Removal of polycyclic aromatic hydrocarbons from aqueous solution using plant residue materials as a biosorbent

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ABSTRACT

To elucidate biosorption mechanism and removal efficiency of plant residues as a biosorbent to abate polycyclic aromatic hydrocarbons (PAHs) in wastewater, sorption of PAHs onto wood chips (WC), ryegrass roots (RR), orange peels (OP), bamboo leaves (BL), and pine needles (PN) were investigated. The structural characterization of the biosorbents was analyzed by elemental composition, BET-N_2 surface area, and Fourier transform infrared spectroscopy. PAHs sorption to the selected biosorbents were compared and correlated with their structures. Biosorption isotherms fit well with Freundlich equation and the mechanism was dominated by partition process. The magnitude of phenanthrene partition coefficients (K_d) followed the order of PN > BL > OP > RR > WC, ranged from 2484 ± 24.24 to 5306 ± 92.49 L/kg. Except the WC sample, the K_d values were negatively correlated with sugar content, polar index [$(N+O)/C$] of the biosorbents, while the aromatic component exhibited positive effects. For a given biosorbent of bamboo leaves, the carbon-normalized partition coefficients (K_{oc}) were linearly correlated with octanol–water partition coefficients (K_{ow}) of PAHs, i.e., $\log K_{oc} = 1.16 \log K_{ow} - 1.21$. The structure–effect relationship provides a reference to select and modify plant residues as a biosorbent with high efficiency to tackle organic pollutants.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are mainly formed from the incomplete combustion of fossil and biomass, which have been detected at elevated concentrations in municipal sewage and surface water [1,2]. PAHs, typical persistent organic pollutants (POPs), are among toxic pollutants of most concern due to their high bioaccumulation and adverse health effects such as mutagenic, carcinogenic and teratogenic properties [1,3]. Because of their low aqueous solubility and bioavailability, PAHs are resistant to biodegradation and are difficult to be removed by conventional physicochemical techniques such as coagulation, flocculation, sedimentation and filtration [4,5].

Sorption is one of the most economical and effective techniques for removing organic pollutants at low concentration, and active carbon (AC) is the most widely used as a conventional sorbent [4,6]. However, high cost and difficult regeneration limit its application in large-scale wastewater treatment [7,8]. Biosorbents, including algae, bacteria, yeasts, fungi, industrial wastes, agricultural wastes and natural residues, are potential alternatives of conventional sorbents owing to their inherent sorption capability, environmental compatibility, and cost effectiveness [9,10]. In the last decade, different kinds of microbial biosorbents were applied to remove heavy metals and some polar organic pollutants such as basic dyes from waste effluents [11–13]. Recently, increasing interests have been focused on the removal of POPs by biosorbents [7,8,14–19].

Plant residues which mainly derived from wood-processing industries, agricultural production, and tree harvesting and pruning, is a ubiquitous green waste in the environment and may cause some serious environmental pollution when filling at a fixed site. More and more interests are focused on developing these plant residues as biosorbent for wastewater treatment due to their relative high sorption affinity with POPs, ubiquitous presence in the environment, and ease being modified to materials with higher efficiency [8,18,20]. Chung et al. [21] found brown seaweed (*Sargassum hemiphyllum*) powder showing high phenanthrene removal efficiency at different conditions and it was viewed as a potential candidate for tackling POPs pollutions. High sorption affinity of tea leaf powder with phenanthrene was reported [22]. The characteristics of plant materials, such as polar and aromatic components, impose a significant influence on their sorptive behavior [18,23]. Lignin is assumed to be the main storage medium of organic pollutants [8,18,24], and sorbents with higher lignin contents show higher affinity with POPs [4,15]. However, Li et al. [8] reported that

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the powerful sorption potential of lignin was seriously masked by the coexisting polysaccharide component (polar composition), and the pre-removal of polysaccharide from raw materials was suggested to promote sorption capability.

POPs sorption to geosorbent (e.g., char and kerogen) revealed that the polar carbon fractions play a negative role in sorption and the aromatic carbon fractions exhibit a d positive effect although there is a debate about the role of aromatic carbons on sorption of fresh plant materials. Several authors dealing with relatively fresh organic matter pointed out that aliphatic carbons rather than aromatic carbons play a regulating role on the sorption behavior of natural organic matter, especially the aliphatic-rich natural organic matter [16,25]. However, biosorption mechanisms and removal efficiency of POPs in wastewater by plant residues as a biosorbent are wanted.

