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# Effect of hexadecyltrimethyl ammonium bromide on the modified rice straw characteristics and its sorption behavior of phenanthrene

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ABSTRACT

A rice straw-derived sorbent for the removal of phenanthrene (PHE) was prepared by graft method using hexadecyltrimethyl ammonium bromide (HTAB) as a modifier. The surface morphology, electrostatic, and hydrophobic characteristics of the sorbent altered significantly after modification. The sorption performance of the modified rice straw, including sorption kinetics and isotherms, was evaluated by batch sorption experiments. The sorption process is strongly enhanced by grafted HTAB and could be appropriately described by pseudo-second-order model and linear sorption isotherms. As compared to adsorption, partition plays a more important role in the sorption of PHE to MRS. Correlations between sorbent properties and sorption capacity indicate that (O+N)/C, relative contact angle, and zeta potential are the key factors that govern the PHE sorption behavior.

*Keywords:* Rice straw; Sorbent; Phenanthrene; Modification; Enhanced sorption; Surfactant

## 1. Introduction

In the past decade, adsorption has become one of the low-cost and effective technologies for pollutant removal [1]. Agricultural wastes are considered as an alternative to replace the conventional adsorbents due to their availability in abundance and renewable [2,3]. Previous studies have shown that a variety of adsorbents are prepared from agricultural wastes, such as wheat/rice husk, bagasse, wheat/rice straw, peanut hull, exhausted coffee, and various nutshells [4–8]. Recent researches have focused on enhancing the effectiveness of agricultural wastes by modifying their specific properties to enable the affinity for certain organic contaminants [9,10].

The modification methods for adsorbent preparation consist of Soxhlet extraction, plasma technique, acid hydrolysis, ion exchange, and crosslinking [11–14]. Compared with the methods like Soxhlet extraction and acid hydrolysis, minor modification method such as ion exchange could be an even better choice due to its less chemical use and less environment impact [2]. Ding et al. [15] demonstrated that modification with long-chain hexadecyltrimethyl ammonium bromide (HTAB) enhanced organic matter adsorption significantly. In our previous studies, quaternary ammonium surfactant modification significantly enhanced the adsorption capability of polystyrene resin [14]. The beneficial effects of

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modification by grafting quaternary ammonium surfactants for organic matter sorption were profound.

However, the mechanism of enhanced sorption behavior for modified agricultural wastes remains unexplored. Having undergone different growth conditions, even one same crop tend to show chemically and structurally much more heterogeneous characteristics with different sorption behavior [16]. There is a strong need to conduct extensive research to reveal this kind of relationship and enhance sorption interaction.

As one kind of polycyclic aromatic hydrocarbons, phenanthrene (PHE) is often generated during incomplete burning of organics, and is extremely harmful to humans due to high toxicity and long-term persistence. Once released into the environment, PHE can transport long distance through air and water flow, and are difficult to biodegrade because of its chemical persistence and semi-volatile nature [17]. The average concentration of PHE in surface seawater from Yangpu Bay, China in summer 2014 was 369.92 ng/L [18], which was higher than the average concentration (44.9 ng/L) studied by Zhu et al. in Zhejiang Province, China [19].

Thus, sorption of PHE to the modified rice straw (MRS) with various amounts of surfactant was investigated in this study. The aim was to elucidate the mechanisms for the sorption of PHE by MRS, by establishing intercorrelations between sorption equilibrium, degree of modifications, and different sorbent properties, as well as to investigate the potential feasibility of using of rice straw-derived sorbent for removing toxic organics from water. Then, the correlations between sorption capacity and sorbent properties ((O+N)/C, relative contact angle, and zeta potential) were studied.

## 2. Materials and methods

### 2.1. Preparation and characterization of the adsorbent

The raw rice straw from Shanghai local countryside was washed and ground first to remove dust and soluble material. Then, the raw rice straw was milled and sieved to retain the 0.15–0.30 mm (60–100 mesh) fractions for further pretreatment and modification. The ground rice straw was treated with 0.1 mol $L^{-1}$ NaOH solution at the ratio of 1:12 (straw/liquid, w/v) to improve the reactivity at 30℃. After thoroughly washed with distilled water, the alkali-treated straw was dried at 105℃ for 24 h and preserved in a desiccator (named as RS). The cation-exchange capacity (CEC) of RS was measured by acid–base titration (0.564 mmol $g^{-1}$). 200 mL of the HTAB solution with desired concentration (6, 15, 30, and 45 mmol $L^{-1}$, respectively) was vigorously mixed with 10 g of RS at 40℃ for 4 h, in which the theoretical amounts of HTAB were 0.2, 0.5, 1.0, and 1.5 times the CEC.

