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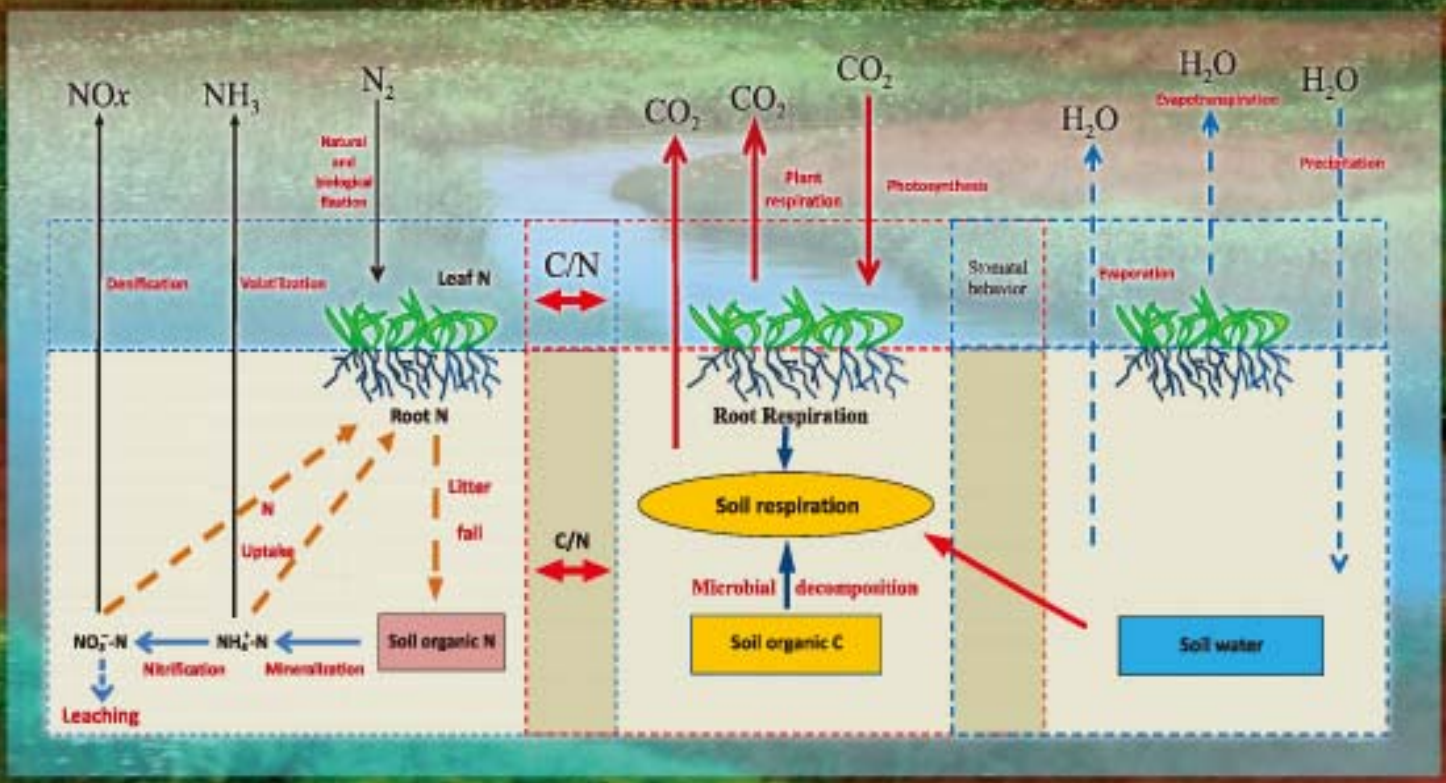

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Removal of polycyclic aromatic hydrocarbons from aqueous solution by raw and modified plant residue materials as biosorbents

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ABSTRACT

Removal of polycyclic aromatic hydrocarbons (PAHs), e.g., naphthalene, acenaphthene, phenanthrene and pyrene, from aqueous solution by raw and modified plant residues was investigated to develop low cost biosorbents for organic pollutant abatement. Bamboo wood, pine wood, pine needles and pine bark were selected as plant residues, and acid hydrolysis was used as an easily modification method. The raw and modified biosorbents were characterized by elemental analysis, Fourier transform infrared spectroscopy and scanning electron microscopy. The sorption isotherms of PAHs to raw biosorbents were apparently linear, and were dominated by a partitioning process. In comparison, the isotherms of the hydrolyzed biosorbents displayed nonlinearity, which was controlled by partitioning and the specific interaction mechanism. The sorption kinetic curves of PAHs to the raw and modified plant residues fit well with the pseudo second-order kinetics model. The sorption rates were faster for the raw biosorbents than the corresponding hydrolyzed biosorbents, which was attributed to the latter having more condensed domains (i.e., exposed aromatic core). By the consumption of the amorphous cellulose component under acid hydrolysis, the sorption capability of the hydrolyzed biosorbents was notably enhanced, i.e., 6–18 fold for phenanthrene, 6–8 fold for naphthalene and pyrene and 5–8 fold for acenaphthene. The sorption coefficients (K_d) were negatively correlated with the polarity index [(O+N)/C], and positively correlated with the aromaticity of the biosorbents. For a given biosorbent, a positive linear correlation between logK_{oc} and logK_{ow} for different PAHs was observed. Interestingly, the linear plots of logK_{oc}–logK_{ow} were parallel for different biosorbents. These observations suggest that the raw and modified plant residues have great potential as biosorbents to remove PAHs from wastewater.

Introduction

Polycyclic aromatic hydrocarbons (PAHs), predominantly originating from the combustion of fossil fuels and biomass, have been widely detected in numerous surface water and groundwater (Boving and Zhang, 2004; Chen et al., 2004). PAHs are of significant environmental concern due to their high bioaccumulation and potential mutagenic and carcinogenic properties (Nizzetto et al., 2008; Chen et al., 2010; Pan et al., 2011). Due to their low solubility and resistance to mineralization, some typical treatment methods, including chlorination, oxidation and ultrasonic irradiation, are not effective in removing PAHs from aqueous solution (Changchaivong and Khaodhiar, 2009).

Sorption is one of the most effective methods to remove organic pollutants at low concentration, and conventional sorbents such as activated carbon and resin have been widely used and displayed good performance in PAHs removal (Zimmerman et al., 2004). However, their comparably high cost limits the treatment of large amounts of wastewater and storm water. Biosorption is considered a

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cost-effective method to remove pollutants from wastewater. For example, the biosorption of heavy metal, dyes and pesticides by biomaterials such as fungi, bacteria, algae, peat and wood fiber have been extensively investigated (Ho et al., 2005; Montazer-Rahmati et al., 2011; Aksu, 2005; Boucher et al., 2007; Calderóna et al., 2008; Eberhardt et al., 2006). However, the use of biosorbents for removing PAHs in the environment has received considerably less attention (Chung et al., 2007). So far, studies on the biosorption of PAHs have mainly concentrated on microorganism and algae biomass, and the roles of raw and modified plant residues on the removal of PAHs need more study (Aksu, 2005; Huang et al., 2006; Chen et al., 2010, 2011; Li et al., 2010).

