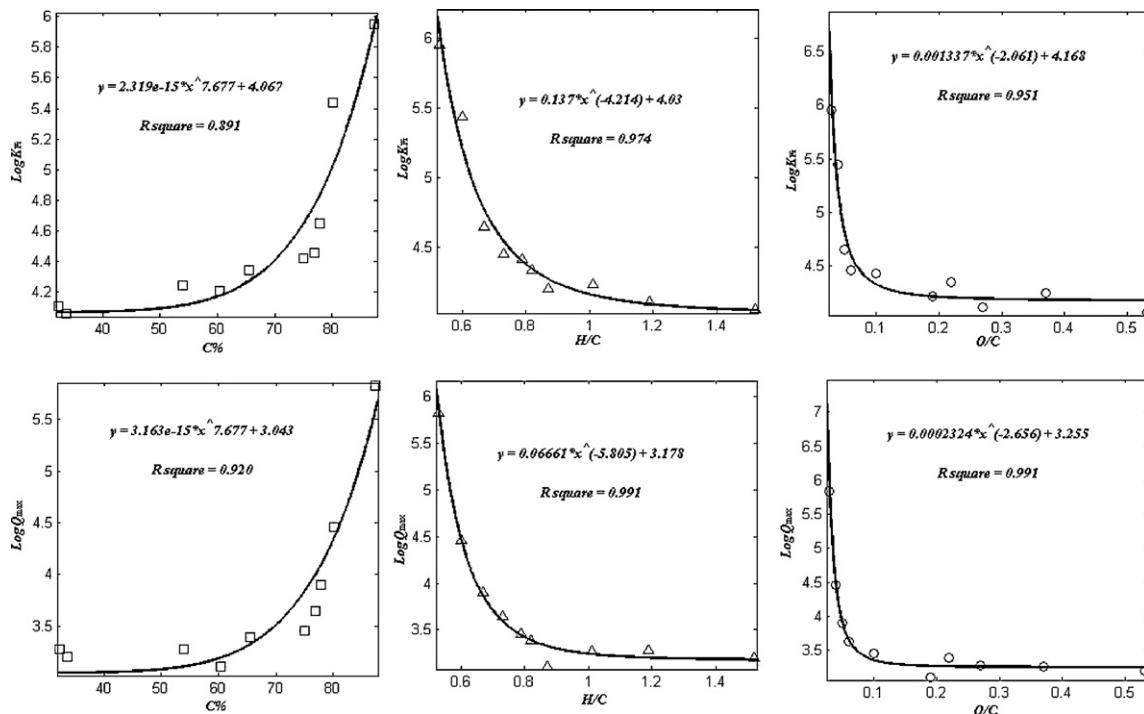


Fig. 6. Correlation analysis for sorption parameters and coal properties.

Table 4
Correlations between H/C and O/C ratios and $\log K_{oc}$ at different concentration.

C_w/S_w	Fitting equation	R^2	Fitting equation	R^2
0.001	$\log K_{oc} = -0.82(H/C)^3 + 1.68(H/C)^2 - 0.76(H/C) + 5.32$	0.039	$\log K_{oc} = -41.76(O/C)^3 + 32.14(O/C)^2 - 6.25(O/C) + 5.58$	0.096
0.010	$\log K_{oc} = -4.04(H/C)^3 + 12.95(H/C)^2 - 13.38(H/C) + 9.56$	0.277	$\log K_{oc} = -54.66(O/C)^3 + 46.52(O/C)^2 - 10.90(O/C) + 5.72$	0.361
0.100	$\log K_{oc} = -7.26(H/C)^3 + 24.23(H/C)^2 - 26.00(H/C) + 13.80$	0.853	$\log K_{oc} = -67.56(O/C)^3 + 60.91(O/C)^2 - 15.55(O/C) + 5.86$	0.632

