Sorption characteristics and mechanisms of organic contaminant to carbonaceous biosorbents in aqueous solution

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A series of carbonaceous biosorbents was prepared by pyrolyzing pine needles, a model biomass, at various temperatures (100－700℃) under an oxygen-limited condition for 6 h. The elemental compositions and the specific surface areas (BET-N_2) of the biosorbents were analyzed. Sorption properties of 4-nitrotoluene to the biosorbents and their mechanisms were investigated, and then correlated with the structures of the biosorbents. The result shows that with the increase of the pyrolytic temperature, the aromaticity of the carbonaceous biosorbents increases dramatically and the polarity (the (N+O)/C atomic ratio) decreases sharply. Correspondingly, conformations of the organic matter in the biosorbents transform gradually from a "soft-state" to a "hard-state" and the specific surface areas of the resultant biosorbents extend rapidly. The sorption isotherms fit well with the Freundlich equation. The regression parameters (i.e., N and $\lg K_f$) are linearly related to the aromaticity indices (the H/C atomic ratio). Contributions of adsorption and partition to total sorption of the carbonaceous biosorbents are quantified. The adsorption of the carbonaceous biosorbents increases quickly with the increase of the pyrolytic temperature. The saturated adsorption amounts (Q_{max}) increase linearly with the increase of the specific surface areas (SA) of the biosorbents. For the carbonaceous biosorbents with hard-state carbon, the calculated normalized-Q_{max} values by SA are comparable to the theoretical estimation (2.45 $\mu mol/m^2$). In comparison, for the carbonaceous sorbents with soft-state carbon, the calculated normalized-Q_{max} values by SA are much higher than the theoretical estimation. The partition coefficients (K_{om}) increase with the decrease of the polarity of the biosorbents, reaching a maximum, and then decrease sharply with further decreasing the polarity, suggesting that partition mechanism be dominated by the compatibility and accessibility of the sorbent medium with organic pollutant. These observations will provide a theoretical and practical reference to design a cost-effective and high-efficient sorbent, and to accurately predict sorption properties and mechanisms of a given sorbent.

carbonaceous biosorbent, organic contaminant, partition, adsorption, wastewater treatment

Water micropollution with organic compounds, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and nitroaromatic compounds, has been increasingly concerned due to the high bioaccumulation, and potential mutagenic and carcinogenic properties of these organic compounds[1,2]. These organic compounds often remain and persist during the conventional wastewater treatment process, and then mostly they will be discharged into the water body. This

scenario, along with the less-efficient removal of persistent organic pollutants (POPs) during producing drinking-water, has resulted in hazard to drinking-water safety and then to human health[1]. Consequently, several

kinds of novel sorbents, such as modified activated-carbon, organoclay[3,4] and triolein-embedded activated carbon composites[5], have been developed for high-efficient and cost-effective performance in abating POPs in wastewater and drinking-water treatment[6]. However, more studies are needed to develop environmentally friendly sorbents, such as carbonaceous biosorbents.

Sorption is a typical interfacial behavior of organic pollutants in soil and sediment systems, which plays a critical role in the transport, fate, and ecotoxicological activities, and even in the abatement and remediation measures of the organic pollutants. Therefore, sorption properties and mechanisms have been extensively concerned by scientific communities of environmental science and soil chemistry[7−9]. Recently, ubiquitous presence of black carbon species such as charcoals, chars and soots in soil, sediment and aerosols has been observed[10,11], and these particles function as supersorbents for organic pollutants[12,13]. However, correlations of sorption mechanisms with structures of the carbonaceous biosorbents are scarcely described in quantitative results[14], which are a prerequisite to prepare powerful sorbents for the purpose of their environmental benefits.

Pine is one of the most important forest species whose foliage, either on the trees (green or alive needles) or on the ground (dry or dead needles) is very flammable[15]. Biomass burning and pyrolyzing is a potential source of black carbon in forest and agricultural soils[14,15]. 4-Nitrotoluene, widely used in dye, pesticide, plastic, fabricated-fiber and adjuvant industries, is a typical organic pollutant in environments and a representative metabolite of these productions. The objective of the current study is to elucidate the relationship between the sorption mechanisms and the structures of carbonaceous biosorbents, and then to provide a theoretical and practical reference to design a cost-effective and high-efficient sorbent. By doing so, we hope to accurately predict sorption properties and mechanisms of a given sorbent. To serve these purposes, eight carbonaceous biosorbents were prepared by pyrolyzing dry pine needles, used as a precursor, at a given temperature (i.e., 100, 200, 250, 300, 400, 500, 600, and 700°C) under an oxygen-limited condition. The elemental composition (CHNO) and the specific surface areas of the carbonaceous biosorbents were analyzed. The sorption of 4-nitrotoluen to these biosorbents was investigated using a batch equilibration technique.