After that, the mixture was centrifuged and the HTAB concentration of the supernatant was determined by an UV–visible spectrophotometer (UV2100, Unico Shanghai). The MRS was separated by suction filtration, washed until no foam observed, and was dried at 105℃ for 24 h in order to avoid the loss of HTAB. The MRS samples are hereafter referred to as MRS-0.2, MRS-0.5, MRS-1.0, and MRS-1.5, respectively, where the suffix number represents the theoretical ratio of HTAB amount to CEC.

Elemental analyses of rice straws were conducted by an elemental analyzer (Elementar Vario ELIII, Germany), and the atomic ratios were calculated to assess the polarity and aliphatic characteristics of the adsorbents. Zeta potential of the rice straws at pH value of 7.0 was measured by an electro-kinetic analyzer (JS94H, Shanghai Zhongchen, China). Capillary rise test was conducted by a wettability analyzer (JF99A, Shanghai Zhongchen, China) and the relative contact angles were calculated according to Washburn's equation [14]. Scanning electron microscopy (SEM) images were obtained on JSM-6360LV scanning electron microscope. BET surface areas were measured on a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer using $N_2$ adsorption at −196℃.

### 2.2. Sorption experiments

PHE (>98.9% purity) was purchased from AccuStandard Chemical Co. (CT, USA) and the stock solution was prepared at high concentrations (10,000 μg $L^{-1}$) in methanol before being added to aqueous solutions. Desired test solutions of PHE were prepared using appropriate subsequent dilutions of the stock solution. Sorption kinetics and equilibrium isotherms were studied. In each batch study, an accurately weighed quantity of straw was added to 50 mL of PHE solution taken in screw cap glass vials and the reaction mixture was agitated at 200 rpm at 30℃ in incubator shakers. Controls without adsorbent were prepared in the same way to account for the possible loss of PHE. A glass fiber filter, which had a proven negligible sorption of PHE, was used to separate the adsorbent from the solution. The concentration of PHE was analyzed using a HPLC system (D2000, Hitachi, Tokyo, Japan) equipped with an Agilent (Santa Clara, CA, US) LiChrospher PAH reverse-phase column (25 cm × 3 mm, 5 μm) at 30℃. The detection at 251 nm was performed using an ultraviolet detector at an isocratic operation (1 mL min$^{-1}$) of the mobile phase comprising 93/7 (*v*/*v*) methanol/water. Each determination was repeated three times and the results obtained were their average value.

The kinetics of PHE sorption was studied by varying the contact time from 0 to 360 min (0, 5, 10, 15, 20, 30, 40, 60, 120, 240, 360 min) at an initial PHE concentration of 500 μg L$^{-1}$. The sorption equilibrium experiments were conducted at 30°C with the initial PHE concentration of 50–1,000 μg L$^{-1}$ and continuous shaking of 8 h. The amount of PHE adsorbed per unit mass of adsorbent at time $t$ ($q_t$, μg g$^{-1}$) and the amount at equilibrium ($q_e$, μg g$^{-1}$), were calculated by the following equations:

$$q_t = (C_0 - C_t)V/m \tag{1}$$

$$q_e = (C_0 - C_e)V/m \tag{2}$$

where $C_0$ and $C_e$ (μg L$^{-1}$) are the initial and the equilibrium concentrations of PHE in solutions, respectively, $C_t$ (μg L$^{-1}$) is the concentration of PHE at time $t$. $V$ is the volume of the solution (L) and $m$ is the mass of dry adsorbent used (g).

All of the described experiments were repeated at least three times, and data values were averaged. In addition, error bars were introduced to prevent interference from uncertain factors.

## 3. Results and discussion

### 3.1. Characterization of RS and MRS

The characterization is important to understand and identify the different phenomena of retention (adsorbent–adsorbate) as well as to the interpretation of the kinetic results. As represented in Table 1, elemental analysis of the selected samples indicated that C, H, and N values substantially increased and the O contents decreased as a result of the modification. The difference could be due to the removal of considerable organic by-products and various amounts of HTAB present in the rice straw surface. Moreover, the zeta potential values of MRS were more positive than those of unmodified rice straws at the same pH. The low negative charge clearly establishes the presence of positive ionic surfactants on the MRS surface.

The amount of HTAB in MRS-0.2, MRS-0.5, MRS-1.0, and MRS-1.5, measured by spectrophotometry, was 0.11, 0.27, 0.53, and 0.71 mmol g$^{-1}$, respectively, which is close to the results calculated from the N content data. The changes of atomic ratio of the H/C and (O+N)/C should be noticed. The values of H/C increased while the (O+N)/C decreased after modification. The unmodified straw had the lowest C content and the highest O content, and displayed the highest polarity [(O+N)/C = 1.04]. In contrast, MRS-1.5 exhibited the highest C content and the lowest O content, and hence the lowest polarity [(O+N)/C = 0.53].