Plant residues, mainly generated from the agricultural industry, are significant components of bio-solid waste, and are considered one of the most abundant, cheap and renewable resources (Santana-Méridas et al., 2012). Developing plant residues as biosorbents for wastewater treatment is of increasing concern due to their relative high sorption capacities for persistent organic pollutants and ease of modification to higher sorption capacity materials (Ho et al., 2005; Huang et al., 2006; Li et al., 2010). Boving and Zhang (2004) found that aspen wood was an effective sorbent for PAH removal. High sorption affinity with phenanthrene by raw and brewed tea leaves was also reported (Lin et al., 2007). However, the sorption of PAHs by modified plant residues has drawn less attention.

The sorption properties of biosorbents are significantly influenced by their structural characteristics, such as polarity and aromaticity. Li et al. (2010) reported that lignin was the main aromatic component of natural plant residues, and the powerful sorption potential of lignin was seriously restricted by the coexisting polysaccharide (polar component). By removing the sugar component with acid hydrolysis, the sorption capacity of modified plant residues could be notably enhanced. However, more studies on raw and modified biosorbents are needed to further elucidate the relationship between sorption properties and kinetics of biosorbents with their structural characteristics, providing an engineering basis for the application of modified plant residues in persistent organic pollutants removal.

The main objective of this study was to elucidate the relationship between PAH sorption with the structural characteristics of biosorbents. To this end, four plant residues including bamboo wood (BW), pine wood (PW), pine needles (PN) and pine bark (PB) were selected and modified via acid hydrolysis to obtain different biosorbents. All samples were characterized by elemental analysis, Fourier transform infrared (FT-IR) spectroscopy and scanning electron microscopy (SEM). Naphthalene, acenaphthene, phenanthrene and pyrene were chosen as the model PAHs because they are widespread in wastewater and surface water.

1 Materials and methods

1.1 Preparation of plant samples

Four plant residues samples, i.e., BW, PW, PN and PB, were collected from Zhejiang Province, China on October 2012. These plant samples were washed with deionized distilled water to remove dust and were then oven-dried for 12 hr at 70°C, ground with a pulverizer, and sieved to less than 0.154 mm, yielding raw biosorbent samples. The raw plant samples were modified by acid hydrolysis, using a reported method (Chen et al., 2008). Acid hydrolysis, conducted in 6 mol/L HCl solution with refluxing for 6 hr at 100°C, was used to eliminate the polysaccharide component from BW, PW, PN and PB, and produced de-sugared bamboo wood (BW-DS), de-sugared pine wood (PW-DS), de-sugared pine needles (PN-DS) and de-sugared pine bark (PB-DS), respectively. All de-sugared residues were separated from the acidic solution by filtration and then were washed with deionized distilled water to adjust these residues to neutral conditions and to remove dissolved organic matter sorbed by the residues. All raw and modified plant samples were oven-dried at 60°C, ground, and sieved to less than 0.154 mm before analysis and sorption experiments. The sugar contents of the four raw plant samples were calculated from the yields of the modified fractions.

1.2 Characterization of plant samples

The contents of C, H and N in the raw and modified biosorbents were determined via a Flash EA 1112 CHN elemental analyzer (ThermoFinnigan), while the oxygen content was calculated by the mass difference. The atomic ratios of H/C and (O+N)/C were calculated to measure the aromaticity and polarity of samples, respectively. FT-IR spectra of plant samples were obtained over a wave number range of 4000 to 400 cm^{-1} on a Nicolet 6700 FT-IR with a resolution of 4.0 cm^{-1}. Plant samples (1.5 mg) were mixed with 100 mg KBr (to ensure 20%–80% transmittance rate) and compressed into pellets, then subjected to FT-IR analysis. The raw and modified plant samples were examined with a Hitachi S4800 scanning electron microscope (Japan) under high vacuum conditions and at an accelerating voltage of 3.0 kV in order to observe the surface morphology of the samples. For SEM, all samples were coated with gold in a sputter coater before being examined.

1.3 Kinetic sorption experiments

Phenanthrene, naphthalene, acenaphthene and pyrene were chosen as representative PAHs due to their different molecular properties and ubiquity in the environment. Their respective physicochemical properties are listed in **Table 1**. All chemicals were of analytical grade, and used without

Table 1 Physicochemical properties of selected PAHs

PAHs	MF	MW	S_w (mg/L)	K_{ow}
Naphthalene	$C_{10}H_8$	128.2	31.02	1.95×10^3
Acenaphthene	$C_{12}H_8$	154.2	3.47	8.4×10^3
Phenanthrene	$C_{14}H_{10}$	178.2	1.29	2.8×10^4
Pyrene	$C_{16}H_{10}$	202.3	0.13	8.0×10^4

MF: molecular formula; MW: molecular weight; S_w: aqueous solubility at 25°C; K_{ow}: octanol-water partition coefficient.

further treatment. Initial PAH water solutions were made by dissolving certain amounts of PAH into a background solution containing 0.01 mol/L $CaCl_2$ and 200 mg/L NaN_3 (as a bioinhibitor) in deionized water. To conduct the sorption kinetic experiments, the initial concentration was 1 mg/L for phenanthrene, 25 mg/L for naphthalene, 2.8 mg/L for acenaphthene and 0.1 mg/L for pyrene. After the initial PAH amount and a given biosorbent were added to sample vials, the vials were placed on a rotating shaker and agitated end-over-end in the dark at 30 r/min and 25 ± 1°C for time periods of 0.5 to 90 hr. Thereon, two sample vials for each biosorbent were centrifuged at 3500 r/min for 15 min, and 500 μL aliquots of the supernatants were taken to determine the PAH concentration in the solution by high performance liquid chromatography (HPLC, Agilent 1200). The amount sorbed by biosorbents was calculated from the sorbate concentration difference in solution. To take the centrifugation time into consideration, each sampling time of kinetic sorption experiment was adjusted by extending it 15 min.

1.4 Batch sorption experiments

Sorption isotherms of phenanthrene to the eight biosorbents (including raw and modified biomass samples) were obtained to elucidate the effects of biosorbent structural characteristics on the sorption capacities. To clarify the effect of PAH properties on sorption, the raw PW and PN, and PW-DS and PN-DS were selected as representative biosorbents to sorb phenanthrene, naphthalene, acenaphthene and pyrene. In brief, the initial concentrations ranged from 0.008 to 1 mg/L for phenanthrene, from 0.2 to 25 mg/L for naphthalene, from 0.022 to 2.8 mg/L for acenaphthene, and from 0.0008 to 0.1 mg/L for pyrene. All sorption isotherms were obtained in a background solution (pH = 7) containing 0.01 mol/L $CaCl_2$ in double-distilled water with 200 mg/L NaN_3 as a biocide. Each isotherm contained ten concentration points including the blank control (containing sorbent without PAHs); each point, including calibration control (containing PAHs without sorbent), was run in duplicate. The desired amount (1–40 mg) biosorbent was placed into 8 mL, 22 mL or 40 mL screw cap vials that were then filled completely with sorbate solution to minimize evaporation and ensure 30%–80% removal rate of sorbate, sealed aluminum foil and agitated in the dark for 3 days at 25 ± 0.5°C to reach an apparent equilibrium (prior tests indicated that sorption equilibrium was achieved in less than 2 days). After 3 days equilibration, the solution was separated by centrifugation at 3500 r/min for 15 min, and then 500 μL supernatant was mixed with 500 μL acetonitrile for HPLC analysis. The equilibrium concentrations of PAHs were measured by an Agilent 1200 HPLC fitted with a G1321A fluorescence detector and Agilent Eclipse XDB-C 18 column (4.6 mm × 250 mm × 5 μm). Injection volumes of 15 μL, a mobile phase of 90% acetonitrile/10% water for phenanthrene, naphthalene, acenaphthene and 95% acetonitrile/5% water for pyrene, with a flow rate of 1 mL/min, were used. The respective excitation wavelengths of phenanthrene, naphthalene, acenaphthene and pyrene were 244, 220, 220 and 237 nm, and the emission wavelengths were 360, 325, 315 and 385 nm. Because sorption by the vials was negligible, and the losses by evaporation, biodegradation and photodegradation were insignificant, the sorbed solute was calculated by the aqueous concentration difference of sorbate between the control and calibration.