1 Materials and methods

1.1 Materials

The dry pine needles were collected from Xixi campus, Zhejiang University and washed four times with tap water to remove dust. After being air-dried for 2 d and subsequently oven-dried overnight at 70−80°C, the dry pine needles were ground and then passed through a 0.154 mm sieve for further treatment. For comparison, powdered activated-carbon (AC) was selected as a control. 4-Nitrotoluene was chosen as a sorbate. AC and 4-nitrotoluene of analytical grade were purchased from Shanghai Chemical Co. and used without further purification. The molecular weight, aqueous solubility, and octanol-water partition coefficient (K_{ow}) of 4-nitrotoluene are 137.1, 350 mg·L^{-1} (25°C) and 235, respectively. Based on van de Waals radii, the calculated molecular surface, defined as the occupying-surface by one tiled molecule, is 0.678 nm^2 for 4-nitrotoluene.

1.2 Preparation of carbonaceous biosorbents

The carbonaceous biosorbents were produced by pyrolyzing the pretreated pine needles at various temperatures under an oxygen-limited condition, which was modified from a previous report[14]. The oxygen to the biomass supply was controlled by this method allowing the material to be charred rather than combusted completely. In brief, the powdered pine needle sample (20 g) was placed in a ceramic pot, covered with a fitting lid and pyrolyzed under the oxygen-limited conditions for 6 h at a given temperature (i.e., 100, 200, 250, 300, 400, 500, 600 and 700°C). The resulting charred residues were pulverized for subsequent demineralization with acid. The samples were treated in a 1 mol/L HCl solution of 200 mL for 12 h and centrifuged to remove the supernatants. The residues were rinsed with deionized distilled water until the aqueous phase became neutral. The charred samples were then oven-dried overnight at 70−80°C. The carbonaceous biosorbent samples are hereafter referred to as P100, P200, P250, P300, P400, P500, P600 and P700, respectively, where the suffix numbers represent the pyrolytic temperatures.

1.3 Characterization of biosorbents

Elemental (C, H, N) analyses were conducted using an EA 112 CHN elemental analyzer (Thermo Finnigan) for all the eight carbonaceous biosorbents and the activated-carbon control in duplicate. Oxygen contents were

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calculated from mass balance because of the low ash content after the samples were treated with hydrochloride acid. The H/C and (N+O)/C atomic ratios were calculated to evaluate the aromaticity and polarity of the samples. The surface areas were measured with the N_2 adsorption method at the liquid nitrogen temperature (i.e., −196°C) using a NOVA-2000E surface area analyzer. Four data points were used to construct the plot to derive the monolayer adsorption capacity with relative pressures between 0.05 and 0.3, from which the surface areas of the biosorbents were calculated using the N_2 molecular cross-sectional area of 0.162 nm^2.

1.4 Batch sorption experiment

Sorption isotherms of 4-nitrotoluene to the eight carbonaceous biosorbent samples and one commercial activated carbon from water were plotted. All the sorption isotherms were obtained using a batch equilibration technique at room temperature ((25±0.5)°C) in Teflon screw cap vials with an aluminum foil-liner. The background solution comprised 0.01 M $CaCl_2$ made with distilled deionized water to simulate environmental water, and 200 mg/L NaN_3 to inhibit degradation of the solution by incidental bacteria. Initial concentrations of the samples ranged from 0 to 320 mg/L. The isotherms consist of ten concentration points and each point, including the blank, is in duplicate. The vials were placed on a rotating shaker and agitated in the dark at 20 r/min for 3 d. Preliminary tests indicated that the apparent equilibrium was reached before 3 d. The solution was separated from the remaining solids by centrifugation at 4000 r/min for 15 min. The equilibrium concentrations were measured by using a UV-2550 spectrophotometer at a wavelength of 284 nm. Because of minimal sorption by the vials and no biodegradation, the adsorbed amount of 4-nitrotoluene by the biosorbents was calculated by the mass difference before and after the treatment. The isotherms were plotted between the equilibrium concentration and the adsorbed amount of 4-nitrotoluene.