The main objective of this study is to elucidate biosorption mechanism and efficiency of plant residues as a biosorbent to remove polycyclic aromatic hydrocarbons (PAHs) from wastewater. To this end, five plant residues, i.e., wood chips (WC), ryegrass roots (RR), orange peels (OP), bamboo leaves (BL) and pine needles (PN), were selected as biosorbents. Their structural characteristics were analyzed by elemental composition, BET-N_2 surface area, and Fourier transform infrared spectroscopy. Naphthalene, acenaphthene, fluorene, phenanthrene, pyrene were chosen as model PAHs because they are widely spread in the wastewater. PAHs sorption to the selected biosorbents were compared and correlated with their structures. Plant residues waste tackling POPs in wastewater should obtain a win–win situation.

2. Materials and methods

2.1. Biosorbents

Five plant residues samples of wood chips (WC), ryegrass roots (RR), orange peels (OP), bamboo leaves (BL), and pine needles (PN) were chosen as model biosorbents. Wood chip, including residues from industrial transformation to forest waste, is a common material which present as fill at many industrial sites and is also a main component of solid waste [15,19]. Ryegrass is a potential candidate for POPs remediation and the sorption of pollutants to the root tissue may be an important process for this end [26]. Orange peel is a valuable agriculture biomass wastes and take up 75% of the total citrus fruits around the world, and China is one of the major producers [27]. Both bamboo and pine are widely spread plants in China, and are important sources of soil organic matter through leaf senescence. Five plant residues were collected and washed with tap water to remove dusts. After air-dried and ground with a pulverizer, the litters were passed through a 0.154 mm sieve to obtain well-proportioned biosorbent samples.

2.2. Characterization of sample

The contents of C (f_C), H (f_H), N (f_N) in the five biosorbents were determined using an EA 112 CHN elemental analyzer (Thermo Finnigan), and the oxygen contents were calculated on the ash-free basis. Because the content of other elements were negligible, and hence the O content (f_O) was calculated by equation of $f_O = 100 - f_C - f_H - f_N$. The H/C and (O + N)/C atomic ratios of five biosorbent were calculated to evaluate their aromaticity and polarity, respectively. FTIR spectra were recorded in the 4000–400 cm^{-1} region by a Nicolet FTIR spectrophotometer (model 560) with a resolution of 4.0 cm^{-1}. Their surface areas were measured from the BET plot of the N_2 (0.162 nm) adsorption data at liquid nitrogen temperature (77 K) determined by a NOVA-2000E surface area analyzer. Four data points, with relative pressures between 0.05

Table 1
The selected physicochemical properties of tested PAHs.

PAHs	MF[a]	MW[b]	S_w (mg/L)[c]	K_{ow}[d]
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
Fluorene	$C_{13}H_{10}$	116.2	1.90	1.5×10^4
Phenanthrene	$C_{14}H_{10}$	178.2	1.18	2.8×10^4
Pyrene	$C_{16}H_{10}$	202.3	0.13	8.0×10^4

[a] MF: molecular formula.
[b] MW: molecular weight.
[c] S_w: solubility in water at 25 °C.
[d] K_{ow}: logarithm of octanol–water partition coefficients.

and 0.3, were used to construct the plot to derive the monolayer adsorption capacity, from which the surface area was calculated using the N_2 molecular area of 16.2E−20 m^2. Acid hydrolysis of five plant residues were conducted in 6 mol/L HCl solution with refluxing for 6 h at 100 °C to eliminate the polysaccharides component, and the fraction removed from plant sample was termed as sugar component.