1.5 Data analysis

The sorption isotherms were fitted by the Freundlich model, and the regression parameters ($\log K_f$ and N) were calculated using the logarithmic form of Eq. (1) by Origin Pro8.5.

$$Q = K_f C_e^N \quad (1)$$

where, Q (μg/g) is the amount sorbed per unit weight of sorbent; C_e (mg/L) is the equilibrium concentration in the aqueous solution; K_f ((μg/g)/(mg/L)^N) is the Freundlich capacity coefficient, and N (dimensionless) describes the isotherm curvature. Sorption coefficients (K_d) were calculated from the slope of the linear isotherms and K_{oc} values were calculated by normalizing K_d to the carbon level (f_{oc}) of each plant sample.

2 Results and discussion

2.1 Characterization of plant samples

The sugar contents and elemental compositions of the raw and modified plant samples are presented in **Table 2**. The four selected raw plant residues contained a high content of carbon, hydrogen and oxygen, and low content of nitrogen. Compared with the other three raw plant residues, the BW presented the lowest carbon content and highest oxygen content, thus producing the highest polarity index [(O+N)/C = 0.75] and highest aliphatic carbon (H/C = 1.58). The result was attributed to the high sugar content of BW (67.2%). In contrast, the PN exhibited the highest carbon content and lowest oxygen content, thus producing the lowest polarity index [(O+N)/C = 0.65] and high aromaticity, which was consistent with the result that the

Table 2 Elemental analysis, atomic ratios and sugar contents of plant samples

Sample	Sugar (%)	C (wt%)	H (wt%)	N (wt%)	O* (wt%)	H/C	O/C	(O+N)/C
BW	67.2	46.83	6.18	0.42	46.57	1.58	0.75	0.75
BW-DS	–	64.64	4.78	0.35	30.23	0.89	0.35	0.36
PW	56.8	50.01	6.32	0.45	43.22	1.52	0.65	0.66
PW-DS	–	64.98	5.68	0.36	28.98	1.05	0.33	0.34
PN	51.9	50.22	6.30	0.65	42.83	1.51	0.64	0.65
PN-DS	–	63.87	5.49	0.42	30.22	1.03	0.35	0.36
PB	52.6	49.96	5.93	0.63	43.48	1.42	0.65	0.66
PB-DS	–	63.93	4.90	0.37	30.80	0.92	0.36	0.37

BW, PW, PN and PB are the raw samples of bamboo wood, pine wood, pine needles and pine bark; while BW-DS, PW-DS, PN-DS and PB-DS are the modified samples of de-sugared bamboo wood, de-sugared pine wood, de-sugared pine needles and de-sugared pine bark, respectively.

* Oxygen content was calculated by mass difference.

PN presented the lowest sugar content (51.9%). After acid hydrolysis, the organic carbon content of the modified samples increased with the decrease of oxygen content; correspondingly, the polarity indexes dropped markedly and aromaticity enhanced notably due to the removal of polysaccharides (polar components). The raw BW, having the highest sugar content, presented the greatest changes in polarity and aromaticity after acid hydrolysis, i.e., the (O+N)/C ratio decreased from 0.75 to 0.36 and the H/C ratio decreased from 1.58 to 0.89. With the lowest sugar content, the raw PN presented relatively less change in polarity and aromaticity after acid hydrolysis. The BW-DS exhibited the highest aromaticity among the tested samples. Presumably, the different structural characteristics would significantly affect the sorption properties and kinetics of the raw and modified plant residues with organic pollutants (Chen et al., 2005; Huang et al., 2006; Li et al., 2010).

The FT-IR spectra between 4000 and 400 cm^{-1} for the plant samples are shown in **Fig. 1**. The large band at 3426 cm^{-1} represents the stretching vibration of hydroxyl groups. The peaks at 2925, 2854, 1460, 1377 and 1324 cm^{-1} are assigned mainly to CH_2 units in biopolymers (Chen et al., 2005). For the raw samples, the bands at 1705, 1737 and 1160 cm^{-1} are assigned to C=O and C–O stretching vibrations of ester bonds. The band at 1605 cm^{-1} is assigned to aromatic C=C and C=O and the peak at 1510 cm^{-1} represents the C=C ring stretching vibration of lignin (Chen et al., 2008). The band at 1270 cm^{-1} is assigned to the aromatic CO– and phenolic –OH stretching (Chun et al., 2004). The peaks at 1041 and 1028 cm^{-1} are assigned to C–O–C stretching of polysaccharides.

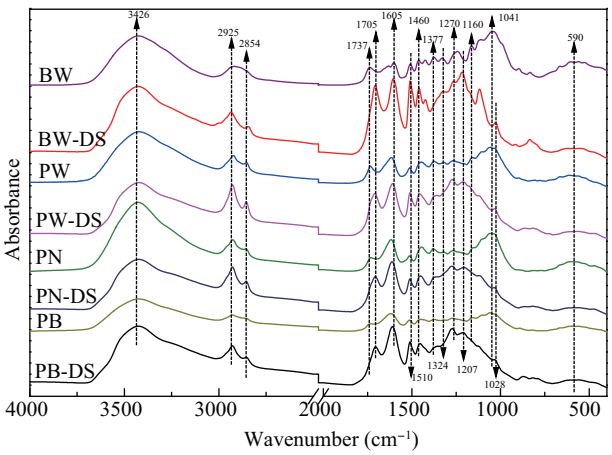

Fig. 1 Fourier transform infrared spectra of the raw and modified plant samples.

The BW was dominated by C–O–C bands due to its high polysaccharide content. After acid hydrolysis, the polysaccharides were removed, and then the FT-IR spectrum of de-sugared samples were dominated by peaks at 1705 (carbonyl stretch of –COOH group), 1605 and 1510 cm^{-1} (C=C stretching vibration in the aromatic ring) as well as phenolic –OH (1270 cm^{-1}), indicating that aromatic bands were the major functional groups in de-sugared fractions. Therefore, it can be seen in **Fig. 1** that the BW-DS presented the highest aromaticity compared with the other plant samples, which is consistent with the elemental analysis. Peaks of –OH (3426 cm^{-1}) and C–O–C (1041 and 1028 cm^{-1}) of carbohydrates were sharply reduced and CH_2 bands (2925, 2854 and 1460 cm^{-1}) became stronger after acid hydrolysis. The aliphatic moieties and aromatic core were exposed by removing polysaccharides (Chen et al., 2008; Li et al., 2010).