As expected, the BET surface areas of these adsorbent samples were quite small (see in Table 1). The surface area of unmodified rice straw is 1.34 m$^2$ g$^{-1}$, similar to the value reported by Chen et al. [20]. After modification, the specific surface areas of MRS-0.2, MRS-0.5, and MRS-1.0 showed a remarkable decrease. This could arise from pore blockage by adsorbed HTAB molecules. Because of its small molecular size, HTAB can easily access the outer pores of the rice straw. This finding is consistent with the results reported by Chen et al. [21], indicating that the surface area of activated carbon decreased from 648 to 431 m$^2$ g$^{-1}$ after adsorption of citric acid. It implies that the sorption kinetics in MRS may be much slower than that in RS since clogging of the cracks and cavities can lead to resistance in the PHE molecules transport.

However, the interesting thing is the surface area of MRS-1.5 with highest HTAB content is little higher than other MRS, even higher than that of RS. This could be because the adsorbent surface roughness increases with the increase in the HTAB content, which leads to more new preiection bonds created by the graft or deposition process. The result of SEM measurement with 200 and 500 magnification times (as shown in Fig. 1) is anastomosing with the above assumptions. According to the comparison results, the unmodified straws (RS) appeared to have smoother surface and contained more square-shaped lattices than MRS-1.5, while the modified RS (MRS-1.5) had rough areas containing various rounded projections and irregular-shaped protuberances. This may be partially attributed to the grafted surfactants, which are precipitation or crystallization on the surface.

### 3.2. Effect of contact time on PHE sorption

The influence of contact time on PHE sorption is shown in Fig. 2. The sorption capacity has a rapid increase as soon as the contact happens and the removals were rapid during the first hour, reaching more than 90% of the maximum sorption capacity, and then gradually leveled off. Such a fast kinetics will benefit a highly efficient pollutant removal. And the contact time of 240 min was sufficient for the

Table 1
Relative elemental composition, atomic ratio, BET-$N_2$ specific surface area, zeta potential, and relative contact angle of five sorbents

| Sorbent | Graft amount (mmol $g^{-1}$) | Elemental analysis C% | H% | N% | O% | Atomic ratio H/C | (O+N)/C | Specific surface area ($m^2$ $g^{-1}$) | Zeta potential (mV) | Relative contact angle (°) |
|---|---|---|---|---|---|---|---|---|---|---|
| RS | 0.00 | 39.30 | 6.30 | 0.60 | 53.80 | 1.92 | 1.04 | 1.34 | −44.5 | 67.2 |
| MRS-0.2 | 0.11 | 40.54 | 6.56 | 0.73 | 52.17 | 1.94 | 0.98 | 1.05 | −38.2 | 42.1 |
| MRS-0.5 | 0.27 | 43.38 | 7.15 | 1.03 | 48.44 | 1.98 | 0.86 | 0.87 | −32.3 | 22.8 |
| MRS-1.0 | 0.53 | 48.18 | 8.14 | 1.54 | 42.14 | 2.03 | 0.68 | 0.94 | −28.6 | 11.2 |
| MRS-1.5 | 0.71 | 53.54 | 9.25 | 2.10 | 35.10 | 2.07 | 0.53 | 1.77 | −21.5 | 0 |