2.3. Batch biosorption experiment

Naphthalene, acenaphthene, fluorene, phenanthrene, pyrene were chosen as model PAHs due to their different molecular properties and prevailing presence in the environment. Their physicochemical properties are presented in Table 1. Sorption of phenanthrene to the five biosorbents was investigated to elucidate the different sorption capacities of various plant residues. To illustrate the effect of PAHs properties on sorption, the bamboo leaves was selected as a typical biosorbent to sorb naphthalene, acenaphthene, fluorene, phenanthrene and pyrene, because few studies on sorption of bamboo leaves were available. All sorption isotherms by plant residues were obtained in a background solution comprised 0.01 mol/L CaCl$_2$ to simulate environmental water and 200 mg/L NaN$_3$ to inhibit the degradation by incidental bacteria. The PAHs solution was made in methanol and then diluted using the background solution. Methanol concentrations were maintained at less than 0.1% of the total solution volume to avoid any co-solvent effects. The initial concentrations ranged from 0.06 to 24 mg/L for naphthalene, from 0.003 to 3.5 mg/L for acenaphthene, from 0.001 to 1.4 mg/L for fluorene, from 0.0006 to 0.6 mg/L for phenanthrene and from 0.00002 to 0.08 mg/L for pyrene. Preliminary experiments were conducted to obtain a solid-to-water ratio and ensure that final PAHs solution concentration remained in the range of 20–80%. Each sorption experiment consisted of 10 initial concentration points including the blank control (contained sorbent without PAHs). Each point, including calibration control (contained PAHs without sorbent) was run in duplicate. The 8-mL vials were filled with a sorbate solution to minimize the headspace volumes of vials and sealed with aluminum foil-lined Teflon screw caps to avoid evaporation of sorbate, and then gentle agitated at 30 rpm on an end-over-end rotary shaker for 3 days at 25 ± 0.5 °C to reach apparent equilibrium (kinetic tests indicated that sorption equilibrium was achieved in less than 48 h). The solution was separated by centrifugation at 4000 rpm for 15 min and the PAHs concentration in solution was measured. The difference of PAHs concentration in calibration control before and after sorption experiments were minimal, so the edge effect of the 8-mL vials on sorption results was negligible. Because of a minimal sorption by the vials (i.e., a minimal edge effect of the 8-mL vials), and negligible losses by evaporation, biodegradation and photodegradation, the amount-sorbed of PAHs to biosorbent was calculated by mass difference between nominal concentration without sorbent and with sorbent in aqueous solutions.

Table 2
Relative elemental composition, atomic ratios, BET-N_2 specific surface area (SA), sugar contents of five plant samples.

Sorbents	SA (m^2/g)	Sugar (%)	Element analysis				$(O+N)/C$[a]	H/C[b]
			C (%)	H (%)	N (%)	O (%)		
WC[c]	25.97	60.6	47.8	6.34	0.33	45.5	0.720	1.592
RR[c]	–	82.7	35.9	5.32	3.80	55.0	1.239	1.778
OP[c]	5.40	72.0	42.9	6.24	1.18	49.7	0.892	1.745
BL[c]	3.41	68.2	44.0	6.20	2.57	47.2	0.855	1.691
PN[c]	9.82	44.2	49.1	6.36	0.86	43.7	0.682	1.554

[a] $(O+N)/C$: atomic ratio of sum of nitrogen and oxygen to carbon.
[b] H/C: atomic ratio of hydrogen to carbon.
[c] WC, RR, BL, OP, PN are powder of wood chip, ryegrass root, bamboo leaves, orange peel, pine needle, respectively.

2.4. PAHs analysis

The equilibrium concentrations of PAHs in solution were measured by high-performance liquid chromatography (Agilent 1200 HPLC) with a fluorescence detector and a 4.6 mm × 150 mm reverse phase XDB-C18 column, using acetonitrile–water (v:v, 90/10) as the mobile phase at a flow rate of 1 mL/min. The respective excitation wavelengths of naphthalene, acenaphthene, fluorene, phenanthrene and pyrene were 240, 240, 220, 244 and 237 nm, and the emission wavelengths were 360, 360, 315, 360 and 385 nm.

