

Cosorption of Phenanthrene and Mercury(II) from Aqueous Solution by Soybean Stalk-Based Biochar

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ABSTRACT: Soybean [*Glycine max* (L.) Merr.] stalk-based biochar was prepared using oxygen-limited pyrolysis. We evaluated phenanthrene (PHE) and Hg(II) sorption, from single and binary component solutions, onto prepared biochar. We found that the prepared biochar efficiently removed PHE and Hg(II) from aqueous solutions. The isotherms for PHE and Hg(II) sorption could be described using linear and Tóth models, respectively, both with high regression coefficients ($R^2 > 0.995$). When PHE and Hg(II) coexisted in an aqueous solution, we observed direct competitive sorption, each one suppressing another. Our results provide insight into the recycling of agricultural residues, and also a new application for removal of polycyclic aromatic hydrocarbons and heavy metals from contaminated water utilizing biochar from agricultural residue.

KEYWORDS: phenanthrene, Hg(II), biochar, cosorption, soybean stalk

INTRODUCTION

Soybean stalk is a plentiful, inexpensive, and renewable resource. China is a large agricultural country, and over 16 million metric tons of soybeans are produced annually. However, most soybean stalk is arbitrarily discarded or destroyed, resulting in loss of a valuable resource and environmental pollution.¹ The development of renewable bioenergy technologies makes it possible to convert waste biomass into value-added material, such as biochar. Biochar refers to a carbon-enriched and porous material derived from oxygen-limited pyrolysis of biomass. Biochars currently used by commercial and research facilities include wood materials (wood chips, wood pellets, and tree bark), crop residues (straw, nutshells, and rice hulls), switch grass, organic wastes (paper sludge, sugar cane bagasse, distillers grain, olive waste), chicken litter, dairy manure, and sewage sludge.² Recent studies have highlighted the benefits of biochar technologies, particularly with respect to carbon sequestration.^{3,4} Also, there are numerous advantages to applying biochar to soils including enhanced soil fertility and crop productivity, increased nutrient concentrations and water holding capacity, and reduced emissions of other greenhouse gases.⁵

In addition to its carbon sequestration and soil amelioration applications, biochar is recognized as a highly efficient and cost-effective sorbent for pollutant removal. For example, pine needle derived biochar (which sorbs naphthalene, nitrobenzene, and *m*-dinitrobenzene) can be used as an engineered environmental sorbent to remove aqueous organic contaminants.⁶ Straw-based biochar is an excellent substitute for activated carbon in treating dyed water.⁷ Rice straw-derived biochar significantly lowers the pentachlorophenol concentration in adsorbed liquid extracted from sediments, thus reducing pentachlorophenol's toxicity on wheat seed growth.⁸ Biochar prepared from a mixture of maple, elm, and oak woodchips and bark exhibits a high sorption affinity

for atrazine and simazine from water.⁹ Furthermore, biochar has a strong sorption affinity for some water-soluble inorganic pollutants, such as phosphate¹⁰ and some heavy metal ions.¹¹

Polycyclic aromatic hydrocarbons (PAHs) are priority pollutants due to their carcinogenic, mutagenic, and toxic properties.¹² They have been found widespread with high concentrations in water bodies all over the world.¹² Environmental pollution by heavy metals is related to military, industrial, and agricultural processes.¹³ PAHs and heavy metals, two typical pollutants, are often found together at many contaminated sites.^{14,15} Many studies have evaluated the uptake of heavy metal ions or PAHs from water, while the study of PAH-heavy metal ion mixtures has been neglected.

Phenanthrene (PHE) is commonly found in wastewater and is difficult for treatment plants to remove using conventional physicochemical methods.^{16,17} PHE was chosen in this study as a representative PAH to investigate PAH removal from aqueous solutions. Hg is one of the most harmful heavy elements to humans and other organisms, and it is cumulative and persistent in both the human body and the environment. Hg has also been found in surface water.¹⁸ Thus, determining if it is present in water is important for human health. The discharge concentration limit for Hg in wastewater, set by China, is $50.0 \mu\text{g L}^{-1}$ (GB8978-1996), while the upper concentration limit for Hg in surface water is only $1.0 \mu\text{g L}^{-1}$ (GB3838-2002). We chose to investigate the removal of Hg, as a representative heavy metal, from aqueous solutions.

In the present study, we prepared a novel, cost-effective biochar sorbent to simultaneously remove PHE and mercury(II) from contaminated water. An agricultural biomass waste, soybean

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[*Glycine max* (L.) Merr.] stalk, was selected as the raw material to reduce the cost of biochar preparation. Soybean stalk-based biochars were prepared using oxygen-limited pyrolysis at different temperatures. In addition, we evaluated the removal efficiencies and sorption isotherms of PHE and Hg(II) from single and binary component solutions onto the prepared biochar. This work provides insight into the reuse of agricultural residue and a new way to remove PAHs and heavy metals from contaminated water using biochar from agricultural residue.