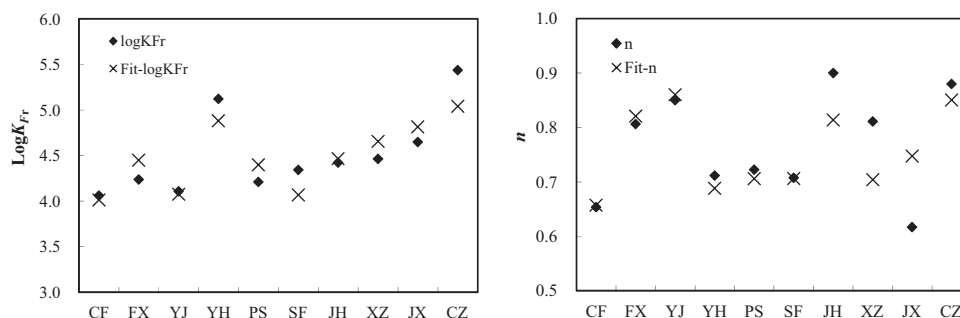


Fig. 7. Comparison of experimental and fitting values of $\log K_{Fr}$ and n in coal samples.

concentrations and adsorption by organic carbon (OC) at high concentrations [5,31]. Adsorption contribution to the whole sorption was estimated at C_w/S_w in a wide range (Fig. 5). At low concentration ($<0.1 \mu\text{g/L}$), adsorption contribution varied from 97% for YH to 65% for JH. However, the contribution decreased dramatically when the concentration was higher than 0.01 mg/L . For anthracite TX, the adsorption contribution was relatively constant (about 70%) in the overall sorption.

3.4. Correlation between sorption parameters and coal geochemical properties

Carbon content is an important indicator of coal maturity [24], as carbon content increases with increasing coal maturity. A power function can describe the relationship between $\log K_{Fr}$ values and C% when YH sample was excluded (Fig. 6). $\log K_{Fr}$ values generally increased as C% increased. YH sample was an exception probably due to its lower carbon, oxygen and hydrogen content compared to other bituminous coal. Similarly, when YH was excluded, significant relationships were observed between $\log K_{Fr}$ and the H/C and O/C atomic ratios respectively (Fig. 6), indicating that H/C and O/C ratios were a key factor controlling the sorption properties. We did not investigate a significant relationship between n values and coal properties. However, as the aqueous concentration was increased, more significant correlations between $\log K_{oc}$ and H/C and O/C ratios could be found (Table 4). Grathwohl [32] observed a correlation between the sorption of nonionic organic compounds and the elemental composition of natural organic matter, and sorption increased considerably with an increasing H/O ratio. Huang et al. [7] reported that $\log K_{oc}$ values, calculated at $C_w = 1 \mu\text{g/L}$, increased as the O/C atomic ratios decreased in soils and sediments; Yang et al. [14] simulated the diagenetic alterations for a lignite coal and found the similar relationship between sorption capacity and O/C ratio in the less matured kerogen samples, while for the more matured samples, an opposite trend was observed. Based on sorption study with heterogeneous Chinese coals, it can be concluded that the carbon content, O/C and H/C values are the key factors that govern the sorption behavior of Phen. The positive correlations between $\log Q_{max}$ values and C% and the H/C and O/C ratios were also shown with similar trend to $\log K_{Fr}$ (Fig. 6). It can be interpreted that the adsorption was the primary sorption relied on C%, H/C and O/C ratios. In addition, extensive sorption was often observed in natural sorbents when BC was existed [9]. In the present study, BC content was analyzed in each sample and correla-

tion analysis showed that BC contents had significant correlation to $\log K_{Fr}$ values when TX was excluded ($R^2 = 0.787$, $p < 0.001$). Therefore, compared to carbon content, BC might play more important role in the sorption of Phen to coal samples.