2 Results and discussion

2.1 Structural characteristics of the carbonaceous biosorbents

The elemental contents (CHNO) and specific surface areas of the carbonaceous biosorbents prepared under different pyrolytic temperatures are presented in Table 1. From Table 1 it can be seen that with the increase of

pyrolytic temperature, the carbon content increases from 50.34% (P100) to 84.61% (P700), while the oxygen and hydrogen contents decrease from 6.09% and 42.87%, respectively, to 1.25% and 13.04%. The atomic ratios of H/C and (N+O)/C have been widely used to represent the respective aromaticity and polarity of natural organic matter[16]. According to Table 1, the P100 sample exhibits the highest polarity ((N+O)/C=0.65) and aliphaticity (H/C=1.44) among all the samples. From P100 to P700, the polarity of the biosorbents decreases quickly and the corresponding aromaticity increases sharply. This result shows that the resultant biosorbents transformed from soft-carbonaceous matter to hard-carbonaceous matter with the increase of the pyrolytic temperature because of the condensed property of the resultant aromatic components[17]. Simultaneously, the specific surface areas increase gradually from 0.65 m^2/g (P100) to 19.92 m^2/g (P300), and jumps to 112.4 m^2/g for sample P400, and then reaches 491 m^2/g for sample P700. However, the SA of sample P500 (236.4 m^2/g) shows an exception of the trend, which is larger than that of sample P600 (206.7 m^2/g). Obviously, the pyrolytic temperature is clearly an important regulating factor on the final residue's structures, including surface areas and phase polarity, which dominate sorption properties and mechanisms of the carbonaceous biosorbents with organic pollutants. The roles of surface areas and phase polarity in sorption will be elucidated further in the following context.

2.2 Sorption properties

Sorption isotherms of 4-nitrotoluene to samples P100-P700 and the activated carbon control in aqueous solution are demonstrated in Figure 1. The sorption isotherms fit well to the Freundlich equation. The regression parameters are listed in Table 2.

From Figure 1(a) it can be seen that the sorption capacities of the samples increase in an order of P100, P200, P250, P300, and P400. However, there is an exception for this trend. With a low solute concentration, the sorption of 4-nitrotoluene to sample P400 is lower than that to sample P500, while with a higher solute concentration the result is reversed, suggesting that multi-mechanisms be involved in the sorption process. From Figure 1(b), it can be seen that the sorption capacities increase in an order of P600, P500, P700, and AC, which is in line with their specific surface areas (Table 1). The Freundlich N value (dimensionless) de-

Table 1 Elemental compositions (C, H, N and O) and atomic ratios and specific surface areas (SA, BET-N$_2$) of the carbonaceous biosorbents prepared at a given temperatures

Sample	Pyrolytic Temperature (℃)	Mass percentage				Atomic ratio			SA (m$^2 \cdot$ g^{-1})
		C (%)	H (%)	N (%)	O (%)	(N+O)/C	O/C	H/C	
P100	100	50.34	6.09	0.70	42.87	0.651	0.639	1.440	0.65
P200	200	56.58	5.66	0.87	36.88	0.502	0.489	1.191	6.22
P250	250	60.48	5.47	0.85	33.20	0.424	0.412	1.077	9.52
P300	300	67.55	4.23	1.06	27.15	0.315	0.301	0.746	19.92
P400	400	76.04	2.88	1.13	19.94	0.209	0.197	0.451	112.4
P500	500	79.38	2.20	1.08	17.34	0.175	0.164	0.329	236.4
P600	600	83.00	1.80	0.95	14.24	0.139	0.129	0.258	206.7
P700	700	84.61	1.25	1.10	13.04	0.127	0.116	0.176	490.8
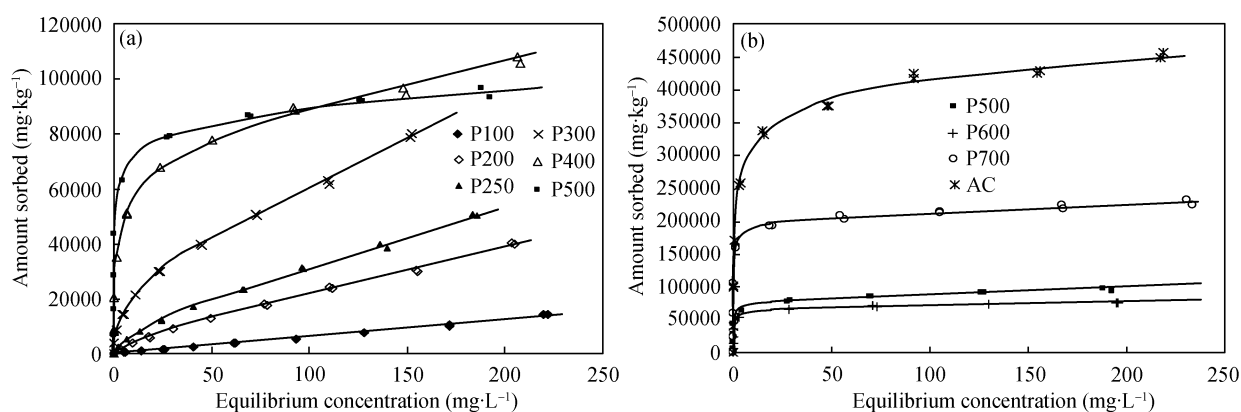
Figure 1 Sorption isotherms of 4-nitrotoluene to the carbonaceous biosorbents (P100-P700) and the activated carbon (AC) in aqueous solution.