MATERIALS AND METHODS

Soybean Stalk Samples. Soybean stalk was collected from a local farmer in Nanjing City, Jiangsu Province, China. It was washed four times with deionized water, and then dried at 105 °C for 3 h. After cooling, the soybean stalk was ground and sieved to 60 mesh and stored in a glass jar at room temperature.

Reagents. PHE, as a representative PAH, was provided by Aldrich Chemical Co. with a purity of >98%. Its molecular weight, solubility in water at 25 °C, and log K_{ow} are 178.23 g mol⁻¹, 1.18 mg L⁻¹, and 4.46, respectively.¹⁹ PHE and methanol were chromatographic grade. CaCl₂, NaN₃, NaHCO₃, and HgCl₂ were analytical grade, and deionized water was used in all experiments. The sorption background solution (0.005 mol L⁻¹ CaCl₂, 500 mg L⁻¹ NaN₃) was prepared by dissolving 0.555 g of CaCl₂ and 0.500 g of NaN₃ in water and diluting to 1 L. The pH was adjusted to 7.0 by NaHCO₃ (5 mg L⁻¹). A stock solution of PHE (100 mg L⁻¹) was prepared by dissolving 0.100 g of PHE in 1 L of methanol and stored at 4 °C. The stock solution of Hg(II) (1 mg L⁻¹) was prepared by dissolving 1.354 mg of HgCl₂ salts in 1 L of deionized water. The individual PHE working solutions (1, 2, 3, 4, 5, and 10 mg L⁻¹) were prepared by diluting the stock solution with the sorption background solution. The individual Hg(II) working solutions (2, 4, 8, 16, 32, 64, 120, 250, and 500 μg L⁻¹) were prepared by dilution with deionized water. The pH was adjusted to 7.0 with NaHCO₃ (5 mg L⁻¹). The dual working solution of PHE and Hg(II) was prepared by diluting the PHE and Hg(II) stock solution with sorption background solution.

Soybean Stalk-Based Biochar Preparation. Preparation of soybean stalk-based biochar was performed as described by Peng et al.²⁰ Powdered soybean stalk (60 g) was sealed in a crucible and heated from room temperature to carbonization temperature (300, 400, 500, 600, and 700 °C) for 8 h in a muffle furnace. After cooling to room temperature, the crucible was removed from the furnace and the biochar sample was obtained.

Characterization of Soybean Stalk-Based Biochar. Specific surface area of the soybean stalk-based biochar was determined by nitrogen adsorption at 77 K using model JW-004 surface area analyzer (Beijing JWGB Sci & Tech Co., Ltd.), and the determination complied with the Standard Test Method (GB/T 19587-2004, testing standard of activated carbon in China). Iodine number was tested according to a standard method of China (GB/T 12496.8-1999). The determination of the sorption amount of methylene blue was referred to a standard method of China (GB/T 12496.10-1999). The ash content was measured according to the standard method of China (GB/T 12496.3-1999). The values were accurate to the second decimal place. Scanning electron microscope (SEM) imaging analysis was conducted using a HITACHI S-3000N SEM to observe the morphological properties of the biochar prepared at a carbonization temperature of 700 °C.

Sorption of Phenanthrene and Hg(II). The removal experiments were divided into two stages: PHE and Hg(II) removal from single component solutions, and PHE and Hg(II) removal from a binary component solution. All experiments for PHE and Hg(II) removal were conducted in a 35 mL centrifuge tube. Prepared biochar (0.010 g) was weighed and set in a 35 mL centrifuge tube, and an accurate volume (30 mL) of individual PHE working solution or individual Hg(II) solution, or dual working solution of PHE and Hg(II), was added. To

Table 1. Characteristics of the Prepared Soybean Stalk-Based Biochars at Five Different Carbonization Temperatures

carbonization temp (°C)	sp surf area (m ² g ⁻¹)	iodine no. (mg g ⁻¹)	amt of methylene blue sorption (mg g ⁻¹)	ash content (%)
300	144.14	203.04	14.51	11.62
400	138.76	204.54	14.58	20.49
500	152.98	210.38	14.72	21.99
600	179.03	250.73	14.87	23.87
700	250.23	337.12	45.43	25.49

prevent loss of PHE, a tube cap layered with tinfoil was applied immediately and tightly, and then sealed with parafilm. The centrifuge tubes containing the biochar/working solution mixture were oscillated continuously for 24 h at a temperature of 25 °C. Afterward, the mixture was centrifuged at 6000g for 30 min and the PHE and Hg(II) concentrations in the supernatant were determined. During the oscillation and centrifuge steps, the centrifuge tubes were kept in the dark. All experiments were performed in triplicate.