The surface morphologies of the raw and modified plant residues were observed using a SEM (**Fig. 2**). It can be seen that the surface morphologies of the raw BW and PN were abundant, and the availability of pores and internal surface is clearly displayed in the image. After acid hydrolysis treatment, the skeleton structure still existed in the samples of BW-DS and PN-DS. The surface morphologies of BW-DS and PN-DS was more uneven and rougher than the raw BW and PN. The acid hydrolysis did not induce any obvious damage to the structure of raw samples.

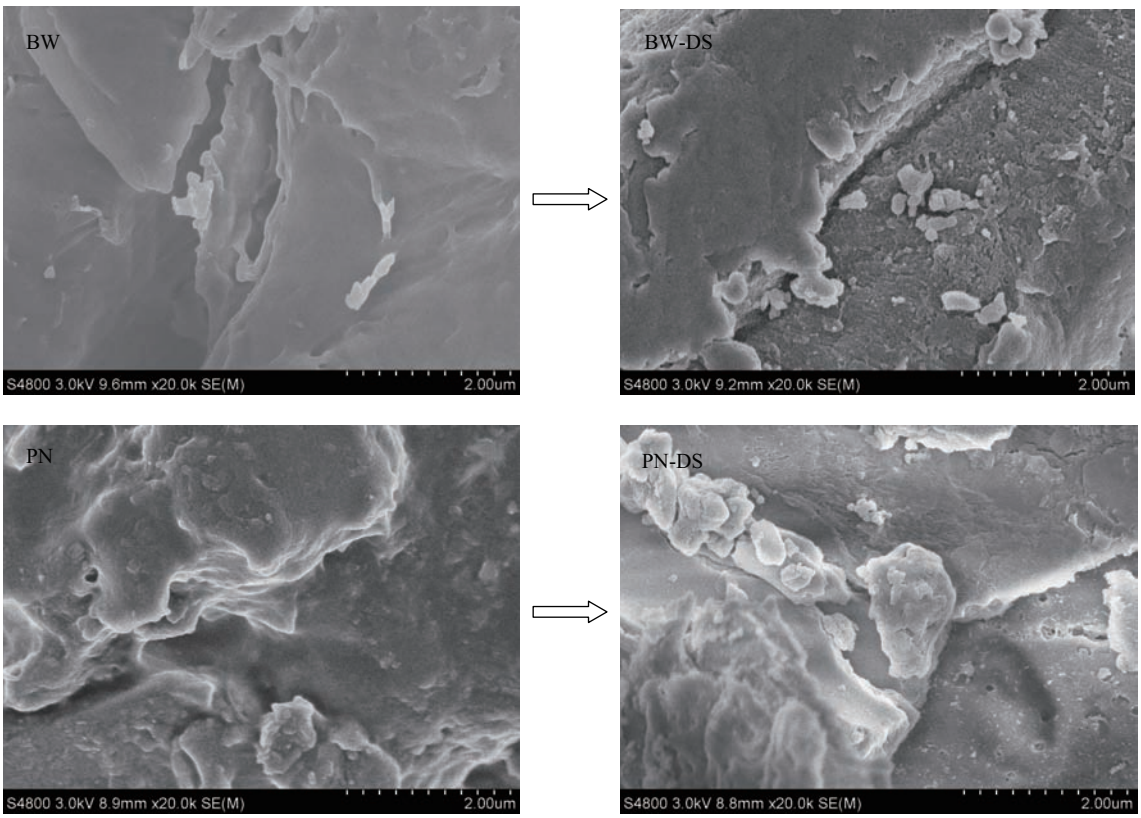

Fig. 2 SEM images of the raw and hydrolyzed plant residues including BW, PN, BW-DS and PN-DS.

2.2 Sorption properties of plant samples with PAHs

In order to investigate the sorption properties of plant samples with PAHs, sorption kinetics experiments were carried out and the kinetic curves are presented in **Fig. 3**. To better elucidate the mechanism of rate-controlling step in the sorption process of the raw and modified biosorbents, Lagergren's pseudo first-order and pseudo second-order kinetic models were used to fit the experimental data (Chen et al., 2011; Dawood and Sen, 2012).

The pseudo first-order Lagergren model is expressed as Eq. (2) (Sen et al., 2011):

$$\log(q_e - q_t) = \log q_e - k_1 t/2.303 \quad (2)$$

where, q_e (μg/g) and q_t (μg/g) represent the amounts of PAHs sorbed at equilibrium and at time t (hr), respectively, and k_1 (hr^{-1}) is the pseudo first-order rate constant. The pseudo second-order kinetic model is expressed as Eq. (3) (Sen et al., 2011):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where, k_2 (g/(μg·hr)) is the pseudo second-order rate constant. The values of kinetic model parameters (q_e, k_1 and k_2) along with the corresponding correlation coefficients can be derived using Origin Pro8.5. The regression results are presented in **Table 3**. It is clear that the correlation coefficients for the pseudo second-order kinetic model are higher in comparison with the pseudo first-order kinetic model, and the former presents a good fit ($R^2 > 0.90$). The calculated values of q_e based on the pseudo second-order kinetic model agreed fairly well with the experimental data, indicating that the sorption kinetics of the biosorbents follows pseudo second-order kinetics.

As shown in **Fig. 3**, for phenanthrene, the sorption processes of the four raw samples were mostly completed within the first 2 hr of reaction and then became more gradual until equilibrium was reached within 24 hr; while the sorption processes of the four modified samples were mostly completed within the first 10 hr and equilibrium was reached within 40 hr. For naphthalene, the sorption processes of PW and PN were mostly completed within the first 1 hr of reaction, and then became more gradual until the equilibrium was reached after 24 hr, while the equilibrium time of PW-DS and PN-DS became longer, increasing to 40 hr. For acenaphthene, the equilibrium time of PW and PN was 24 hr, and PW-DS and PN-DS presented a longer equilibrium time, rising to 48 hr. For pyrene, the equilibrium times of the raw plant residues (PW and PN) and the modified samples (PW-DS and PN-DS) were 28 hr and 50 hr, respectively. These observations suggest that the de-sugared samples exhibited a slower