2.5. Data analysis

The sorbed amounts (Q) of PAHs by sorbents were estimated as follows:

$$Q = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where V is the volume of solution and m is the mass of sorbent used in this study. C_0 (mg/L) and C_e (mg/L) are the initial and equilibrium concentration of PAHs, respectively. The partition coefficients (K_d) derived from the batch sorption experiment were calculated from the equation $K_d = Q/C_e$, so the removal efficiency (RE) of PAHs could be calculated as follows:

$$RE = \frac{C_0 - C_e}{C_0} \times 100\% = \frac{mK_d}{V + mK_d} \times 100\% \tag{2}$$

3. Results and discussion

3.1. Characterization of plant residues

The elemental compositions and surface area of five plant residues are listed in Table 2. The selected plant residues contained large number of C, O, H element and little N element. The ryegrass roots had the lowest C content and highest O content, and displayed the highest polarity [$(O+N)/C = 1.239$]. In contrast, pine needles exhibited the highest C content but lowest O content, hence the lowest polarity [$(O+N)/C = 0.682$]. Correspondingly, the sugar content for ryegrass roots was the highest one (82.7%), and the lowest one was pine needles (44.2%). Pine needles with the low polarity and sugar content may contribute to the high sorption capacity for POPs [8,18]. In addition, pine needles show the lowest ratio of H/C (1.554), expressing the highest aromaticity. As expected, the BET-N_2 specific surface areas of all plant samples were quite small with a range of 3.41–25.97 m^2/g (see in Table 2).

The FTIR spectra of the plant residues samples are shown in Fig. 1. All plant residues samples except for wood chips were dominated by the large band at 3400 cm^{-1} which represents the stretching vibration of hydroxyl groups. The peak of –OH together with C=C and C=O in the aromatic ring (large peak at 1640 cm^{-1})
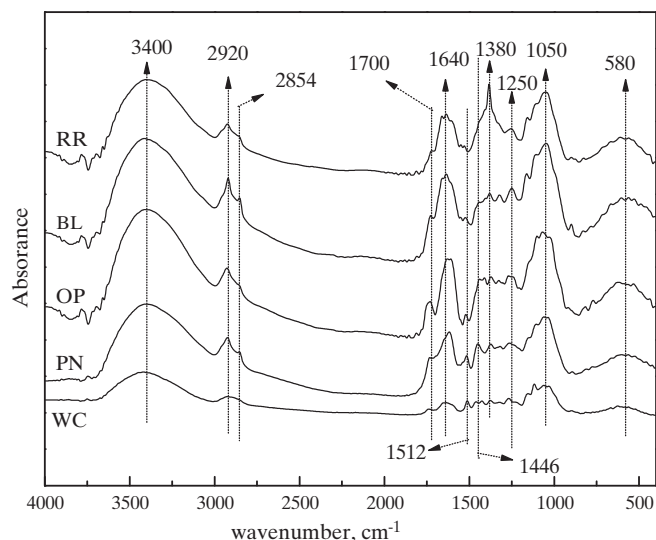

Fig. 1. FTIR spectra of plant residue samples. The symbols of RR, BL, OP, PN, WC represent ryegrass root, bamboo leaves, orange peel, pine needle, wood chip, respectively.

indicates the presence of plenty of polyphenols [22]. The peaks at 2920, 2854, 1446 and 1380 cm^{-1} are assigned mainly to CH_2 units in biopolymers [28]. The band at 1700 cm^{-1} were unconspicuous for all samples except orange peels in which it is assigned to –COOH stretching vibrations of ester bonds [22,29]. The peak at 1512 cm^{-1} represents the C=C ring stretching vibration of lignin [29]. The bands at 1250 cm^{-1} and 1050 cm^{-1} were C–O stretching of polysaccharides [30]. The peak of 580 cm^{-1} was assigned to the aromatic CH components. All these bands showed lower band intensities for wood chips compared to other four plant samples.

3.2. Biosorption of phenanthrene to plant samples

Biosorption isotherms of phenanthrene to five biosorbents of plant residues are presented in Fig. 2, and their linear and Freundlich regression parameters are listed in Table 3. Sorption isotherms fit well with the Freundlich model and the Freundlich N values approximated to 1 (ranging from 0.982 ± 0.049 to 1.091 ± 0.031). The practically linear isotherms indicated that the
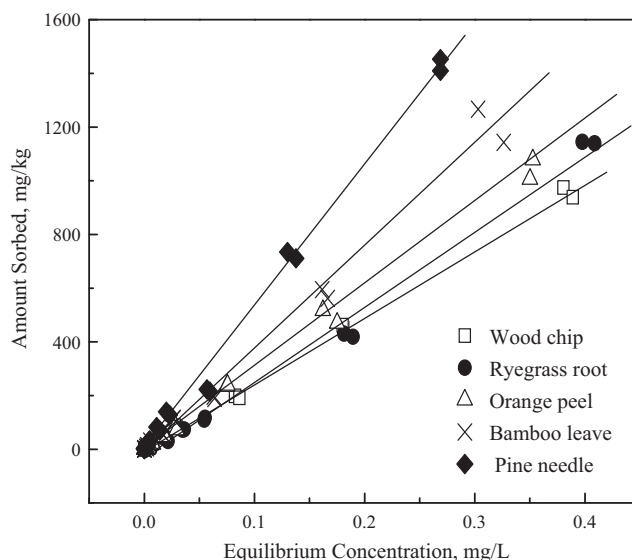