Table 2 Regression parameters of isotherms of 4-nitrotoluene to the carbonaceous biosorbents in aqueous solution

Sample	Freundlich regression parameter[a]				Linear regression over high conc. range[b]		K_{om} (mg $\cdot$ g^{-1})	Q_{max} (mL $\cdot$ g^{-1})	$Q_{max, SA}$[c] (μmol $\cdot$ m^{-2})
	N	lgK_f	R^2	K_f	Linear equation	R^2			
P100	1.001	1.760	0.997	57.58	$Q = 57.71C_e$	0.998	57.71	0	0
P200	0.765	2.802	0.999	633.4	$Q = 172.4C_e + 3685$	0.997	172.4	3.685	4.32
P250	0.695	3.098	0.999	1254	$Q = 226.3C_e + 7414$	0.995	226.3	7.414	5.68
P300	0.499	3.768	0.999	5864	$Q = 369.9C_e + 20447$	0.995	369.9	20.45	7.49
P400	0.236	4.468	0.991	29343	$Q = 180.4C_e + 65399$	0.982	180.4	65.40	4.24
P500	0.126	4.675	0.996	47326	$Q = 102.8C_e + 72367$	0.919	102.8	72.37	2.23
P600	0.081	4.671	0.996	46914	$Q = 67.28C_e + 60355$	0.927	67.28	60.36	2.13
P700	0.070	5.167	0.987	146757	$Q = 140.0C_e + 186578$	0.896	140.0	186.6	2.77
AC	0.135	5.323	0.987	210572	$Q = 276.6C_e + 367361$	0.883	276.6	367.4	2.59

a) The Freundlich parameters (K_f and N) were calculated using the logarithmic form of equation $Q = K_f C_e^N$, where Q is the amount sorbed per unit weight of sorbent, mg $\cdot$ kg^{-1}; C_e is the equilibrium concentration, mg $\cdot$ L^{-1}; K_f [(mg $\cdot$ kg^{-1})/(mg $\cdot$ L^{-1})^N] is the Freundlich capacity coefficient, and N (dimensionless) describes the isotherm curvature. R^2 is the regression coefficient; b) linear isotherms over a high concentration range were regressed, and the slope and the intercept of the linear equation were used to calculate partition coefficient (K_{om}) and the saturated amount of adsorption (Q_{max}, mg $\cdot$ g^{-1}), respectively; c) the normalized-Q_{max} by SA (i.e., $Q_{max, SA}$) is calculated by the equation of $Q_{max, SA} = Q_{max}/SA/137.1$, where SA is the specific surface area of sorbents; 137.1 is the relative molecular weight of 4-nitrotoluene.

scribes the isotherm curvature, thus the sorption isotherm of 4-nitrotoluene to sample P100 is practically linear ($N = 1.001$), suggesting that the solute partitioning into the sorptive phase of sample P100 is the dominant mechanism. For the other samples, the isotherms are of a typical concave-downward shape at low solute concentrations, and then the concave intensity increases with increasing the pyrolytic temperatures (200℃→700℃). Correspondingly, the isotherms show transitional shapes, from moderate nonlinearity for samples P200-P300 (i.e.,