Based on the original concentration and sorption equilibrium concentration of PHE or Hg(II) in solution, we calculated the sorption capacity of prepared biochar using the following equation:

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where Q_e is the amount of sorbate sorbed by the prepared biochar at equilibrium, in mg g⁻¹ for PHE and μg g⁻¹ for Hg(II); C_0 and C_e are the original concentration and the equilibrium concentration of sorbate in solution, respectively, in mg L⁻¹ for PHE and μg L⁻¹ for Hg(II); V is the volume of the solution, in L; and m is the mass of the biochar, in g.

Controls included PHE working solutions in the absence of biochar to examine any loss of PHE other than to biochar sorption, such as photochemical decomposition, volatilization, and sorption to the glass tubes. Such losses were found to be negligible.

The PHE concentration in an aqueous solution was analyzed using a high-performance liquid chromatography (HPLC) system (SHIMADZU LC-20A) coupled with a programmable fluorescence detector. Aliquots of aqueous solution containing PHE (3 mL) were mixed with 7 mL of methanol. The mixture was filtered through a 0.22 mm filter, and the PHE concentration was determined by HPLC. The HPLC system was fitted with a 4.6 × 250 mm reverse phase C₁₈ column, using methanol as the mobile phase at a flow rate of 1 mL min⁻¹ (40 °C). Sample solutions (30 μL) were injected into the HPLC system using an autosampler. The excitation wavelength of PHE was 244 nm, and the corresponding emission wavelength was 360 nm. The detection limit was 17.14 ng L⁻¹. The Hg(II) concentration in aqueous solution was analyzed using cold-vapor atomic fluorescence spectrometry. Measurement of Hg(II) followed the United States Environmental Protection Agency Method 1631.²¹

RESULTS AND DISCUSSION

Characteristics of Soybean Stalk-Based Biochar. Specific surface area, iodine number, amount of methylene blue sorption, and the ash content of the soybean stalk-based biochars prepared at five different carbonization temperatures were determined, and the data are listed in Table 1. As seen, the ash content of the biochar prepared at 700 °C was 25.49%, which was slightly higher than that of the biochars prepared at 400, 500, and 600 °C; Similarly, the specific surface area, iodine value, and sorption amount of methylene blue of the 700 °C prepared biochar were 250.23 m² g⁻¹, 337.12 mg g⁻¹, and 45.43 mg g⁻¹, respectively,

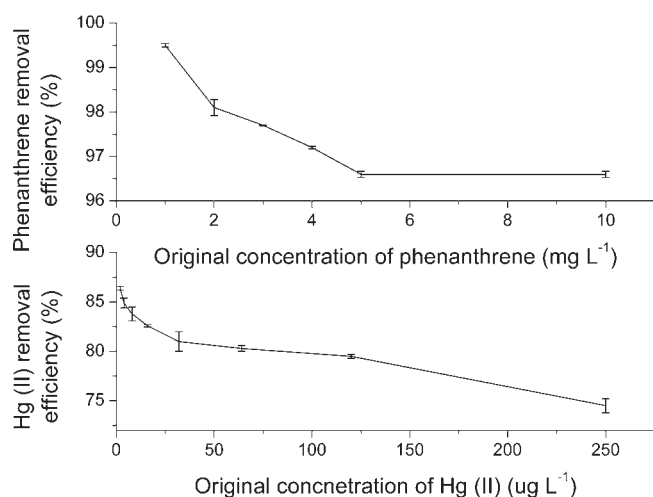


Figure 1. The removal efficiencies of phenanthrene and Hg(II) from solution by the prepared biochar.

and the values were much higher than those of the biochar prepared at the lower carbonization temperatures.

We found that the biochars with the highest qualities were prepared at a carbonization temperature of 700 °C. As such, the 700 °C prepared biochars were used to evaluate the sorption performance of PHE and Hg(II) from solutions with single and binary contaminant components. In addition, it was observed from the SEM micrograph (1000×) that the biochar sample had a rough and convoluted structure with a highly complex network of pores, channels, and otherwise fibrous ridged surfaces. The rough surface and numerous pores of the biochar provided larger surface areas, resulting in the increase of the sorption capability for PHE and Hg(II).