Fig. 2. Biosorption isotherms of phenanthrene by five plant residue samples.

Table 3
Regression parameters of biosorption isotherms of PAHs onto plant residues.

Sorbents	PAHs	Linear equation			Freundlich equation			S-T-W (mg/mL)[a]
		K_d (L/kg)	R^2	K_{oc} (L/kg)	N	$\log K_f$	R^2	
WC	Phen	2484 ± 24.24	0.998	5197	1.018 ± 0.032	3.420 ± 0.056	0.986	3.62
RR	Phen	2777 ± 58.62	0.992	7735	1.048 ± 0.046	3.404 ± 0.069	0.981	3.24
OP	Phen	2970 ± 39.80	0.997	6923	1.091 ± 0.031	3.551 ± 0.052	0.989	3.03
PN	Phen	5306 ± 92.49	0.995	10,810	0.982 ± 0.049	3.692 ± 0.092	0.967	1.69
BL	Naph	179.0 ± 2.973	0.995	406.8	0.956 ± 0.012	2.279 ± 0.010	0.997	50.3
BL	Acen	1357 ± 17.83	0.997	3084	0.974 ± 0.032	3.075 ± 0.039	0.984	6.63
BL	Fluo	1440 ± 22.69	0.995	3273	1.046 ± 0.035	3.194 ± 0.062	0.981	6.25
BL	Phen	3746 ± 96.54	0.988	8513	0.999 ± 0.029	3.581 ± 0.057	0.987	2.40
BL	Pyr	15,430 ± 710	0.961	35,070	1.002 ± 0.079	4.223 ± 0.210	0.941	0.58

[a] S-T-W: The solid-to-water ratio as the removal efficiency of PAHs reach up to 90%.

dominant mechanism for different plant residues biosorbents was partition process, which is in line with the quite small BET-N$_2$ specific surface areas of the biosorbents. Similar phenomena were observed for POPs sorption by other type of raw and modified plant materials such as pine bark [8], tea leaves [22], grass roots and shoots [24], ryegrass roots [26], aspen wood fibers [31].

Partition coefficient (K_d) is a good parameter to describe the distribution of organic pollutants between solid and solution phases, and then to evaluate sorption capacity of sorbents. The magnitude of K_d values were increased in the order of wood chip (2484 ± 24.24 L/kg) < ryegrass roots (2777 ± 58.62 L/kg) < orange peels (2970 ± 39.80 L/kg) < bamboo leaves (3746 ± 96.54 L/kg) < pine needles (5306 ± 92.49 L/kg). According to Eq. (2), the removal efficiency of phenanthrene could be up to 90% when the solid-to-water ratio (mg:mL) reached 1.7–3.6 (Table 3). As shown in Table 4, biosorption of phenanthrene to pine needles is much lower than some natural or modified sorbents such as algae, lignin, humic acid [16], fibric peat [25], fruit cuticles [32], and some geosorbents and conventional abiotic materials (char and activated carbon) [33], but higher than those of pink bark [8], cellulose, aspen wood fibers [18], and tender tea leaves [22]. In view of its ubiquity, environmental compatibility, and cost effectiveness, plant materials could be a favorable biosorbent for PAHs pollution treatment.