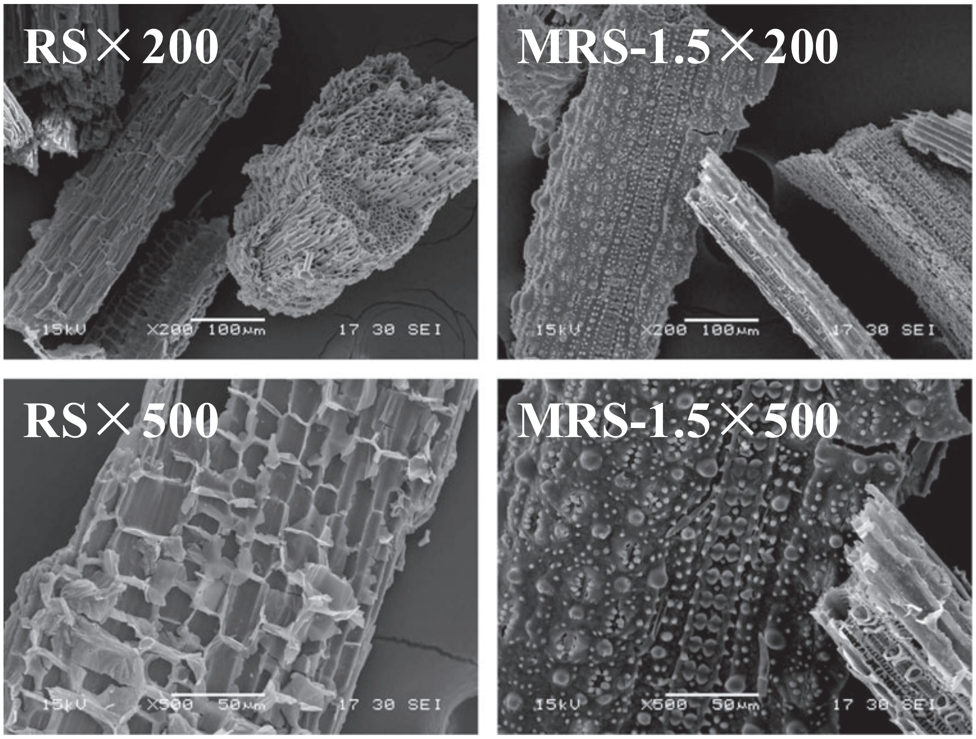

Fig. 1. SEM morphology of RS and MRS-1.5 enlarged 200 and 500 times.

equilibrium sorption, and 8 h was used in the following sorption isotherms study.

Besides, a significant difference was found between the RS and MRS at the same initial concentration. We may easily find that the sorption capacity of MRS was much greater than that of RS. In order to further explore the sorption mechanism of PHE onto MRS and rate-controlling steps, an investigation on kinetics was conducted next.

### 3.3. Sorption kinetics

Pseudo-first-order [22], pseudo-second-order [22,23], and intraparticle diffusion [24,25] kinetic models were used for testing experimental data in this section. The kinetic equations are given below as (3)–(5), respectively.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

$$q_t = k_i t^{1/2} + I \tag{5}$$

where $q_e$ and $q_t$ refer to the sorption capacity (μg $g^{-1}$) at equilibrium and at certain time, $t$ (min), respectively,

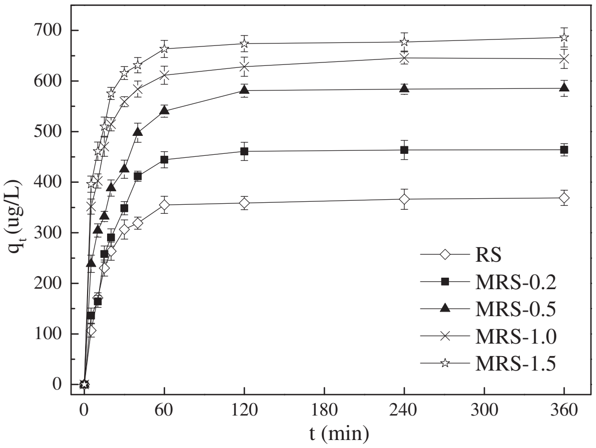

Fig. 2. Effect of contact time on the sorption of RS and MRS with different graft amounts.

$k_1$ ($\text{min}^{-1}$), $k_2$ ($\text{g}\ \mu\text{g}^{-1}\cdot\text{min}^{-1}$), and $k_i$ ($\mu\text{g}\ \text{g}^{-1}\ \text{min}^{-1/2}$) is the rate constant of the pseudo-first-order sorption, the pseudo-second-order sorption, and the intraparticle diffusion, respectively. $I$ ($\mu\text{g}\ \text{g}^{-1}$) is a constant that suggests the thickness of the boundary layer [25].

The initial sorption rate, $h$ ($\mu\text{g}\ \text{g}^{-1}\ \text{min}^{-1}$) can be determined from fitted $k_2$ and $q_e$ values based on [22],

$$h = k_2 q_e^2 \tag{6}$$

Also, half of the sorption time, $t_{0.5}$, is the time required for the adsorbent to take up half as much PHE as it would have taken up at equilibrium (i.e. $t = t_{0.5}$ as $q_t = q_e/2$) [26]:

$$t_{0.5} = 1/kq_e \tag{7}$$

The fitted curves of above-mentioned models were plotted in Fig. 3(a), (b), and (c). It was found that a close fit was obtained for the pseudo-first-order model and the pseudo-second-order model, respectively. However, the fitted kinetic parameters in Table 2 show that the pseudo-second-order model has a better correlation coefficient ($R^2 > 0.99$) than that of the pseudo-first-order model ($R^2 > 0.81$) and intraparticle diffusion model ($R^2 > 0.65$). In addition, the calculated value of $q_{e,cal}$ by pseudo-second-order model is much closer to the experimental value $q_{e,exp}$, which also confirms that the sorption of PHE follows pseudo-second-order kinetic [27].

According to intraparticle diffusion model, if the plot of $q_t$ vs. $t^{1/2}$ gives a straight line, then the sorption process is controlled by intraparticle diffusion; but the fitting result indicated that the model was not able to adequately describe the sorption behavior in our experiment [24,25]. In other words, the PHE uptake on the rice straw-based adsorbent functionalized with HTAB could be influenced by two or more steps due to the data exhibit multi-linear plots.