$N = 0.765-0.499$) to high nonlinearity for samples P400-P700 (i.e., $N = 0.236-0.070$). This observation may be accounted by the transitional structures of bio-sorbents, i.e., a soft matter evolving to a hard matter along with the increase of specific surface areas. Linear relationships between the isotherm regression parameters (i.e., N and $\lg K_f$) of 4-nitrotoluene and the carbonaceous biosorbent's aromaticity (represented by the H/C atomic ratio) are demonstrated in Figure 2. The N values are positively relative to the H/C ratios, while the $\lg K_f$ values are reversely dependent on the H/C ratios. According to these linear relationships, the sorption characteristics of a given biosorbent pyrolyzed at a specific temperature can be predicted. The transitional sorption will be further elucidated by the view of quantitative mechanisms of adsorption and partition.
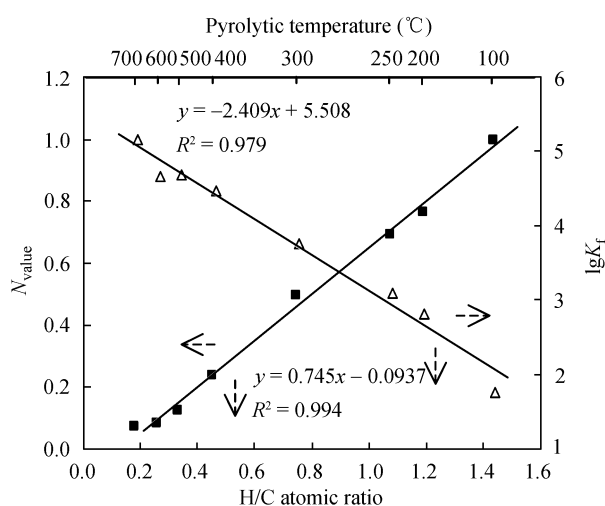
Figure 2 Relationships between the regression sorption parameters (i.e., N and $\lg K_f$) of 4-nitrotoluene to carbonaceous biosorbents and the aromaticity (i.e., H/C atomic ratio) of the biosorbents.

2.3 Sorption mechanisms

Sorption of nonionic organic pollutants from water to soil is widely believed to be dominated by partition, which was conceptualized for the first time by Chiou et al.[7,18], rather than adsorption due to suppression by co-existed water molecules. The sorption processes of organic solutes into solid phase by dissolution are regulated by soil organic matter contents rather than specific surface areas[7,18]. For sample P100 with a low SA (0.65 m²/g), the sorption capacity increases linearly with the solute equilibrium concentration, suggesting that partition of 4-nitrotoluene to the sorptive phase of sample P100 is the dominant mechanism again. The partition

coefficient (K_{om}) is used to describe the magnitude of partition as follows:

$$K_{om} = K_d / f_{om} = Q_P / C_e. \quad (1)$$

where Q_P is the sorbed-amount contributed by partition in mg/kg; C_e is the solute equilibrium concentration in water in mg/L; f_{om} is the organic matter contents and $f_{om} = 1$ for samples P100-P700; K_{om} is the f_{om}-normalized partition coefficient (K_d). According to the definition, the K_{om} value should be equal to the slope of the linear isotherms, thus $K_{om} = K_d = 57.71$ mL/g for sample P100 (Table 2). Because of the nonlinear isotherms, multi-mechanisms, including partition and adsorption, should be derived to explain the sorption to samples P200-P700. As well-known, a partition mechanism results in linear isotherms, relatively weak uptake and non-competitive behavior, while an adsorption mechanism demonstrates nonlinear isotherms, strong uptake and competitive behavior[3,4,7-9]. The quantitative contributions of partition and adsorption to total sorption of organo-clays have been successfully described by the isotherm-separation method in our previous reports[3,4]. The similar method is employed here to elucidate the transitional mechanisms with structural changes of the carbonaceous biosorbents for the purpose of providing theoretical basis to design novel sorbents.

The total sorption amount of 4-nitrotoluene to the biosorbents can be defined as follows:

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

where Q_T is the total sorbed-amount of the solute to a sorbent; Q_A and Q_P are the sorbed-amounts contributed by adsorption and partition, respectively. In a mixed adsorption-partition system, the partition effect is progressively favored by increasing solute concentrations, while the adsorption contribution reaches saturation more rapidly with the increase of the solute concentration. The isotherm at high concentrations should approach linearity. This hypothesis is substantiated by the isotherm shape in the present study, which is nonlinear at low concentrations, but practically linear at high concentrations. Correspondingly, the linear regression covering high concentration ranges was performed, and the linear regression equation is expressed as follows:

$$Q_T = a\, C_e + b. \quad (3)$$

where regression parameters of a and b are the slope and intercept of the line, and the values are listed in Table 2. Apparently linearity over the high concentration range can be observed. Logically, the a values are equal to the

magnitudes of partition coefficients (K_{om}), while the b values should be the saturated adsorption capacity (Q_{max}) of the carbonaceous biosorbents[3]. The calculated K_{om} and Q_{max} values for various biosorbents are also listed in Table 2. Based on eqs. (1) and (2), the respective contributions of partition and adsorption are calculated by

the following equations: $Q_P = K_{om}C_e$ and $Q_A = Q_T - Q_P = Q_T - K_{om}C_e$, and they are plotted with respect to the equilibrium concentrations in Figure 3.