The sugar content, polarity index [(O + N)/C], aromaticity (H/C) could dramatically affect the sorption capacity of pollutants of sorbents [8,28]. The sorption coefficient in the current study increased with decreasing polarity and sugar content, and with increasing aromaticity of plant residues except for wood chip (Fig. 3). Negative correlation of K_d values with sugar content, (O + N)/C, H/C for ryegrass roots, oragane peels, bamboo leaves and pine needles are obtained and shown as follows:

$$K_d = -69.02 f_{Sugar} + 8309 \quad (n = 4, R^2 = 0.928) \tag{3}$$

$$K_d = -11615 f_{H/C} + 23,353 \quad (n = 4, R^2 = 0.992) \tag{4}$$

$$K_d = -4305 f_{(O+N)/C} + 7400 \quad (n = 4, R^2 = 0.506) \tag{5}$$

where f_{Sugar}, $f_{H/C}$ and $f_{(O+N)/C}$ are the values of sugar content, H/C, (O + N)/C, respectively. These equations confirmed the positive effect of aromaticity [23], and negative effect of polarity [28] and polysaccharide component [8,32] on PAHs sorption. The correlation of sorption capability with structural characteristics of biosorbent provide a fundamental basis to select plant residues with high efficiency to remove POPs from water, and give a gist to enhance the sorption capability of raw plant residues by modification through structure-tailored technique. Some reports [8,22] suggested that not only polar carbons but also aromatic carbons played a negative role in PAHs sorption, and aliphatic carbons govern the sorption of PAHs to natural organic matter. Salloum et al. [16] reported that the dominant role of aliphatic carbons in PAHs sorption by aliphatic-rich natural organic matter. Further research is necessary

Table 4
Sorption coefficients of phenanthrene with selected natural and synthetic sorbents reported in the previous studies and the current wok.

Sorbents		$\log K_d$	Source
Plant residues	Wood chip	3.40	
	Ryegrass root	3.44	Presented study
	Orange peel	3.47	
	Bamboo leaf	3.57	
	Pine needle	3.72	
	Alfalfa root	3.37	
	Ryegrass root	3.32	
	Tomato root	3.40	
	Potato root	3.62	
	Carrot root	3.70	Zhu et al. [35]
	Cucumber	3.52	
	Zucchini root	3.66	
	Pumpkin root	3.62	
	Tender tea leaves	3.52–3.54	Lin et al. [22]
	Mature tea leaves	3.77–4.05	
	Pine bark	3.53	Li et al. [8]
Fungi	White-rot fungi	3.83	Chen et al. [30]
Algae	*Botryococcus braunii*	4.13	Salloum et al. [16]
	Brown seaweed	3.83	Chung et al. [21]
Nature organic matter	Cellulose	2.98	
	Collagen	4.47	Salloum et al. [16]
	Lignin	4.03	
	Cuticle of mangrove	4.21	
	Cuticle of grape	4.54	
	Cuticle of potato	4.21	Li and Chen [32]
	Cuticle of tomato	4.61	
	Cuticle of apple	4.73	
Modified biosorbents	Aspen wood fiber	3.60–3.67	
	Bleaching treatment	3.24–3.26	Huang et al. [18]
	Low-temperature hydrolyzed wood fibers	4.03–4.15	
	High-temperature hydrolyzed wood fibers	4.63–4.75	
	Brewed tender tea leaves	3.76–3.80	Lin et al. [22]
	Brewed mature tea leaves	3.95–4.20	
	Fibric peat	4.11	Tang et al. [25]
	Surfactant modified fibric peat	4.42	
	Acid hydrolysis of pine bark	4.23	Li et al. [8]
Geosorbents and abiotic sorbents	Humic acid	4.45	Salloum et al. [16]
	Pula kerogen	4.76	
	Nature chars[a]	4.83–6.31	
	Artificial wood chars[a]	5.19–7.20	James et al. [34]
	Active carbon[a]	5.70–5.90	

[a] The equilibrium concentration of phenanthrene was 1 μg/L.

Fig. 4. Biosorption isotherms of five PAHs by the biosorbent of bamboo leaves.

tive predicted values from the structure–effect relationships, such as $K_d \sim$ sugar content, $K_d \sim (O+N)/C$, and $K_d \sim H/C$ (Fig. 3), which may be attributed to its relative low content of aliphatic group and high lignin content as reflected by Fig. 1. However, more study are needed to explain this phenomenon.