The rate coefficient, $k_2$, varied from $1.85 \times 10^{-4}$ to $3.32 \times 10^{-4}$ g $\mu\text{g}^{-1}$ $\text{min}^{-1}$. For MRS-0.2 and MRS-0.5, the $k_2$ value of them is lower than that of RS because the sorption of PHE took longer time to reach equilibrium than that on RS, which is mainly due to the much larger sorption amount of MRS. The sorption rate of MRS-0.2 and MRS-0.5 is really close to that of RS at the initial stage.

However, the $k_2$ value of MRS-1.5 is larger than others and obtaining a shortest half of the sorption time. The initial sorption rate $h$ of MRS-1.5 is greater than that of other adsorbents at the initial stage and is nearly four times greater than that of RS. Same trend was previously reported by Dong et al. [10] for the sorption of Bisphenol A onto HTAB-modified zeolite. This variance drops a hint that the sorption ability may not only depend on the specific surface area of the adsorbent, because the specific surface area of RS changed a little after modification. Apparently, the surface modifications had generated new sorption sites for PHE binding. The sorption capacity of PHE by MRS was much higher than unmodified RS, and increased with the increase in amount of HTAB loaded.

### 3.4. Sorption isotherms

In order to clarify the sorption process, the sorption isotherms of PHE on RS and MRS were conducted at a fixed sorbent dosage (0.05 g) by changing initial concentrations and the isotherms were described by Henry linear model (Eq. (8)) and Freundlich model (Eq. (9)) [28]:

$$q_e = K_d C_e \tag{8}$$

$$q_e = K_f C_e^{1/n} \tag{9}$$

where $K_d$ ($\text{L g}^{-1}$) is the apparent sorption coefficient. $K_f$ (($\mu\text{g g}^{-1}$) ($\text{L}\ \mu\text{g}^{-1})^{1/n}$) is the sorption capacity coefficient; $1/n$ is the Freundlich exponent that describes how favorable the sorption process is.

From Fig. 4, the adsorbed amounts of PHE on both types of adsorbent increase with the increase in solute concentrations, but the adsorptive intensities are different. MRS shows a greater sorption capacity than unmodified rice straw under all the conditions