Removal of Phenanthrene and Hg(II) from a Monocomponent Solution. At pH 7.0, a biochar concentration of 0.010 g/30 mL, and a contact time of 24 h, PHE and Hg(II) removal efficiencies from monocomponent solutions onto the prepared biochar are shown in Figure 1. With increasing concentrations of Hg(II), removal efficiencies from monocomponent solutions decreased. In the original concentration range of 2 to 250 µg L⁻¹, Hg(II) removal efficiencies were 86.4–74.5%. The removal efficiency was larger than the maximum Hg(II) removal efficiency (72%) from aqueous solution by adsorption on activated carbons prepared from olive stones with a surface area of 1383 m² g⁻¹.²² Similarly, PHE removal efficiencies decreased as the initial concentration of PHE increased. However, PHE removal efficiencies were very high at the evaluated concentrations. At a concentration of 10 mg L⁻¹, PHE removal efficiency was lowest at 96.6%. The maximum PHE removal efficiency was 99.5% at a concentration of 1 mg L⁻¹. This suggests that biochar prepared from soybean stalk can efficiently remove PHE from aqueous solutions. A few studies have recently evaluated PAH removal from aqueous solutions using carbonaceous materials. Zeledón-Toruño et al.²³ reported that when the amount of leonardite, solution volume, and concentration of PAHs were 0.5 g, 500 mL, and 100 µg L⁻¹, respectively, the removal efficiencies of PAHs (fluorene, pyrene, etc.) from water by leonardite exceeded 82% at equilibrium. A PHE removal efficiency of 95.2% was reported for petroleum coke-derived porous carbon under the conditions of 0.1 g of porous carbon, 100 mL of solution volume, and initial PAH concentration of 6.4 mg L⁻¹.²⁴ Li et al.²⁵ reported that the phenanthrene removal efficiency was

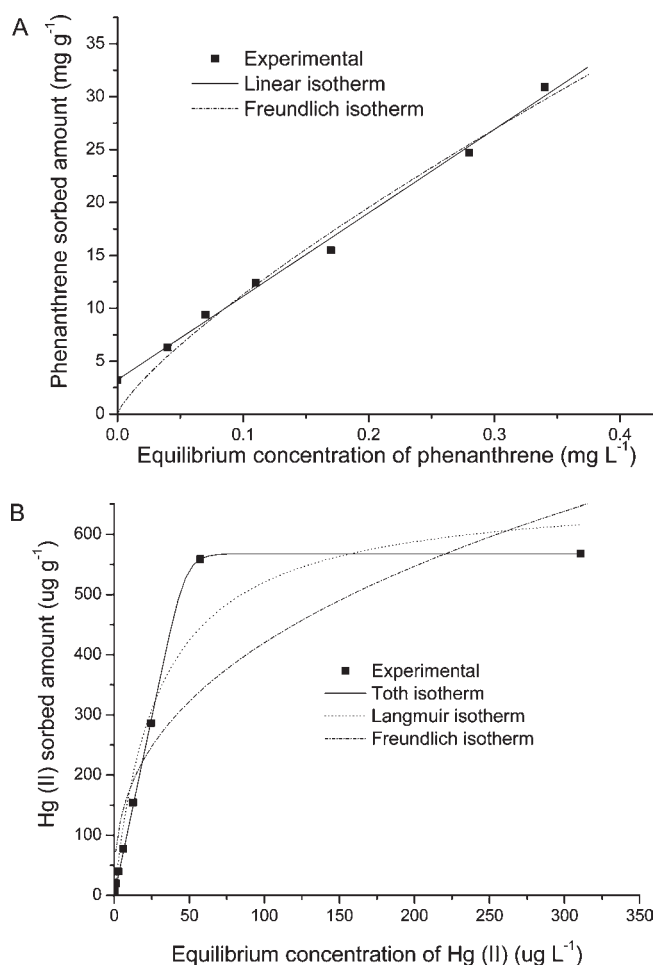


Figure 2. The isotherms for phenanthrene (A) and Hg(II) (B) sorption from monocomponent solution onto the prepared biochar.

89.41–91.16% from aqueous solution with initial phenanthrene concentration of 0.5 mg L⁻¹ using hydrolyzed pink bark at the dose of 0.5 g L⁻¹. Comparatively, biochars are more efficient at removing PAHs than carbonaceous materials.

Phenanthrene and Hg(II) Sorption Isotherms in a Monocomponent Solution. To analyze the removal mechanisms of PHE and Hg(II) from aqueous solution using prepared biochar, we investigated equilibrium sorption. When the biochar concentration was 0.01 g/30 mL, sorption of PHE and Hg(II) from monocomponent solutions onto prepared biochar was evaluated at a constant temperature of 25 °C to obtain a sorption isotherm. The sorption isotherms of PHE and Hg(II) are shown in Figure 2. Linear and Freundlich isotherm equations were applied to interpret the experimental data for PHE sorption.