3.3. Biosorption of PAHs to bamboo leaves

Biosorption isotherms of naphthalene, acenaphthene, fluorene, phenanthrene, pyrene to bamboo leaves are compared in Fig. 4, and their regression parameters are listed in Table 3. Biosorption isotherms of PAHs onto bamboo leaves fit well with the Freundlich equation with Freundlich N approximate to 1, indicating that the dominant mechanism is still partition process for different sorbates. Organic carbon-normalized distribution coefficient (K_{oc}) was calculated from organic carbon contents (f_{oc}) of bamboo leaves and K_d values as $K_{oc} = K_d/f_{oc}$, and listed in Table 3.

The respective partition coefficient (K_d) by bamboo leaves were 179.0 ± 2.973, 1357 ± 17.83, 1440 ± 22.69, 3746 ± 96.54, $15,430 \pm 710.3$ L/kg for naphthalene, acenaphthene, fluorene, phenanthrene and pyrene. Hence, the removal efficiency would reach up to 90% when the solid-to-water ratio (mg/mL) were 50.3 for naphthalene, 6.63 for acenaphthene, 6.25 for fluorene, 2.40 for phenanthrene, and 0.58 for pyrene (Table 3). A positively linear correlation between $\log K_{oc}$ and $\log K_{ow}$ (Fig. 5) was observed as follows:

$$\log K_{oc} = 1.16 \log K_{ow} - 1.21 \quad (n = 5, R^2 = 0.974) \tag{6}$$

where K_{ow} is octanol–water partition coefficient of PAH. In contrast, the relationship between $\log K_{oc}$ and $\log K_{ow}$ for PAHs on heat-killed fungi [30], river sediments [34], raw and surfactant modified fibric peat [25] were reported as follows:

$$\log K_{oc} = 1.13 \log K_{ow} - 0.84 \quad \text{(heat-killed fungi,}$$
$$n = 5, R^2 = 0.996) \tag{7}$$

$$\log K_{oc} = 1.00 \log K_{ow} - 0.21 \quad \text{(river sediments,}$$
$$n = 10, R^2 = 0.996) \tag{8}$$

$$\log K_{oc} = 1.14 \log K_{ow} - 0.66 \quad \text{(raw fibric peat,}$$
$$n = 3, R^2 = 0.992) \tag{9}$$

Fig. 3. Relationship between sorption coefficients (K_d) of phenanthrene with the structural characterization of biosorbents of plant residues excluding the wood chip (WC).

to clarify the respective role of aromatic carbons and aliphatic carbons in POPs sorption to different types of nature organic materials. Li et al. [8] pointed out that lignin is the main aromatic constitutes of natural sorbents and its strong sorption affinity with PAHs could be seriously restricted by the coexisting polysaccharide component. Therefore, removal of polar components (i.e., mainly sugar) through acid hydrolysis was a necessary modification process to enhance the sorption capability of biosorbents. The K_d value of phenanthrene for wood chips was much lower than their respec-
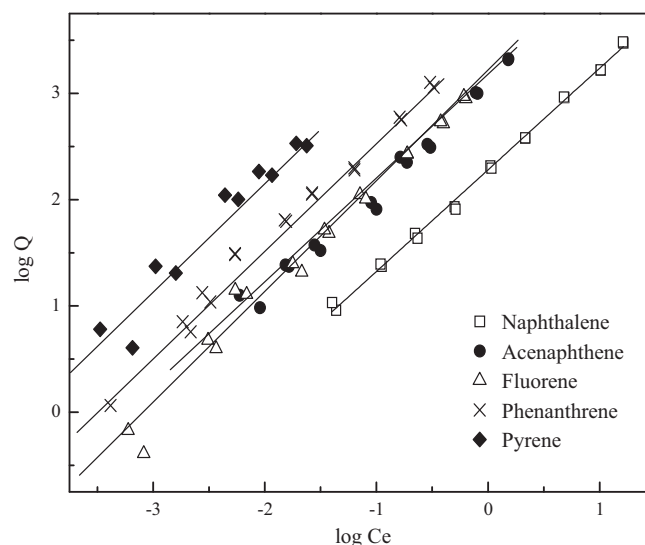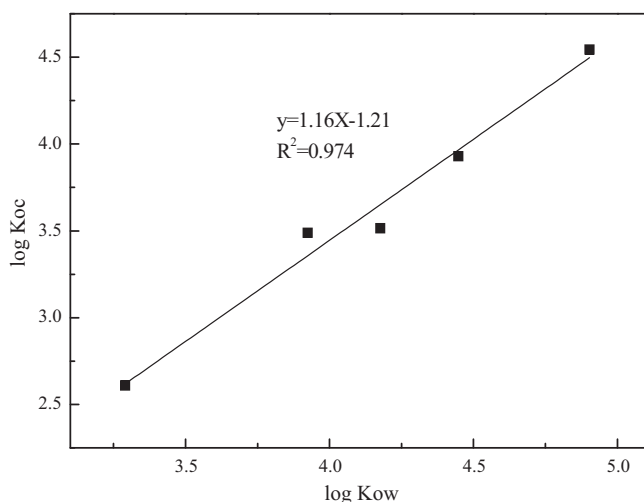
Fig. 5. Relationship between $\log K_{oc}$ and $\log K_{ow}$ of PAHs by the biosorbent of bamboo leaves.