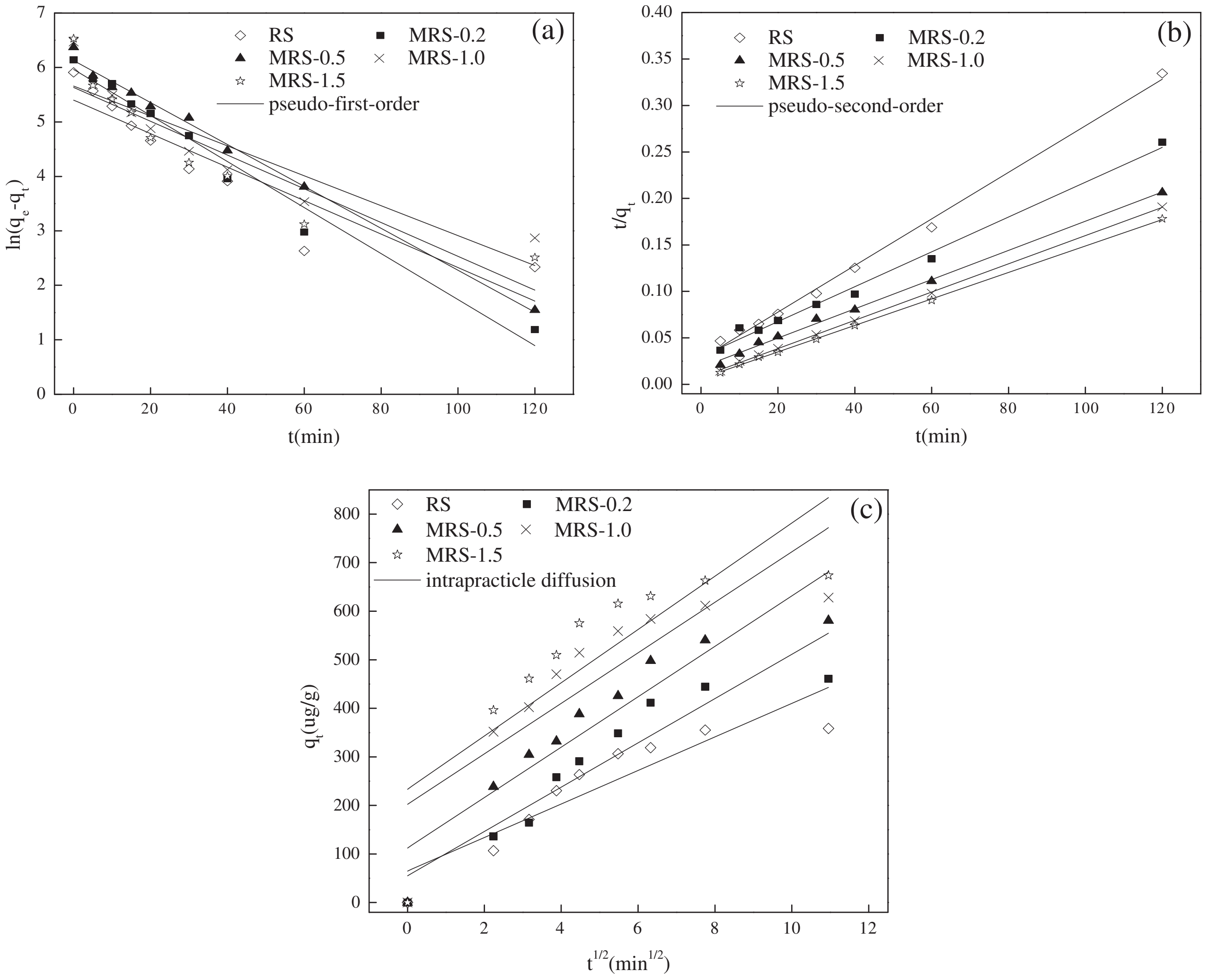

Fig. 3. Fitted kinetic curve based on the (a) pseudo-first-order model, (b) pseudo-second-order model, and (c) intraparticle diffusion model.

Table 2
Pseudo-second-order kinetic parameters for PHE sorption on RS and MRS ($C_0$ = 500 μg L$^{-1}$)

| | | pseudo-second-order model | | | | |
|---|---|---|---|---|---|---|
| Sorbent | $q_{e,exp}$ (μg g$^{-1}$) | $k_2$ (g μg$^{-1}$ min$^{-1}$) | $t_{0.5}$ (min) | $q_e^2$ (μg g$^{-1}$) | $H$ (μg g$^{-1}$ min$^{-1}$) | $R^2$ |
| RS | 387.2 | 2.90E-4 | 9.0 | 384.6 | 42.9 | 0.999 |
| MRS-0.2 | 461.2 | 1.88E-4 | 11.1 | 476.2 | 42.7 | 0.998 |
| MRS-0.5 | 586.2 | 1.85E-4 | 9.2 | 588.2 | 64.1 | 0.999 |
| MRS-1.0 | 661.9 | 2.88E-4 | 5.2 | 666.7 | 128.2 | 0.999 |
| MRS-1.5 | 687.7 | 3.32E-4 | 4.2 | 714.3 | 169.5 | 0.999 |

Notes: $q_{e,exp}$: Equilibrium adsorption capacity from experimental results.
$q_e^2$: Equilibrium adsorption capacity calculated using pseudo-second-order model.

studied. In comparison with RS, PHE sorption on MRS is greatly enhanced after intercalating with HTAB$^+$, indicating that the sorption capacity of rice straw was notably improved by modification. Results in Table 3 indicated that Linear and Freundlich models both described the isotherm data well [28]. But the isotherm model fitness was dependent on the HTAB graft amount. For RS, the comparison of the magnitude of $R^2$ indicates that Freundlich isotherm fitted the data more precisely compared to linear isotherm. But after modification, linear model generally fitted better than Freundlich model, especially in the case of higher HTAB graft amount. The rice straw adsorbents exhibited varied degrees of model fitness, which implied that the PHE sorption mechanisms by MRS may be different between the low and high graft amount, which was likely caused by heterogeneous interactions of functional groups with the PHE on the MRS surface.

### *3.5. The contribution of adsorption and partition: structural features affecting sorption*

According to the above analysis, sorption of PAHs to the surface of surfactant-modified adsorbent is a complex and cumulative function of multiple processes [28]. Based on the dual-mode concept, the sorption process involves a combination of at least two principal sorption domains: (1) amorphous soft phase domain (partitioning); and (2) more rigid, condensed phase domain (adsorption) [29,30]. The organic matrixes of MRS could be regarded as mainly consist by aliphatic moieties (soft phase) and aromatic backbones (hard phase), so micropores adsorption and linear partition all play a role in the whole sorption process [31].

Generally, adsorption capacities were probably correlated with sorbents surface areas. In this study, for MRS, the contribution of adsorption on condensed phase to the whole sorption was relatively small due to the small specific surface area. There is no significant relationship between PHE removal and MRS surface area. Therefore, the sorption by partition in a soft phase makes a major contribution to the whole sorption [32].