It was known that the organic matrixes of coal consist mainly of both aliphatic moieties and aromatic backbones [14]. Studies on heterogenous geosorbents including sediments, soils and kerogens lead to a controversial conclusion that either aromatic [33–35] or aliphatic [16,36,37] groups control the sorption of HOCs. In this study, neither aromatic nor aliphatic carbon alone was found to fit the experimental data well. However, when combined carbon, aromatic and aliphatic carbon content were considered simultaneously, significant nonlinear relationships with $\log K_{Fr}$ and n values in coal samples (except TX sample) was established. The fitting equations were as follows:

$$\log K_{Fr} = 0.002 \times C\%^2 - 0.169 \times C\% - 0.017 \times C_{arom} - 0.026 \times C_{alip} + 10.391 \quad (R^2 = 0.876, \quad p < 0.001)$$

$$n = -0.030 \times C_{arom} - 0.029 \times C_{alip} + 3.609 \quad (R^2 = 0.745, \quad p < 0.013)$$

where C_{arom} and C_{alip} were the proportion of aromatic carbon and aliphatic carbon based on the CP/MAS ^{13}C NMR spectra analysis, respectively. As shown in Fig. 7, the fitting results indicated that carbon content, aliphatic and aromatic carbon played dominant roles in the Phen sorption by coal sorbents.

4. Conclusions

As an important carbonaceous geosorbent in the environment, coal has gained attentions concerning its sorption of organic contaminants. Coal sorption behavior tends to be related to its degrees of geochemical alterations and physicochemical properties. In this study, sorption experiment with heterogeneous Chinese coals showed high sorption capacity and distinct nonlinearity. In contrast to the Freundlich sorption isotherm, combined partitioning and adsorption model fitted the experimental data well. Adsorption contributed most in the overall sorption behavior of the coal samples being examined. According to elemental analysis (e.g. H/C and O/C ratios), all coal samples were classified into different types and metamorphic evolutionary stages. Correlation analysis showed that C%, H/C and O/C ratios could be key factors that controlled

the sorption behavior of coal, which was dominated by adsorption. When C% was increased, $\log K_{Fr}$ and $\log Q_{max}$ values were generally increased; whereas, when the H/C and O/C atomic ratios were increased, both $\log K_{Fr}$ and $\log Q_{max}$ values were decreased. Compared to total carbon, BC might play more important role in the sorption of Phen to coal samples. Moreover, neither aliphatic carbon nor aromatic carbon showed a significant correlation to sorption data. However, with combined carbon content, aliphatic and aromatic carbon were considered simultaneously, a significant nonlinear relationship with $\log K_{Fr}$ and n values respectively was established, indicating that carbon content, aliphatic and aromatic carbon played an important role in coal's sorption behavior.