The linear isotherm can be described by the following equation:²⁶

$$Q_e = K_d C_e \quad (2)$$

where K_d is the partition coefficient of PHE between biochar and solution, in L g⁻¹.

The Freundlich isotherm can be described by the following equation:²⁷

$$Q_e = K_F C_e^n \quad (3)$$

where K_F (L g⁻¹) and n (dimensionless) are Freundlich adsorption isotherm constants, indicative of the extent of adsorption

Table 2. Parameters of Linear, Freundlich, Langmuir, and Tóth Isotherms for the Sorption of Phenanthrene and Hg(II) onto Soybean Stalk-Based Biochars in a Single Component System^a

sorption isotherms	parameters	phenanthrene	Hg(II)
linear	K_d ($L g^{-1}$)	78.898	
	R^2	0.995	
Freundlich	K_F ($L g^{-1}$)	69.668	72.353
	n	0.790	0.382
	R^2	0.986	0.824
Langmuir	Q_m ($\mu g g^{-1}$)		674.909
	b ($L \mu g^{-1}$)		0.034
	R^2		0.953
Tóth	Q_m ($\mu g g^{-1}$)		567.951
	K_T ($L \mu g^{-1}$)		0.0209
	m		9.864
	$\lim_{C_e \rightarrow 0} [(dQ_e)/(dC_e)] =$		11.870
	$Q_{m,T}K_T$ ($L g^{-1}$)		
	R^2		1.000

^a The soybean stalk-based biochar concentration was 0.01 g/30 mL; temperature was 25 °C; and contact time was 24 h.

and the degree of nonlinearity between the solution concentration and adsorption, respectively.

As seen in Figure 2B, the sorption isotherm of Hg(II) plateaued above approximately $57.3 \mu g L^{-1}$. According to Giles classification for isotherms, the shape of the experimental isotherm of Hg(II) was "L2".²⁸ The Freundlich, Langmuir, and Tóth isotherm equations were applied to interpret the experimental data for Hg(II) sorption.²⁹

The Langmuir isotherm can be described by the following equation:³⁰

$$Q_e = \frac{Q_{m,L} b C_e}{1 + b C_e} \quad (4)$$

where $Q_{m,L}$ is the monolayer sorption capacity of the sorbent ($\mu g g^{-1}$) and b is the Langmuir sorption constant ($L \mu g^{-1}$).

Tóth modified the Langmuir equation, reducing the error between experimental data and predicted values of equilibrium adsorption data. The Tóth isotherm can be described by the following equation:³¹

$$Q_e = \frac{Q_{m,T} K_T C_e}{[1 + (K_T C_e)^m]^{1/m}} \quad (5)$$

where $Q_{m,T}$ is the maximum sorption of the sorbent, $\mu g g^{-1}$, and K_T ($L \mu g^{-1}$) and m (dimensionless) are the Tóth sorption constants. It is obvious that, for $m = 1$, this isotherm reduces to the Langmuir sorption isotherm equation. Therefore, the parameter m is said to characterize the system's heterogeneity. If it deviates from unity, the system is said to be more heterogeneous.

Linear and Freundlich plots for PHE sorption onto prepared biochar at 25 °C are shown in Figure 2A. Freundlich, Langmuir, and Tóth plots for Hg(II) sorption are shown in Figure 2B. The parameters of these sorption isotherms are listed in Table 2. For PHE sorption, the regression coefficient R^2 of the linear isotherm model ($R^2 = 0.995$) was larger than that of the Freundlich isotherm model ($R^2 = 0.986$). It is clear that the linear isotherm model is a better fit than the Freundlich isotherm model. Thus, we hypothesized that partitioning is the dominant mechanism for

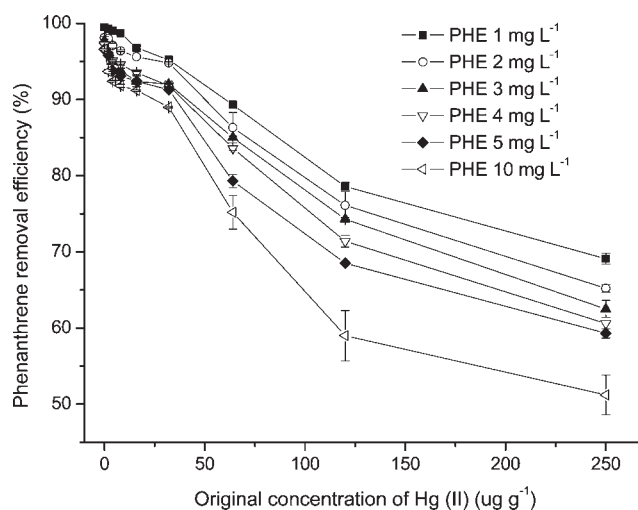


Figure 3. Phenanthrene removal efficiencies from dual-component solution containing Hg(II) onto the prepared biochar.