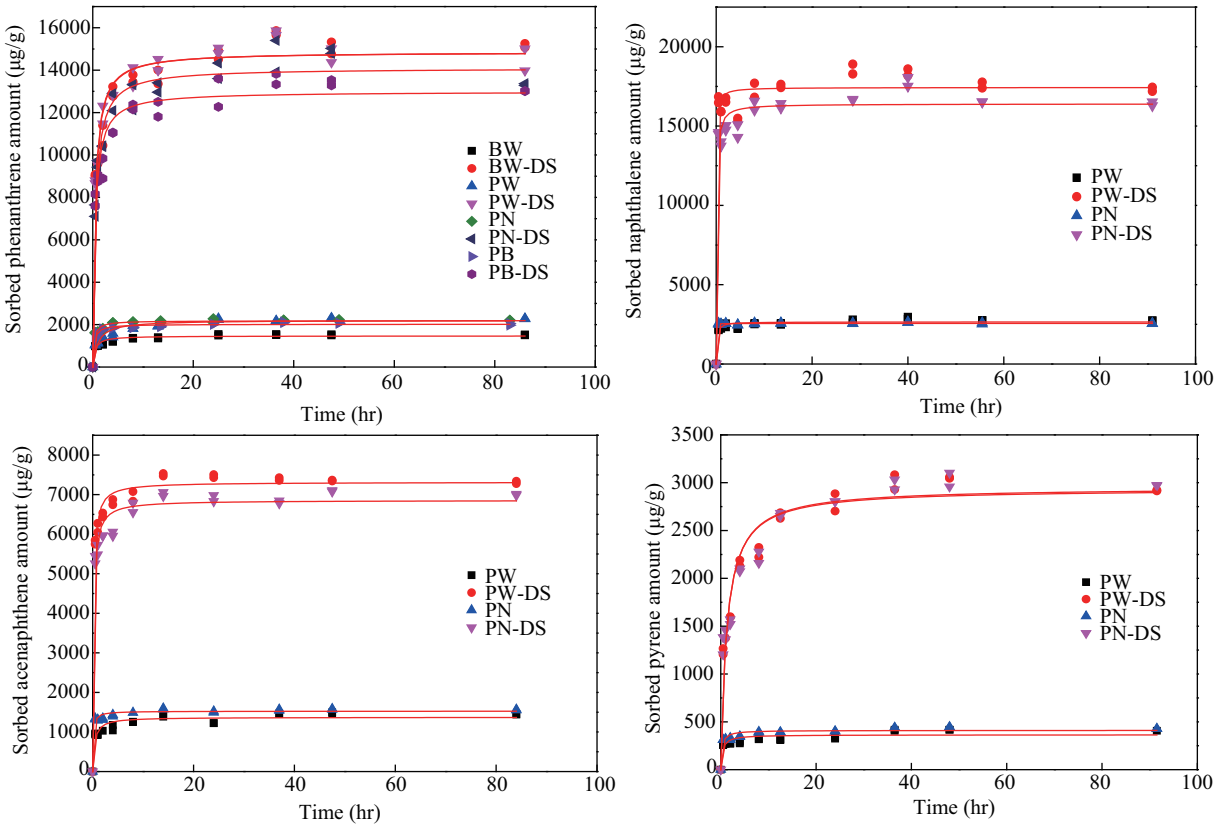

Fig. 3 Lagergren's pseudo-second-order kinetic model for PAHs sorption kinetics by the raw and modified plant samples used as biosorbents.

Table 3 Kinetic parameters of PAH sorption by plant samples by the pseudo first- and second-order models.

Organic pollutants	Sorbent	$q_{e,exp}$ (μg/g)	First-order kinetic model			Second-order kinetic model		
			k_1 (hr^{-1})	$q_{e,cal}$ (μg/g)	R^2	k_2 (g/(μg·hr))	$q_{e,cal}$ (μg/g)	R^2
Phenanthrene	BW	1553.88	0.027	1396.18	0.802	0.00168	1467.03	0.918
	BW-DS	15865.32	0.022	14200.42	0.863	0.0014	14863.16	0.952
	PW	2318.05	0.012	2076.39	0.819	0.00046	2212.02	0.926
	PW-DS	15866.5	0.022	14230.00	0.905	0.00015	14855.63	0.968
	PN	2277.22	0.037	2109.24	0.897	0.0019	2182.90	0.964
	PN-DS	15403.15	0.020	13463.81	0.903	0.00014	14097.71	0.961
	PB	2127.32	0.034	1953.85	0.939	0.0019	2019.59	0.980
	PB-DS	13824.85	0.023	12399.53	0.856	0.00017	12992.47	0.948
Naphthalene	PW	2820.61	0.055	2586.43	0.890	0.00272	2653.52	0.926
	PW-DS	18902.99	0.111	17189.62	0.934	0.00122	17434.17	0.946
	PN	2635.76	0.168	2550.42	0.993	0.04105	2558.39	0.994
	PN-DS	18068.64	0.070	16009.71	0.910	0.00058	16399.21	0.946
Acenaphthene	PW	1497.9	0.029	1307.45	0.768	0.00193	1372.58	0.879
	PW-DS	7533.47	0.049	7120.42	0.943	0.00086	7315.19	0.982
	PN	1597.8	0.067	1487.38	0.920	0.00578	1526.26	0.960
	PN-DS	7106.92	0.047	6644.69	0.912	0.00079	6856.04	0.966
Pyrene	PW	417.7	0.034	344.59	0.682	0.0078	364.11	0.793
	PW-DS	3084.4	0.008	2770.82	0.855	0.00027	2950.95	0.941
	PN	447.56	0.042	393.67	0.820	0.00989	410.78	0.909
	PN-DS	3103.27	0.009	2748.61	0.825	0.00027	2935.91	0.924

sorption rate than that of the corresponding raw samples, which is attributed to the increase of aromaticity of the de-sugared samples as well as the decrease of polarity (**Table 2**).

Based on **Table 3**, the sorption rate (k_2) of PAHs onto the raw biosorbents was relatively faster than that for the hydrolyzed samples. Previous sorption studies have indicated that the condensed domain was mainly composed of aromatic moieties (Chen et al., 2005), while the expanded domain appeared to be enriched mainly in aliphatic carbons (Johnson et al., 2001). Furthermore, the sorption rate of a solute with a natural sorbent is controlled largely by the solute's diffusivity in the sorbent's partition phase, in which the medium's compactness directly affects the solute diffusivity (Chen et al., 2012). The polar moieties of cellulose and hemicellulose in plant residues may strongly interact with water to loosen up the structure of the organic matter for the partition uptake of organic pollutants. Therefore, the fast partitioning with the water-saturated organic phase of the raw plant residues would predominate for PAH uptake. After removal of hemicellulose, the polar moieties in the modified samples were decreased, and the condensed organic domains dominated PAH sorption. The k_2 of biosorbents was affected by the molecular dimensions of the PAHs. Among the tested sorbates, the k_2 of naphthalene, with the smallest size, displayed the largest value, while the k_2 of pyrene was ranked lower due to having the largest size.

2.3 Sorption isotherms of phenanthrene by the raw and modified plant samples

Sorption isotherms of phenanthrene onto the raw and modified plant samples are presented in **Fig. 4a**. The sorption isotherms fit well with the Freundlich model, and their linear and Freundlich regression parameters are listed in **Table 4**. Sorption coefficients (K_d and K_{oc}) and K_{oc}/K_{owc} ratios were also calculated. The sorption isotherms of phenanthrene by the four raw plant residues (BW, PW, PN and PB) were essentially linear as indicated by the Freundlich exponent N ranging from 0.94–1.04, indicating a predominant partition process. The Freundlich exponent N values of the de-sugared samples were all less than those of the corresponding precursor materials for a given PAH compound, which indicated that all de-sugared biosorbents exhibited more nonlinear isotherms compared with the raw biosorbents.