$$\log K_{oc} = 1.23 \log K_{ow} - 0.84 \quad \text{(surfactant modified fibric peat,}$$

$$n = 3, R^2 = 0.998) \tag{10}$$

For bamboo leaves, the slope of linear equation between $\log K_{oc}$ and $\log K_{ow}$ was similar with that of surfactant modified fibric peat, heat-killed fungi, raw fibric peat, and river sediments. However, the y-intercept for bamboo leaves was -1.21, which was much lower than that for the above-mentioned sorbents (-0.21 to -0.88). These phenomena may be attributed to the difference of polar component content among the sorbents.

3.4. Comparison of phenanthrene sorption by various sorbents

It is of great interest to compare the sorption capacity of various sorbents and partition coefficient (K_d) is an effective parameter to evaluate the sorption efficiency. Table 4 listed the K_d values of various sorbents including different kinds of biosorbents and some conventional abiotic materials. The $\log K_d$ values for phenanthrene in the current study are 3.40–3.72, which are comparable to several plant root and residues [8,22,35], white-rot fungi [30] and brown seaweed [21], but much lower than algae reported by Salloum et al. [16]. Plant cuticles also present much higher sorption capability than the raw plant materials [28]. Because algae and cuticles own comparable aromaticity (H/C = 1.53–1.73), their high sorption affinity with PAHs may be attributed to their aliphatic-rich property (71.5–91.6% of aliphatic carbons). This phenomenon reflects the important role of aliphatic carbons on PAHs sorption by plant residues. Cellulose shows lower sorption capability than lignin, indicating that lignin is a more effective storage medium for PAHs. Hydrolysis (acid or low/high temperature treatment) increases the aromaticity and decreases the polarity of sorbents, and hence dramatically enhances the sorption capability of raw plant materials [8,18]. While surfactant treatment increases the aliphatic carbon content of sorbents, which results in a greater sorption capacity and faster sorption rate of fibric peat [25]. Although the sorption capability of raw plant residues is often much lower than some conventional geosorbents such as kerogen [16], char and active carbon [33], it is still a promising biosorbent for POPs abatement due to its ubiquity, environmental compatibility, and cost effectiveness. Moreover, raw plant materials are easily modified to be more powerful sorbents by simple treatment.

4. Conclusions

Plant residues are of great potential as natural biosorbents for PAHs removal in wastewater treatment. Partition processes play an predominant role in PAHs biosorption by plant residues. The polarity [(O + N)/C], aromaticity (H/C), and sugar content imposed important effects on sorptive behavior of the biosorbents. Negative correlation of K_d values with sugar content, (O + N)/C, H/C for ryegrass roots, orange peels, bamboo leaves and pine needles are obtained. The K_d value of phenanthrene for wood chips was much lower than their respective predicted values from the structure–effect relationships. The structure–effect relationship provide a fundamental basis to select plant residues with high sorption affinity, and give a guide to modify raw plant residues to enhance their sorption capability. Removal of polar components (i.e., mainly sugar) through acid hydrolysis was a promising choice for plant residues modification to enhance the sorption capability of biosorbents. With the properties of low cost, environmental compatibility, high sorption capability, and ubiquity in the environment, plant residues and their modified materials are assumed to be a promising choice for organic pollutants treatment.

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