According to Figure 3, sorption of 4-nitrotoluene to sample P100 is dominated absolutely by the partition mechanism without the presence of adsorption. With the
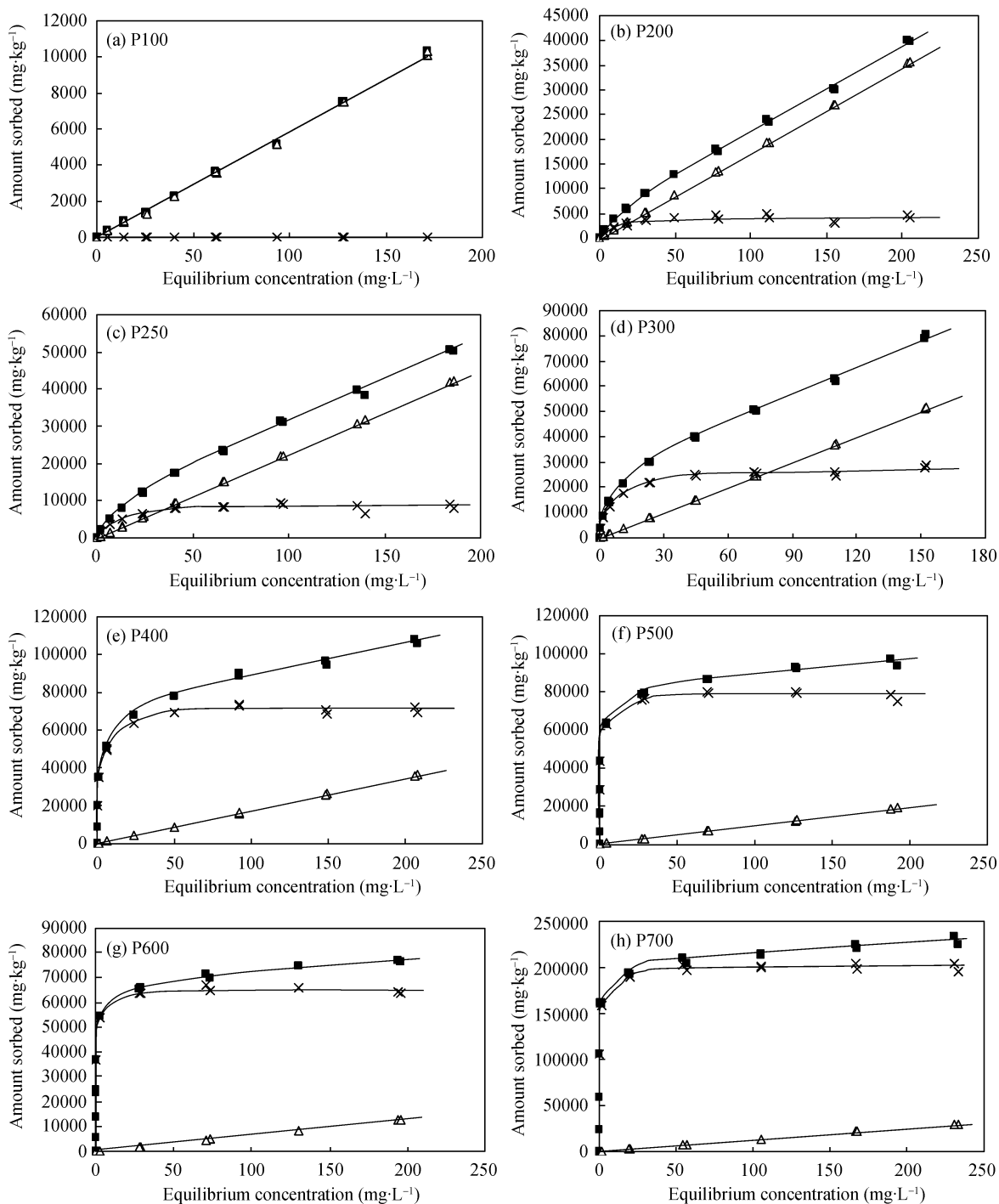

Figure 3 Respective contributions of partition (△) and adsorption (×) to total sorption (■) of 4-nitrotoluene to the carbonaceous biosorbents (samples P100-P700).