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References

- [1] R. Lohmann, J.K. Macfarlane, P.M. Gschwend, Importance of black carbon to sorption of native PAHs, PCBs, and PCDDs in Boston and New York harbor sediments, *Environ. Sci. Technol.* 39 (2005) 141–148.
- [2] J.C. Means, S.G. Wood, J.J. Hassett, W.L. Banwart, Sorption of polynuclear aromatic hydrocarbons by sediments and soils, *Environ. Sci. Technol.* 14 (1980) 1524–1528.
- [3] C.T. Chiou, P.E. Porter, D.W. Schmedding, Partition equilibria of nonionic organic compounds between soil organic matter and water, *Environ. Sci. Technol.* 17 (1983) 227–231.
- [4] S. Kleineidam, H. Rügner, B. Ligouis, P. Grathwohl, Organic matter facies and equilibrium sorption of phenanthrene, *Environ. Sci. Technol.* 33 (1999) 1637–1644.
- [5] S. Kleineidam, C. Schüth, P. Grathwohl, Solubility-normalized combined adsorption-partitioning sorption isotherms for organic pollutants, *Environ. Sci. Technol.* 36 (2002) 4689–4697.
- [6] U. Ghosh, J.R. Zimmerman, R.G. Luthy, PCB and PAH speciation among particle types in contaminated harbor sediments and effects on PAH bioavailability, *Environ. Sci. Technol.* 37 (2003) 2209–2217.
- [7] W.L. Huang, P.A. Peng, Z.Q. Yu, J.M. Fu, Effects of organic matter heterogeneity on sorption and desorption of organic contaminants by soils and sediments, *Appl. Geochem.* 18 (2003) 955–972.
- [8] L. Hong, U. Ghosh, T. Mahajan, R.N. Zare, R.G. Luthy, PAH sorption mechanism and partitioning behavior in lampblack-impacted soils from former oil-gas plant sites, *Environ. Sci. Technol.* 37 (2003) 3625–3634.
- [9] G. Cornelissen, Ö. Gustafsson, T.D. Bucheli, M.T.O. Jonker, A.A. Koelmans, P.C.M. Van Noort, Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments and soils: mechanisms and consequences for distribution, bioaccumulation, and biodegradation, *Environ. Sci. Technol.* 39 (2005) 6881–6895.
- [10] W.J. Weber Jr., P.M. McGinley, L.E. Katz, A distributed reactivity model for sorption by soils and sediments. 1. Conceptual basis and equilibrium assessments, *Environ. Sci. Technol.* 26 (1992) 1955–1962.
- [11] J.J. Pignatello, B. Xing, Mechanisms of slow sorption of organic chemicals to natural particles, *Environ. Sci. Technol.* 30 (1996) 1–11.
- [12] W.L. Huang, T.M. Young, M.A. Schlautman, H. Yu, W.J. Weber Jr., A distributed reactivity model for sorption by soils and sediments. 9. General isotherm non-linearity and applicability of the dual reactive domain model, *Environ. Sci. Technol.* 31 (1997) 1703–1710.
- [13] R.M. Allen-King, P. Grathwohl, W.P. Ball, New modeling paradigms for the sorption of hydrophobic organic chemicals to heterogeneous carbonaceous matter in soils, sediments and rocks, *Adv. Water Res.* 25 (2002) 985–1016.
- [14] C. Yang, W.L. Huang, B.H. Xiao, Z.Q. Yu, P.A. Peng, J.M. Fu, G.Y. Sheng, Interrelations among degree of geochemical alterations, physicochemical properties, and organic sorption equilibria of kerogen, *Environ. Sci. Technol.* 38 (2004) 4396–4408.
- [15] Y. Ran, B. Xing, P.S.C. Rao, J.M. Fu, Importance of adsorption (hole-filling) mechanism for hydrophobic organic contaminants on an aquifer kerogen isolate, *Environ. Sci. Technol.* 38 (2004) 4340–4348.
- [16] U. Ghosh, J.S. Gillette, R.G. Luthy, R.N. Zare, Microscale location, characterization, and association of polycyclic aromatic hydrocarbons on harbor sediment particles, *Environ. Sci. Technol.* 34 (2000) 1729–1736.
- [17] T.D. Bucheli, Ö. Gustafsson, Quantification of the soot-water distribution coefficient of PAHs provides mechanistic basis for enhanced sorption observations, *Environ. Sci. Technol.* 34 (2000) 5144–5151.
- [18] G. Cornelissen, Ö. Gustafsson, Sorption of phenanthrene to environmental black carbon in sediment with and without organic matter and native sorbates, *Environ. Sci. Technol.* 38 (2004) 148–155.