Partition coefficient (K_d) is used to describe the sorption efficiency for organic pollutants. The K_d values of the four raw plant residues for phenanthrene ranked in the order of BW (2896 L/kg) < PB (5445 L/kg) < PN (6370 L/kg) < PW (6754 L/kg). Polysaccharides have been found to play a negative role in the sorption capacity of pollutants on biosorbents (Li and Chen, 2009; Li et al., 2010; Chen and Li, 2007), which was also confirmed in the current study. A negative correlation for K_d values with the sugar content for bamboo wood, pine wood, PN and pine bark was obtained ($K_d = -207.11x + 17197$, $R^2 = 0.709$), indicating that the polar sugars played a crucial role in PAHs sorption to plant residues. With acid hydrolysis treatment of the raw plant residues, the sorption capacities of the de-sugared samples increased greatly. The K_d values of phenanthrene onto the four modified plant residues ranked in the order of PB-DS (32693 L/kg) < PN-DS (38375 L/kg) < BW-DS (51464 L/kg) < PW-DS (55763 L/kg). The K_d ratios of phenanthrene by biosorbents after and before modification were calculated, i.e., $K_{d,BW\text{-}DS}/K_{d,BW} = 17.77$, $K_{d,PW\text{-}DS}/K_{d,PW} = 8.26$, $K_{d,PN\text{-}DS}/K_{d,PN} = 6.02$, $K_{d,PB\text{-}DS}/K_{d,PB} = 6.00$. It is found that the K_d ratios have a positive correlation with the sugar content of the raw samples. Li et al. (2010) pointed out that the powerful sorption capacity of aromatic domains was seriously suppressed by the coexisting polysaccharide component. Therefore, acid hydrolysis was an effective modification method to enhance sorption capacities of biosorbents.

2.4 Effects of PAH properties on the biosorption by plant residues

Sorption isotherms of naphthalene, acenaphthene and pyrene to PW, PN, PW-DS and PN-DS are compared in **Fig. 4**. The regression data are listed in **Table 4**. The sorption isotherms of PAHs by PW and PN were essentially linear, with Freundlich N close to 1, showing that the sorption processes of different sorbates were controlled by a partition mechanism. In contrast, PW-DS and PN-DS exhibited more nonlinear isotherms compared with raw samples. Similarly, with acid hydrolysis treatment of PW and PN, the sorption capacities of naphthalene, acenaphthene and pyrene increased greatly. For example, the K_d of naphthalene to PW-DS was about 8 times larger than that of raw PW, and the naphthalene K_d of PN-DS was about 6 times larger than that of raw PN. For acenaphthene and pyrene, the same phenomena were observed.

The respective partition coefficients (K_d) by PW and PW-DS were 270 and 2124 L/kg for naphthalene, 1365 and 10804 L/kg for acenaphthene, 6754 and 55763 L/kg for phenanthrene, 26833 and 218233 L/kg for pyrene. The individual K_d values by PN and PN-DS were 301 and 1871 L/kg for naphthalene, 1499 and 7808 L/kg for acenaphthene, 6370 and 38375 L/kg for phenanthrene, 30728 and 190706 L/kg for pyrene. For a given biosorbent, the K_{oc}/K_{owc} values of PAHs ranked in the order of naphthalene < acenaphthene < phenanthrene < pyrene (**Table 4**), which is in line with the octanol-water partition coefficients of the PAHs. A positive linear correlation between $\log K_{oc}$ and $\log K_{ow}$ of PAHs was observed (**Fig. 5**).

According to the linear relationships for $\log K_{oc}$–$\log K_{ow}$, the biosorption of other PAHs to the raw and modified biosorbents could be predicted. Similarly, relationships between $\log K_{oc}$ and $\log K_{ow}$ for PAHs on bamboo leaves (Chen et al., 2011), heat-killed fungal biomass (Chen et

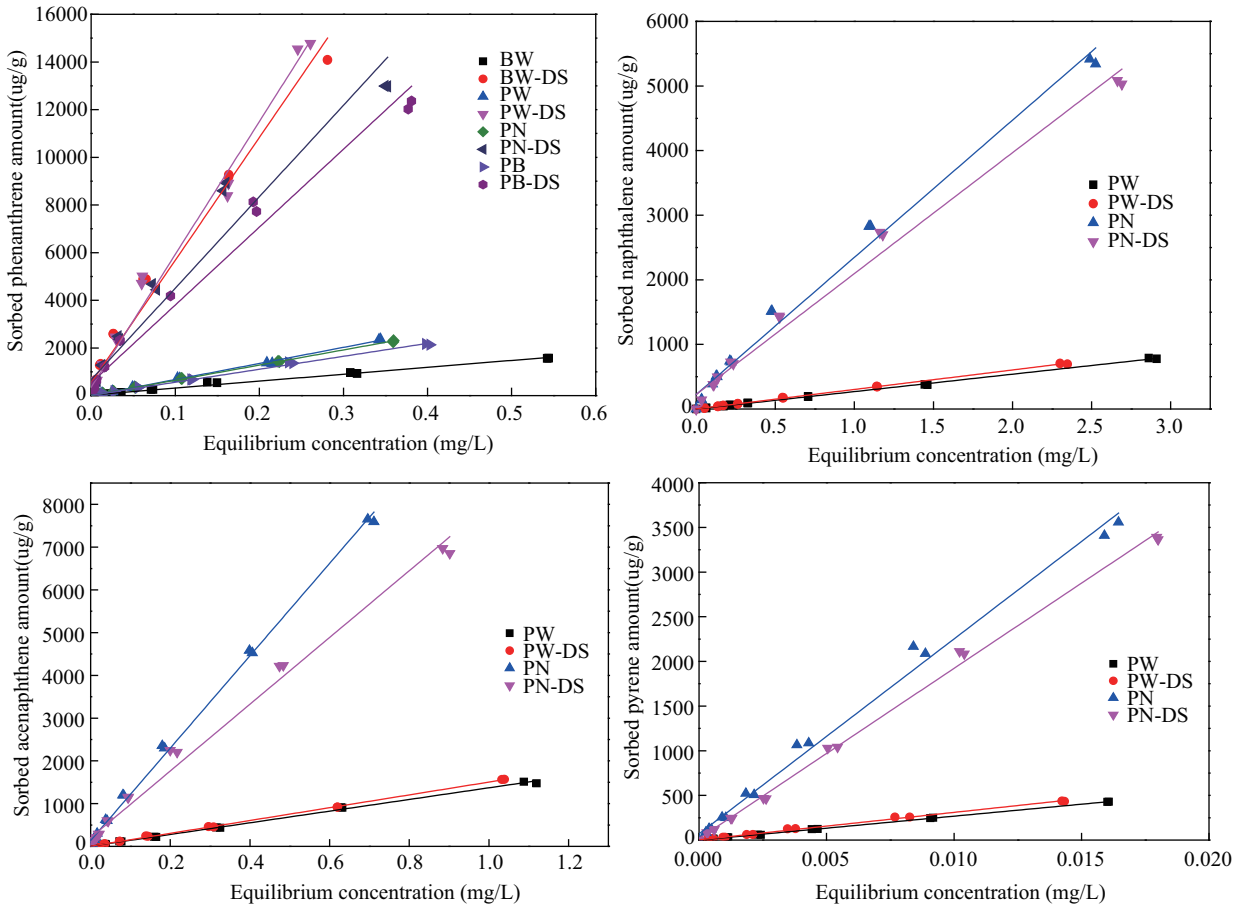

Fig. 4 Sorption isotherms of PAHs onto the raw and modified plant samples.