increase of the pyrolytic temperature, adsorption contributions increase in an order of P200 to P700, positively related to their SA. For samples P200, P250 and P300, sorption is controlled concurrently by partition and adsorption, and the effect of adsorption is larger than that of partition at low solute concentrations, while the effect is reversed at high concentrations. For P400, P500, P600 and P700, the adsorption contribution overwhelms the partition contributions. The correlations of K_{om} values with the polarity indices of the biosorbents (i.e., (O+N)/C) are presented in Figure 4(a). From Table 2 and Figure 4(a), it can be seen that with decreasing polarity of the biosorbents, the partition coefficient increases linearly from 57.71 mL/g (P100) to 172.4 mL/g (P200) and 226.3 mL/g (P250), and then it reaches the maximum (K_{om} = 369.9 mL/g) for P300, which is 6.5 times higher than that for P100. Then it decreases linearly to 180.4 mL/g (P400) and 102.8 mL/g (P500), and it touches the minimum (K_{om}=67.28 mL/g) for P600, which is comparative to the K_{om} value for P100. Interestingly, for sample P700, the K_{om} value rises back to 140 mL/g, which is higher than those for samples P500 and P600. This phenomenon cannot be explained by an enhanced-partition mechanism because the partition phase should be eliminated completely after pyrolyzing at 700°C. Because of the extremely low polarity, and the dramatically high surface area and aromaticity of P700, a pore-filling mechanism may be involved in sorption of sample P700[19]. To the best of our knowledge, this unique curve of K_{om}-(O+N)/C was observed for the first time. Obviously, the increased sorptions from samples P100 to P300 can be attributed to concurrent enhance-

ment of partition and adsorption. In comparison with samples P400 and P500, the dominant adsorption at low concentrations results in the total sorption magnitude in an order of P500 > P400. However, because the adsorption is saturated at high solute concentrations, partition as the controlling factor to sorption leads to an opposite result at high concentrations (see Figure 1(a)).

The observed unique relationship between the partition contribution and the polarity of sorbents can be illustrated by the compatibility and accessibility of 4-nitrotoluen with the carbonaceous biosorbents[16,20]. When pyrolytic temperature increases from 100 to 300°C, the decrease in the polarity of the resultant biosorbent promotes compatibility of the sorbent phase with 4-nitrotoluene according to the principle of "like dissolves like", thus enhancing the K_{om} values. Although the polarity of the biosorbents further decreases at a higher pyrolytic temperature($\geqslant$400°C), the accompanying transition of a "soft matter" to a "hard matter" limits the accessibility of the final biosorbents to 4-nitrotoluene, thus dramatically reducing the K_{om} values. The relationship between the saturated adsorption capacity (Q_{max}) and specific surface areas (SA) of the carbonaceous biosorbents is plotted in Figure 4(b). The Q_{max} values increase linearly with the increase of the SA and they reach maximum (186.6 mg/g) for sample P700, but the maximal Q_{max} value for the biosorbents samples is still less than the Q_{max} value for AC (367.4 mg/g). The good linear relationship of Q_{max} with respect to SA partially suggests that it be reasonable to adopt the isotherm-separation method to quantify the respective contributions of partition and adsorption.
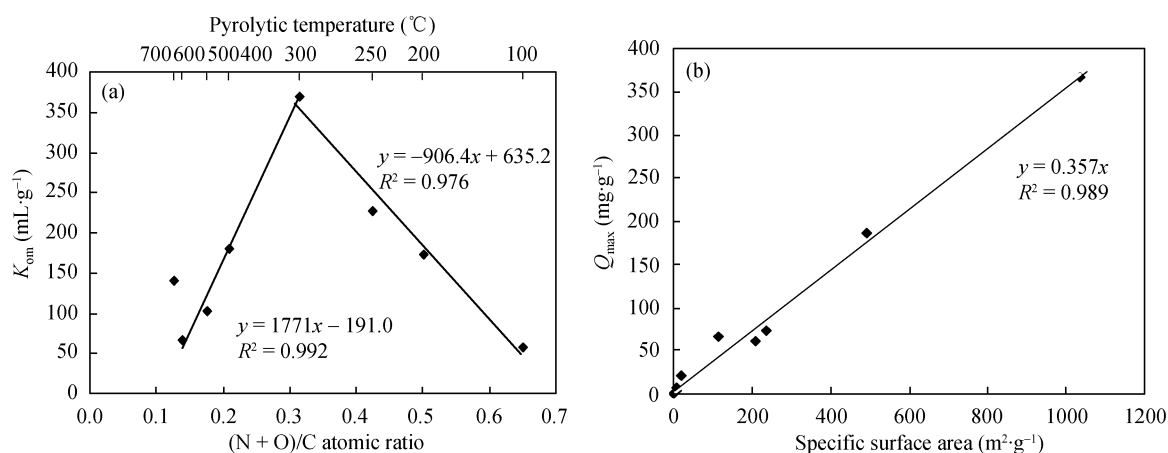

Figure 4 Correlation of 4-nitrotoluen sorption mechanisms with structural characteristics of the carbonaceous biosorbents. (a) Partition coefficient (K_{om}) with the polarity of biosorbents polarities ((N+O)/C); (b) maximal adsorption amount (Q_{max}) with the specific surface areas.