- [19] G. Cornelissen, Z. Kukulska, S. Kalaitzidis, K. Christanis, Ö. Gustafsson, Relations between environmental black carbon sorption and geochemical sorbent characteristics, *Environ. Sci. Technol.* 38 (2004) 3632–3640.
- [20] R.L. Malcolm, P. MacCarthy, Limitations in the use of commercial humic acids in water and soil research, *Environ. Sci. Technol.* 20 (1986) 904–911.
- [21] M. Schnitzer, H. Kodama, J.A. Ripmeester, Determination of the aromaticity of humic substances by X-ray diffraction analysis, *Soil Sci. Soc. Am. J.* 55 (1991) 745–750.
- [22] P. Nkedi-Kizza, P.S.C. Rao, A.G. Hornsby, Influence of organic cosolvents on leaching of hydrophobic organic chemicals through soils, *Environ. Sci. Technol.* 21 (1987) 1107–1111.
- [23] W.L. Huang, W.J. Weber Jr., A distributed reactivity model for sorption by soils and sediments. 10. Relationships between desorption, hysteresis, and the chemical characteristics of organic domains, *Environ. Sci. Technol.* 31 (1997) 2562–2569.
- [24] G. Cornelissen, Ö. Gustafsson, Importance of unburned coal carbon, black carbon, and amorphous organic carbon to phenanthrene sorption in sediments, *Environ. Sci. Technol.* 39 (2005) 764–769.
- [25] W.J. Weber Jr., W.L. Huang, A distributed reactivity model for sorption by soil and sediments. 4. Intraparticle heterogeneity and phase distribution relationships under non-equilibrium conditions, *Environ. Sci. Technol.* 30 (1996) 881–888.
- [26] B. Xing, J.J. Pignatello, Dual-mode sorption of low-polarity compounds in glassy polyvinylchloride and soil organic matter, *Environ. Sci. Technol.* 31 (1997) 792–799.
- [27] G.S. Xia, W.P. Ball, Adsorption-partitioning uptake of nine low-polarity organic chemicals on a natural sorbent, *Environ. Sci. Technol.* 33 (1999) 262–269.
- [28] S.W. Karickhoff, D.S. Brown, T.A. Scott, Sorption of hydrophobic pollutants on natural sediments, *Water Res.* 13 (1979) 241–248.
- [29] C.T. Chiou, D.E. Kile, D.W. Rutherford, G.Y. Sheng, S.A. Boyd, Sorption of selected organic compounds from water to a peat soil and its humic acid and humin fractions potential sources of the sorption nonlinearity, *Environ. Sci. Technol.* 34 (2000) 1254–1258.
- [30] H.K. Karapanagioti, D.A. Sabatini, Impacts of heterogeneous organic matter on phenanthrene sorption: different aquifer depths, *Environ. Sci. Technol.* 34 (2000) 2453–2460.
- [31] G. James, D.A. Sabatini, C.T. Chiou, D. Rutherford, A.C. Scott, H.K. Karapanagioti, Evaluating phenanthrene sorption on various wood chars, *Water Res.* 39 (2005) 549–558.
- [32] Grathwohl, Influence of organic matter from soils and sediments from various origins on the sorption of some chlorinated aliphatic hydrocarbons: implications on K_{oc} -correlations, *Environ. Sci. Technol.* 24 (1990) 1687–1693.
- [33] M.J. Salloum, B. Chefetz, P.G. Hatcher, Phenanthrene sorption by aliphatic-rich natural organic matter, *Environ. Sci. Technol.* 36 (2002) 1953–1958.
- [34] B. Chen, B. Xing, Sorption and conformational characteristics of reconstituted plant cuticular waxes on montmorillonite, *Environ. Sci. Technol.* 39 (2005) 8315–8323.
- [35] Y. Ran, K. Sun, Y. Yang, B. Xing, E. Zeng, Strong sorption of phenanthrene by condensed organic matter in soils and sediments, *Environ. Sci. Technol.* 41 (2007) 3952–3958.
- [36] D.E. Kile, R.L. Wershaw, C.T. Chiou, Correlation of soil and sediment organic matter polarity to aqueous sorption of nonionic compounds, *Environ. Sci. Technol.* 33 (1999) 2053–2056.
- [37] M.D. Johnson, W.L. Huang, W.J. Weber Jr., A distributed reactivity model for sorption by soils and sediments. 13. Simulated diagenesis of natural sediment organic matter and its impact on sorption/desorption equilibria, *Environ. Sci. Technol.* 35 (2001) 1680–1687.