the sorption of PHE onto the prepared biochar. For Hg(II) sorption, the regression coefficient R^2 of the Tóth isotherm model ($R^2 = 1.000$) was significantly larger than that of the Freundlich isotherm ($R^2 = 0.824$) and Langmuir isotherm models ($R^2 = 0.953$). It is also clear that the Tóth isotherm model fits better than the Freundlich and Langmuir isotherm models. The m value was equal to 9.864, significantly larger than unity. This suggests that the sorption of Hg(II) onto soybean stalk-based biochar was highly heterogeneous.

Effect of Hg(II) on Phenanthrene Sorption to Prepared Biochar. At pH 7.0, biochar concentrations of 0.010 g/30 mL, and a contact time of 24 h, PHE removal efficiencies from dual-component solutions onto the prepared biochar were evaluated and are shown in Figure 3. When Hg(II) concentrations were less than $32 \mu g L^{-1}$, PHE removal efficiencies fluctuated based on the initial concentration of PHE. There was a trend toward decreased removal efficiencies as the initial concentration of PHE increased, and Hg(II) concentrations remained between 2 and $250 \mu g L^{-1}$. Similarly, PHE removal efficiencies decreased as Hg(II) concentration increased. At lower Hg(II) concentrations ($<32 \mu g L^{-1}$), the effect of Hg(II) on PHE sorption was less dominant, and the PHE removal efficiencies were always greater than 90%. When the concentration of Hg(II) exceeded $32 \mu g L^{-1}$, it significantly reduced PHE removal efficiencies. For example, at a PHE concentration of $5 mg L^{-1}$, with Hg(II) concentrations of 2, 16, and $250 \mu g L^{-1}$, PHE removal efficiencies were 95.8%, 92.4% and 59.3%, respectively. With an Hg(II) concentration increase from 2 to $16 \mu g L^{-1}$, PHE removal efficiency decreased by only 3.4%. However, with an Hg(II) concentration increase from 16 to $250 \mu g L^{-1}$, PHE removal efficiency decreased significantly by 33.1%.

At eight different concentrations of Hg(II) in dual-component solutions, equilibrium sorption isotherms of PHE onto the prepared biochar were investigated. The plots are shown in Figure 4, and the isotherm parameters are listed in Table 3. The equilibrium sorption isotherms were well described using a linear model, and all the regression constants (R^2) were greater than 0.948. This suggests that when Hg(II) coexisted with PHE in solution, partitioning was the dominant sorption mechanism for PHE. We know that the partition coefficients of PHE decreased (Table 3) as the concentration of Hg(II) increased, and that the

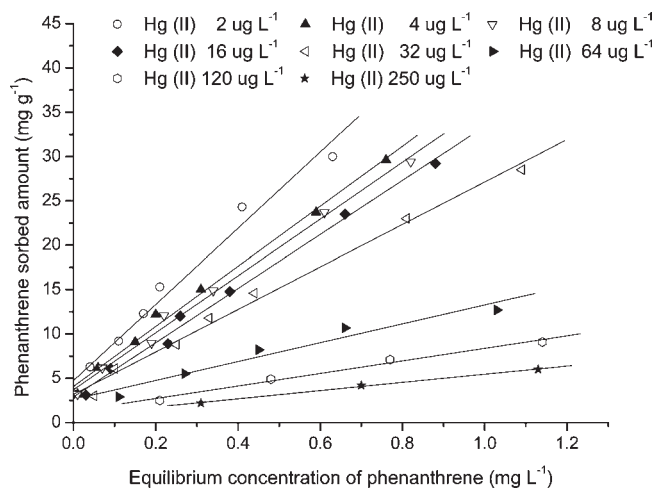


Figure 4. The plots for phenanthrene sorption isotherms in dual-component solution containing Hg(II) onto the prepared biochar.