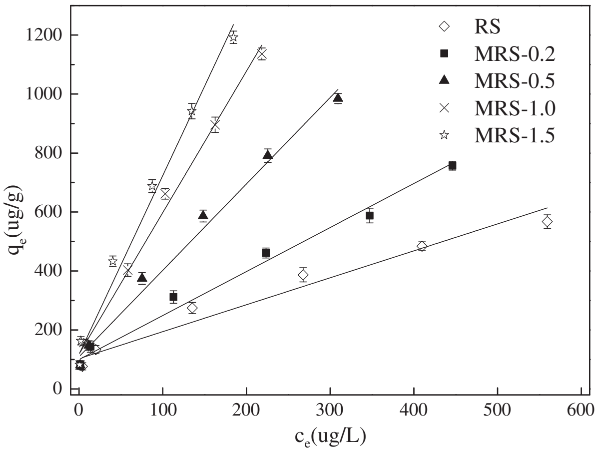

Fig. 4. Sorption isotherms of PHE by five adsorbents.

The distinctive sorption capacity of MRS for PHE further proves that the grafted HTAB play a critical role in partition process. When HTAB grafted onto the sorbent surface, the non-polar portion (alkyl) pointed toward the bulk of solution, and thus formed a soft organic phase over sorbent surface [33,34]. The hydrophobic interaction between the organic phase and the benzene rings of PHE strengthens the retention of PHE [10]. The values of H/C increased while the (O+N)/C decreased after modification. In other words, the aliphatictiy increased and the polarity decreased with the HTAB amount increasing. The hydrophobicity of MRS has been referenced by the atomic ratio coefficient ((O+N)/C) and n-octanol wettability (relative contact angle). Herein, the $q_e$ and $K_d$ are paired for comparing correlation using ((O+N)/C) and relative contact angle (as shown in Fig. 5). $K_d$ values generally increased as ((O+N)/C) and relative contact angle decreased. Similarly, significant relationships were observed between $q_e$ and ((O+N)/C) and relative contact angle, respectively, indicating that ((O+N)/C) and relative contact angle could be used to predict the sorption properties of sorbents.

### *3.6. Mechanism of enhanced sorption behavior*

Adsorbent hydrophobicity, rather than surface area, was the dominant adsorbent parameter affecting sorption in this study. However, given the heterogeneous nature of rice straw, it is unlikely that the sorption mechanism obeys simple hydrophobic partitioning paradigms [11,34]. In fact, the experimental results indicate that, besides hydrophobic effects, other mechanisms also significantly contributed to the sorption of PHE to MRS. Higgins and Luthy [35] have observed weak correlations of perfluorinated surfactants sorption with zeta potential, suggesting that electrostatic interactions may play a role in anionic surfactant sorption. In this study, the successfully grafted quaternary ammonium cations made sorbent surface less negative charged due to the positive-charged head of HTAB. Although the additional charge generated by the grafting surfactants was insufficient to change the total charge of the MRS, electrostatic interaction is still the most likely explanation for the linear relationship observed for sorption capacity and zeta potential according to the discussion mentioned above. PAHs are rich in delocalized

Table 3
Linear and Freundlich model parameters for PHE sorption isotherms

| | Linear equation | | | Freundlich equation | | |
|---|---|---|---|---|---|---|
| Sorbent | $K_d$ (L g$^{-1}$) | $K_{oc}$ (L g$^{-1}$) | $R^2$ | $K_F$ ((μg g$^{-1}$) (L μg$^{-1}$)$^{1/n}$) | $n$ | $R^2$ |
| RS | 0.86 | 2.19 | 0.967 | 41.60 | 0.4027 | 0.994 |
| MRS-0.2 | 1.43 | 3.54 | 0.989 | 59.85 | 0.3851 | 0.972 |
| MRS-0.5 | 2.91 | 6.71 | 0.991 | 55.99 | 0.4752 | 0.976 |
| MRS-1.0 | 4.78 | 9.91 | 0.994 | 66.92 | 0.4992 | 0.985 |
| MRS-1.5 | 5.86 | 10.94 | 0.991 | 105.39 | 0.4369 | 0.985 |