For further illustration of saturated adsorption, the Q_{max} (mg/g) should be normalized by the SA and then its unit (mg/g) should be transformed into the unit of $\mu mol/m^2$ ($Q_{max,SA}$) as follows:

$$Q_{max,SA}(\mu mol/m^2) = \frac{Q_{max}(mg/g) \times 1000(\mu mol/mmol)}{SA(m^2/g) \times M(mg/mmol)}.$$

(4)

where SA is the specific surface area of the carbonaceous biosorbents, m^2/g; M is the molecular weight of 4-nitrotoluene, 137.1 mg/mmol; 1000 is the unit conversion factor. The calculated values of $Q_{max,SA}$ are listed in Table 2. According to the molecular structure and dimension demonstrated in Figure 5, the estimated tiled molecular surface of 4-nitrotoluene is 0.678 nm^2. Correspondingly, the theoretical maximal sorbed-amount ($Q_{max,MN}$) in monolayer arrangement is 2.45 $\mu mol/m^2$. From the last column of Table 2, it can be seen that the $Q_{max,SA}$ values for the biosorbents of a hard-matter state (i.e., P500, P600, P700 and AC) are in the range of 2.13－2.77 $\mu mol/m^2$, which are comparable to the $Q_{max,MN}$ value (i.e., 2.45 $\mu mol/m^2$), suggesting that surface coverage dominates the adsorption mechanism. While for the biosorbents of a soft-matter state (i.e., P200, P250, P300 and P400), the $Q_{max,SA}$ values (i.e., 4.32－7.49 $\mu mol/m^2$) are larger than the $Q_{max,MN}$ value, indicating that an additional adsorption mechanism besides surface coverage may be involved in the total sorption process.
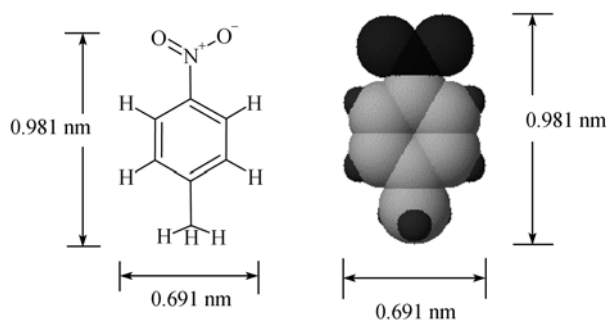
Figure 5 Scheme of 4-nitrotoluene molecular structure and its molecular dimension.

3 Conclusions

(1) The carbonaceous biosorbents produced exhibit powerful sorptive capability for organic pollutant in water. Their sorption properties and mechanisms are dominated by their surface areas and structures, which are regulated by the pyrolytic temperature. With the increase of the pyrolytic temperature, the aromaticity of the biosorbents (the H/C ratios) and the specific surface areas increase dramatically, and the polarity indices ((N+O)/C ratio) decrease sharply; correspondingly the soft matter evolves into a hard matter. The linear relationships between the isotherm regression parameters (i.e., N and lgK_f) and the aromaticity of the biosorbents provide an engineering reference to design a unique biosorbent and to predict its sorption characteristics.

(2) The respective contributions of adsorption and partition were quantified, which correspond to the structures of the biosorbents. Adsorption contributions increase with the pyrolytic temperature, and the saturated sorbed-amount is linearly correlated with the SA. For the sorbents of a hard-matter state (i.e., P500, P600, P700 and AC), the $Q_{max,SA}$ values (2.13－2.77 $\mu mol/m^2$) are comparable to the theoretical estimation (i.e., 2.45 $\mu mol/m^2$), suggesting that surface coverage dominates the adsorption mechanism. While for the sorbents of a soft-matter state (i.e., P200, P250, P300 and P400), the larger $Q_{max,SA}$ values (i.e., 4.32－7.49 $\mu mol/m^2$) indicate that an additional adsorption mechanism besides surface coverage may be involved in the total sorption process.

(3) The unique curve of partition contributions (K_{om}) with respect to the polarity of the biosorbents can be attributed to compatibility and accessibility of the carbonaceous biosorbent with the tested solute. With increasing pyrolytic temperatures, the values of K_{om} increase linearly from 57.71 mL/g (P100) to 369.9 mL/g (P300), and then decrease linearly to 67.28 mL/g (P600). The unexpected restore of K_{om} for sample P700 may result from a pore-filling mechanism rather than a partition mechanism.

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