Table 3. Linear Regression Parameters for Sorption Isotherms of Phenanthrene on Soybean Stalk-Based Biochars at Different Hg(II) Concentrations in Binary Component System^a

orig concn of Hg(II), C_0 ($\mu\text{g L}^{-1}$)	regression coeff, R^2	partition coeff of phenanthrene, K_d (L g^{-1})	decrease rate of partition coeff, $100 - 100K_d/K_{d,0}$ (%)
0	0.995	78.898 ($K_{d,0}$)	
2	0.978	42.954	45.6
4	0.994	33.862	57.1
8	0.994	32.057	59.4
16	0.994	30.490	61.4
32	0.993	23.944	69.7
64	0.948	10.627	86.5
120	0.986	7.082	91.0
250	0.997	4.627	94.1

^a The soybean stalk-based biochar concentration was 0.01 g/30 mL; temperature was 25 °C; and contact time was 24 h.

partition coefficient rates decreased 45.6%–94.1% at Hg(II) concentrations of 2–250 $\mu\text{g L}^{-1}$. PHE sorption was increasingly suppressed as the concentration of Hg(II) increased.

Effect of Phenanthrene on Hg(II) Sorption to Prepared Biochar. In the presence of PHE, Hg(II) removal efficiencies from dual-component solutions onto biochar are shown in Figure 5. Similar to the effect of Hg(II) on PHE sorption, Hg(II) sorption was suppressed by PHE. As seen in Figure 5, at a constant PHE concentration, Hg(II) removal efficiencies decreased as the initial Hg(II) concentration increased. When the initial concentration of Hg(II) remained constant, Hg(II) removal efficiencies decreased as the concentration of PHE increased. When the initial concentration of PHE was greater than 5 mg L^{-1} , it had a very minor effect on Hg(II) removal efficiency with the exception of Hg(II) concentration of 250 $\mu\text{g L}^{-1}$. When the initial concentration of PHE was 10 mg L^{-1} , the reduced Hg(II) removal efficiencies were 2.1, 2.7, 2.5, 4.0, 2.8, 4.1, and 4.2% at Hg(II) concentrations of 2, 4, 8, 16, 32, 64, and 120 $\mu\text{g L}^{-1}$, respectively. When PHE was at low concentrations (<5 mg L^{-1}), there was a significant effect on Hg(II) removal efficiency. At an

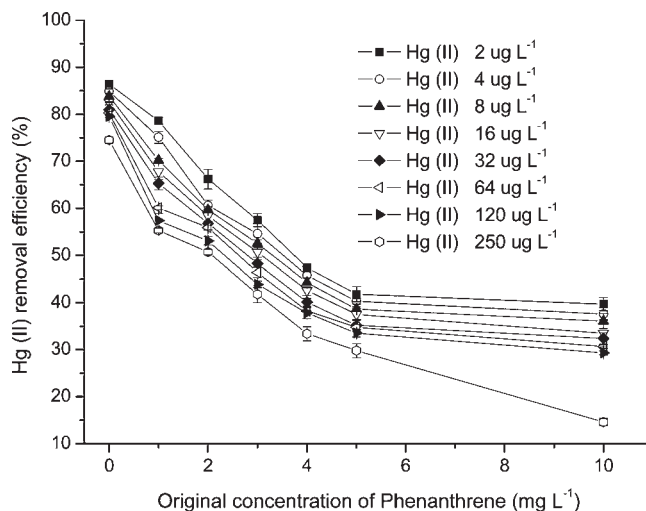


Figure 5. Hg(II) removal efficiencies from dual-component solution containing phenanthrene onto the prepared biochar.

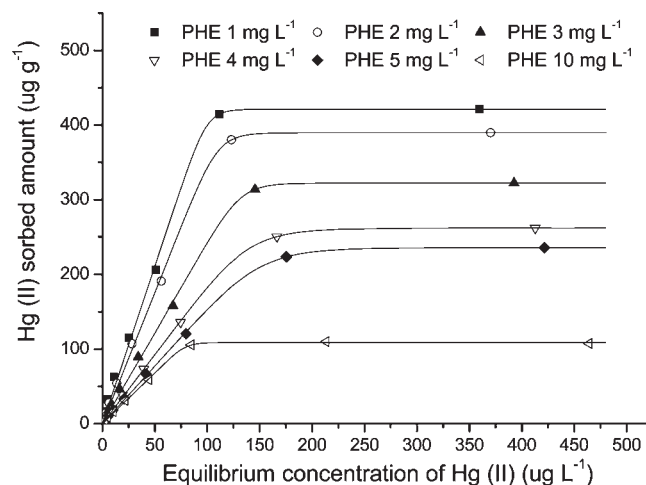


Figure 6. The plots for Hg(II) sorption isotherms in dual-component solution containing phenanthrene onto the prepared biochar.

initial Hg(II) concentration of 2 $\mu\text{g L}^{-1}$, and when the concentration of PHE increased from 1 to 5 mg L^{-1} , the Hg(II) removal efficiency peaked at 36.8%.