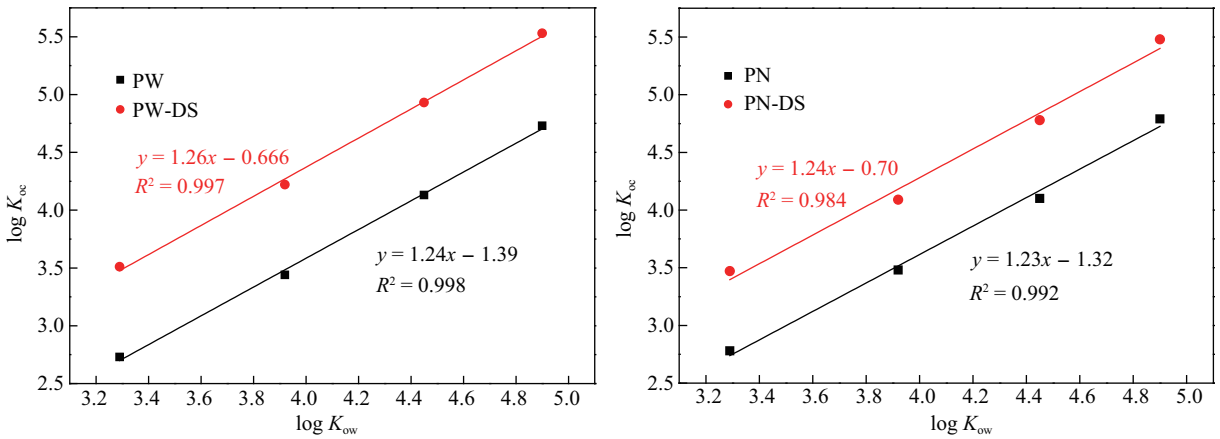

Fig. 5 Relationship between logK_{oc} and logK_{ow} of PAHs by the biosorbent of plant samples ($n = 4$).

al., 2010), and raw and surfactant-modified fibric peat (Tang et al., 2010) were also reported. Interestingly, based on **Fig. 5**, all of the lines relating logK_{oc}–logK_{ow} were parallel regardless the precursor material for biosorbents, and the slopes were similar. It was also found that the Y-intercepts for the raw plant residues were similar, while the Y-intercepts for the modified plant residues were almost the same. The Y-intercept for the raw plant residues was less than that of the modified plant residues, which may mainly due to the difference of the sorbents' polarity.

2.5 Structure-function relationship in biosorption of PAHs by plant residues

The structure characteristics of biosorbent (e.g., aromaticity and polarity) and sorbate properties (i.e., molecule size and K_{ow}) had an important effect on PAH biosorption and kinetic behaviors. The sorption processes of the raw

Table 4 Sorption regression parameters of PAHs by plant samples

Organic pollutants	Sorbent	Linear model		Freundlich model			K_{oc} (L/kg)	K_{oc}/K_{owc}
		K_d (L/kg)	Linear R^2	N	logK_f	R^2		
Phenanthrene	BW	2896 ± 57	0.993	0.939 ± 0.013	3.473 ± 0.021	0.997	6184	0.16
	BW-DS	51464 ± 1798	0.980	0.838 ± 0.024	4.679 ± 0.048	0.988	79616	2.10
	PW	6754 ± 60	0.999	1.004 ± 0.011	3.831 ± 0.019	0.998	13505	0.36
	PW-DS	55763 ± 1480	0.987	0.920 ± 0.045	4.748 ± 0.085	0.964	85816	2.26
	PN	6370 ± 33	0.999	1.040 ± 0.022	3.855 ± 0.036	0.993	12684	0.33
	PN-DS	38375 ± 1971	0.955	0.816 ± 0.020	4.563 ± 0.038	0.990	60083	1.58
	PB	5445 ± 60	0.998	0.997 ± 0.013	3.759 ± 0.021	0.997	10899	0.29
	PB-DS	32693 ± 1119	0.979	0.800 ± 0.028	4.473 ± 0.053	0.981	51139	1.35
Naphthalene	PW	270 ± 2	0.999	1.010 ± 0.011	2.432 ± 0.007	0.998	540	0.20
	PN	301 ± 2	0.999	1.019 ± 0.013	2.490 ± 0.009	0.998	599	0.23
	PW-DS	2124 ± 60	0.988	0.840 ± 0.011	3.421 ± 0.009	0.998	3269	1.24
	PN-DS	1871 ± 55	0.987	0.820 ± 0.010	3.374 ± 0.008	0.998	2929	1.11
Acenaphthene	PW	1365 ± 14	0.998	0.964 ± 0.011	3.127 ± 0.014	0.998	2729	0.24
	PN	1499 ± 8	0.999	0.970 ± 0.007	3.174 ± 0.009	0.999	2985	0.26
	PW-DS	10804 ± 135	0.997	0.893 ± 0.011	4.031 ± 0.017	0.997	16627	1.46
	PN-DS	7808 ± 186	0.990	0.869 ± 0.011	3.921 ± 0.016	0.997	12225	1.07
Pyrene	PW	26833 ± 117	0.999	1.032 ± 0.011	4.494 ± 0.029	0.999	53655	0.49
	PN	30728 ± 433	0.997	1.023 ± 0.017	4.554 ± 0.046	0.997	61187	0.56
	PW-DS	218233 ± 4963	0.993	0.926 ± 0.017	5.218 ± 0.046	0.996	335846	3.10
	PN-DS	190706 ± 2421	0.998	0.955 ± 0.018	5.188 ± 0.049	0.995	298585	2.75

K_d is the sorption coefficient(K_d=Q/C_e), calculated from the slope of the linear equation.

The Freundlich parameters (K_f and N) were calculated using the logarithmic form of the equation $Q = K_f C_e^N$, where, Q (μg/g) is the amount sorbed per unit weight of sorbent; C_e (mg/L) is the equilibrium concentration; K_f ((μg/g)/(mg/L)^N) is the Freundlich capacity coefficient; and N (dimensionless) describes the isotherm curvature. R is regression coefficient.

K_{oc} is the carbon-normalized sorption coefficient ($K_{oc} = K_d/f_{oc}$) and K_{owc} is the carbon-normalized K_{ow} ($K_{owc} = K_{ow}/f_{oc}$, f_{oc} is the percentage of carbon content of octanol, i.e., 73.8%).

samples reached sorption equilibrium more quickly than the modified plant samples, and the sorption rates (k_2) of PAHs to the raw samples were relatively faster than that for the modified samples. The change in the sorption kinetics was attributed to the increase of aromaticity of de-sugared samples as well as the decrease of polarity, which decreased the solute's diffusivity in the biosorbent's partition phase. The sorption rates (k_2) of phenanthrene, naphthalene, acenaphthene and pyrene to the biosorbents were distinct due to the different molecular sizes of the PAHs.

In this study, negative correlation for K_d values with sugar content for the four raw plant residues (K_d = –207.11x + 17197, R^2 = 0.709) was observed, and positive correlation of K_d values with aromaticity (H/C) for the eight plant samples (K_d = –68749x + 110219, R^2 = 0.832) was obtained. The relationships between the K_{oc} values and the polarity index (i.e., (O + N)/C) of the sorbents are presented in **Fig. 6**. The K_{oc} values decreased linearly with increasing polarity of the raw and modified plant samples, showing an apparently negative effect of polarity on PAH sorption. The raw BW, which had the highest sugar content and polarity and the lowest aromaticity (**Table 2**), exhibited the lowest partition coefficient (**Table 4**) compared with the other three raw plant residues and presented the greatest change in polarity (i.e., (O+N)/C) and aromaticity (i.e., H/C) after acid hydrolysis. In addition, the surface morphology of modified BW and PN was more uneven and rougher than raw BW and PN, but presented similar abundant wax (**Fig. 2**). These phenomena gave rise to the enhancement of sorption capacity of raw plant residues after acid hydrolysis, which was attributed to the exposure of aliphatic moieties and aromatic core after the removal of polar polysaccharides. The BW-DS exhibited the greatest change in sorption capacity for phenanthrene after acid hydrolysis, which was in line with the CHN and FT-IR data mentioned above. The PW-DS sample presented the highest sorption capacity for PAHs because it had the lowest polarity. Li et al. (2010) suggested that the relative role of aromatic and aliphatic moieties was regulated by the amorphous cellulose component. The relationship between the sorption capability and characteristics of a sorbent provides a theoretical basis for selecting plant residues having high efficiency for the removal of PAHs from water. Furthermore, it is a theoretical guide to the modification of raw plant residues through acid hydrolysis to enhance their sorption capacity.