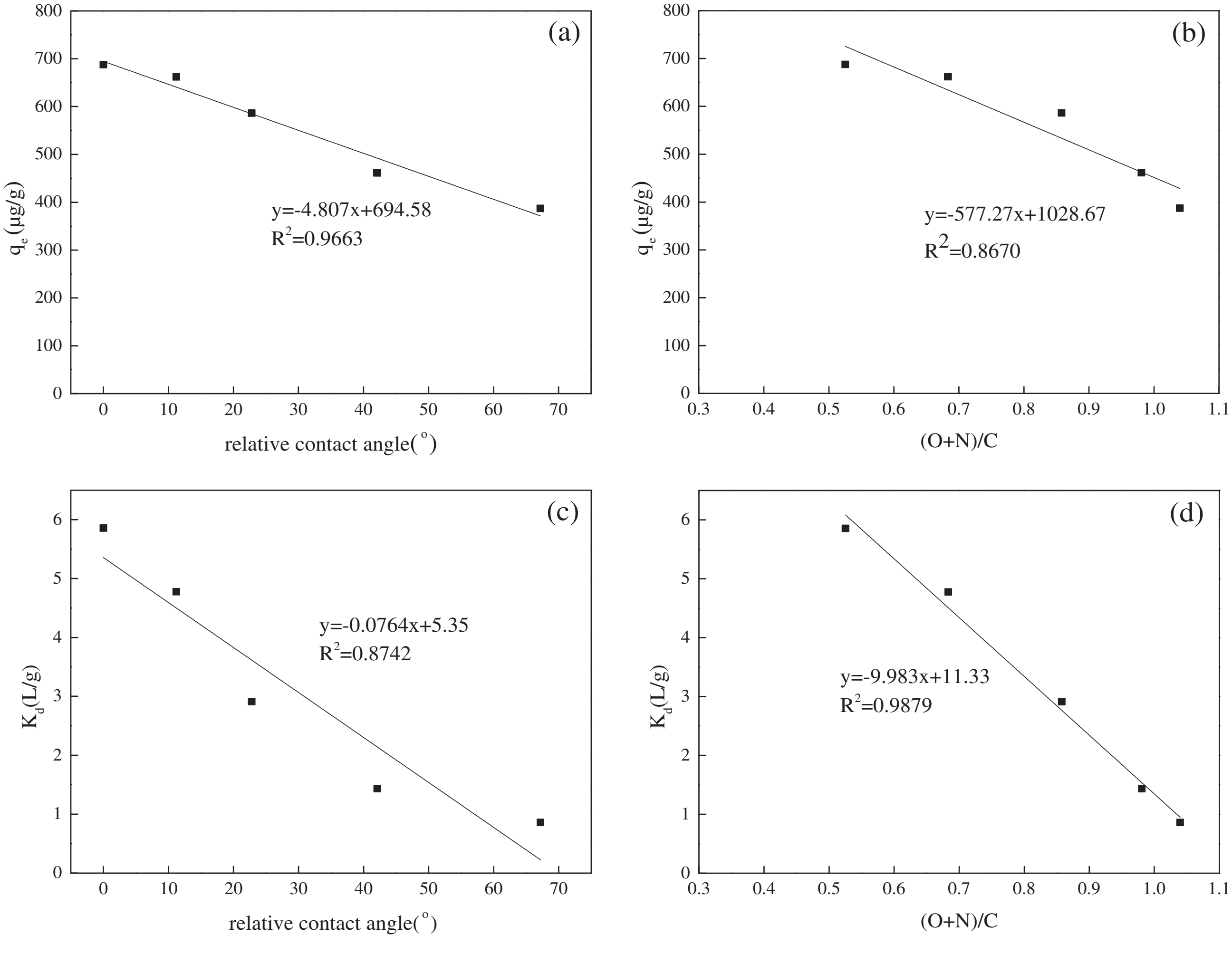

Fig. 5. Correlation analysis for sorption parameters and rice straw hydrophobicity ($C_0$ = 500 μg/L).

π electrons and thus may interact strongly with electron-deficient or positively charged species via electron donor–acceptor interactions or electrostatic attractions (cation-π bonding) [36]. MRS-1.5 has the largest cation amount among all the tested MRS, and the cation-π interactions between MRS-1.5 and PHE in aqueous solution are expected to be the strongest. PHE molecules sorbed on the MRS surface and cation-π bonded with HTAB cations, making microenvironments around the cations more hydrophobic and therefore favoring cation-π interactions with subsequently sorbed PHE molecules.

## 4. Conclusions

In this study, PHE was chosen as probe compound to investigate the unique sorption behavior of MRS. $K_d$ values generally increased as ((O+N)/C) and relative contact angle decreased. The less negative-charged surface clearly confirms the presence of ionic surfactants on the MRS surface. Attachment of HTAB enhanced the hydrophobicity of the RS surface. Kinetic results indicate that the sorption process is more appropriately described by pseudo-second-order model. The sorption capacities of PHE on the MRS increase with HTAB graft amount increasing. Compared to adsorption, the contribution of partition plays more important role in the sorption of PHE to MRS. The enhanced sorptive affinities were due to hydrophobic interactions between PHE and ammonium cations on the MRS surface.

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## Abbreviations

| | | |
|---|---|---|
| PHE | — | phenanthrene |
| HTAB | — | hexadecyltrimethyl ammonium bromide |
| PAHs | — | polycyclic aromatic hydrocarbons |
| RS | — | alkali-treated straw |
| MRS | — | modified rice straw |
| CEC | — | cation-exchange capacity |
| $C_0$ and $C_e$ | — | the initial and the equilibrium concentrations of PHE in solutions |

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