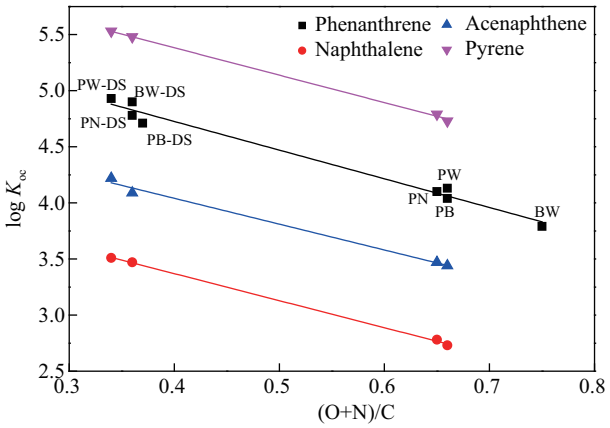

Fig. 6 Relationships between the logK_{oc} of PAHs and the polarity index of the raw and modified plant samples.

2.6 Application implications

To select proper natural sorbents for environmental applications, it is of great importance to compare the sorption capacity of different kinds of sorbents. Sorption coefficients of natural, modified and synthetic sorbents in the previous studies and in this study are summarized in **Table 5**. In the present study, PW and PN with high sorption capacity were selected as model biosorbents to compare with other sorbents. The sorption coefficients of PW and PN for phenanthrene are 6754 L/kg and 6370 L/kg, respectively. The K_d values of PW and PN are higher than that of many natural sorbents such as cellulose (Salloum et al., 2002), aspen wood fiber (Huang et al., 2006), tender tea leaves (Lin et al., 2007), ryegrass root and orange peel (Chen et al., 2011), but lower than those of algae, lignin (Salloum et al., 2002), heat-killed fungal biomass (Chen et al., 2010) and potato cuticle (Li and Chen, 2009). The high sorption affinity for PAHs exhibited by lignin and fruit cuticles may be attributed to their aliphatic-rich nature and thus indicating the important role of aliphatic carbon in the sorption of PAHs by plant residues (Chen et al., 2011).

With acid hydrolysis treatment of raw plant residues, the sorption capacity was enhanced greatly due to the increase of aromaticity and the decrease of polarity of the sorbents. The K_d values of BW-DS, PW-DS, PN-DS and PB-DS are higher than some modified biosorbents such

Table 5 Sorption coefficients of phenanthrene with different kinds of sorbents reported in the previous studies and present work

	Sorbent	Phenanthrene concentration (mg/L)	K_d of phenanthrene (L/kg)	Source
Nature organic sorbent	BW	0.008–1	2896	Present study
	PW	0.008–1	6754	
	PN	0.008–1	6370	
	PB	0.008–1	5445	
	Algae	0.2–1.0	13630	Salloum et al., 2002
	Cellulose	0.2–1.0	951.8	
	Lignin	0.2–1.0	10627	
	Aspen wood fiber	0.01–0.1	3940–4660	Huang et al., 2006
	Heat-killed fungal biomass	0.001–1	6822	Chen et al., 2010
	Tender tea leaves	0.008–0.8	3290–3450	Lin et al., 2007
	Mature tea leaves	0.008–0.8	5880-11200	
	Ryegrass root	0.0006–0.6	2777	Chen et al., 2011
	Orange peel	0.0006–0.6	2970	
	Potato cuticle	0.005–0.95	16222	Li et al., 2009
	Pine needle cuticle	0.005–0.95	6600	Li et al., 2010
Modified biosorbents	BW-SD	0.008–0.1	51464	Present study
	PW-SD	0.008–0.1	55763	
	PN-SD	0.008–0.1	38375	
	PB-SD	0.008–0.1	32693	
	Fibric peat	Not given	12870	Tang et al., 2010
	Surfactant modified peat	Not given	26074	
	Brewed tender tea leaves	0.008–0.8	5820–6270	Lin et al., 2007
	Brewed mature tea leaves	0.008–0.8	8950–15900	
	Hydrolyzed pine needle cuticle	0.005–0.95	38836	Li et al., 2010
	Low-temperature hydrolyzed wood fibers	0.01–0.1	10800–14000	Huang et al., 2006
	High-temperature hydrolyzed wood fibers	0.01–0.1	42600–57500	
Synthetic sorbents	Natural chars	0.052–1.001	79433–1995262	James et al., 2005
	Active carbon	0.052–1.001	501187–794328	
	Organobentonites	Not given	11500–43400	Chen and Zhu, 2001

as fibric peat, surfactant-modified peat (Tang et al., 2010), and brewed tea leaves (Lin et al., 2007), while they are comparable to hydrolyzed wood fibers (Huang et al., 2006) and organobentonites (Chen and Zhu, 2001), but lower than those of some synthetic sorbents, such as natural chars and active carbon (James et al., 2005) (**Table 5**). Synthetic sorbents mainly rely on their huge surface area to adsorb pollutants and the sorption efficiency is easily affected by the coexistence of pollutants. Li et al. (2010) confirmed that hydrolyzed barks retained organic pollutants mainly by the non-competitive partition process. The sorption capacity of hydrolyzed plant samples increased 6–18 fold for phenanthrene, 6–8 fold for naphthalene, 5–8 fold for acenaphthene and 6–8 fold for pyrene compared with their raw samples, presenting higher sorption capacity. In addition, hydrolyzed plant samples are much safer in wastewater treatment than raw samples due to the removal of dissolved organic matter and metals during the acid hydrolysis process (Ribe et al., 2009). In the end, the modification process for raw plant samples was relatively simple and the processing cost was low. Considering their ubiquity, non-competitive sorption process, high sorption capacity, high environmental compatibility and cost effectiveness, the hydrolyzed plant samples are proposed to be promising sorbents for PAHs removal in aqueous solution.

3 Conclusions

The present study shows that raw plant residues and modified plant residues both have great potential as effective low-cost biosorbents for PAH removal from aqueous solution. Sorption took place by a predominant partition process for the raw plant residues, while the modified plant residues exhibited relatively nonlinear isotherms. The adsorption kinetics fit well with pseudo second-order kinetics. Negative correlation of partition coefficients with sugar content, polarity index [(O+N)/C] as well as positive correlation with the aromaticity of the biosorbents was observed. The powerful sorption capacity of aromatic domains was seriously suppressed by the coexisting polysaccharide component. Therefore, the consumption of polar components through acid hydrolysis is a promising choice to enhance the sorption capability of plant residues. The de-sugared pine wood presented the highest sorption capacity for PAHs, attributed to the fact that it had the lowest polarity. The hydrolyzed plant residues are proposed to be promising biosorbents for PAH removal in aqueous solution.

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