Tóth model plots of Hg(II) sorption at different PHE concentrations are shown in Figure 6, and the regression parameters are listed in Table 4. The equilibrium sorption isotherms are well described using a Tóth model, and all the regression constants (R^2) were greater than 0.997. The partition coefficient of Hg(II) K_d ($C_e = 0$) was used to indicate the biochar sorption affinity at lower concentrations. For the Tóth model, the partition coefficient of Hg(II) K_d at $C_e = 0$ is equal to the isotherm slope when the equilibrium concentration approaches zero, and the value is a constant:

$$\lim_{C_e \rightarrow 0} K_d = \lim_{C_e \rightarrow 0} \frac{dQ_e}{dC_e} = Q_m, T K_T \quad (6)$$

As seen from Table 4, m values were significantly larger than unity. This suggests that when PHE is present, the sorption of Hg(II) onto biochar is highly heterogeneous. Both the maximum

Table 4. Tóth Regression Parameters for Sorption Isotherms of Hg(II) at Different Phenanthrene Concentrations in Binary Component System^a

orig concn of phenanthrene, C_0 (mg L ⁻¹)	max sorption of Hg(II), $Q_{m,T}$ ($\mu\text{g g}^{-1}$)	K_T (L μg^{-1})	m	$\lim_{c_e \rightarrow 0} [(dQ_e)/(dC_e)] = Q_{m,T}K_T$ (L g ⁻¹)	regression coeff, R^2
0	567.951	0.0209	9.864	11.870	1.000
1	421.311	0.0100	13.125	4.213	0.997
2	389.719	0.0090	11.037	3.507	0.999
3	322.114	0.0075	11.216	2.416	0.999
4	261.906	0.0071	6.587	1.860	1.000
5	235.650	0.0066	6.394	1.555	0.999
10	108.708	0.0125	12.691	1.359	0.999

^aThe soybean stalk-based biochar concentration was 0.01 g/30 mL; temperature was 25 °C; and contact time was 24 h.

Table 5. Phenanthrene and Hg(II) Sorbed Amounts in Dual-Component Solution by Soybean Stalk-Based Biochars^a

Hg ²⁺ concn ($\mu\text{g L}^{-1}$)	phenanthrene concn (mg L ⁻¹)						
	0	1	2	3	4	5	10
Phenanthrene Sorbed Amount (mg g ⁻¹)							
0		3.18 ± 0.00	6.28 ± 0.01	9.38 ± 0.00	12.44 ± 0.00	15.45 ± 0.01	30.92 ± 0.02
2		3.18 ± 0.00	6.27 ± 0.00	9.24 ± 0.00	12.26 ± 0.01	15.33 ± 0.01	29.98 ± 0.08
4		3.17 ± 0.00	6.21 ± 0.02	9.12 ± 0.01	12.17 ± 0.01	15.01 ± 0.01	29.57 ± 0.02
8		3.16 ± 0.00	6.17 ± 0.00	9.00 ± 0.03	12.11 ± 0.02	14.90 ± 0.09	29.38 ± 0.08
16		3.10 ± 0.01	6.12 ± 0.00	8.87 ± 0.06	11.97 ± 0.03	14.78 ± 0.02	29.18 ± 0.02
32		3.05 ± 0.01	6.07 ± 0.01	8.83 ± 0.03	11.75 ± 0.02	14.61 ± 0.03	28.48 ± 0.04
64		2.86 ± 0.01	5.52 ± 0.13	8.16 ± 0.02	10.70 ± 0.04	12.69 ± 0.14	24.06 ± 0.71
120		2.52 ± 0.02	4.87 ± 0.12	7.13 ± 0.02	9.14 ± 0.11	10.96 ± 0.01	18.88 ± 1.07
250		2.21 ± 0.02	4.17 ± 0.03	6.00 ± 0.10	7.76 ± 0.01	9.49 ± 0.10	16.39 ± 0.82
Hg ²⁺ Sorbed Amount ($\mu\text{g g}^{-1}$)							
2	5.18 ± 0.00	4.72 ± 0.00	3.97 ± 0.13	3.45 ± 0.08	2.84 ± 0.06	2.51 ± 0.10	2.38 ± 0.08
4	10.18 ± 0.01	9.01 ± 0.04	7.27 ± 0.13	6.55 ± 0.25	5.49 ± 0.21	4.83 ± 0.07	4.51 ± 0.15
8	20.11 ± 0.06	16.84 ± 0.15	14.32 ± 0.17	12.61 ± 0.20	10.63 ± 0.24	9.27 ± 0.13	8.66 ± 0.38
16	39.65 ± 0.17	32.55 ± 0.08	28.03 ± 0.66	24.34 ± 0.51	20.45 ± 0.52	18.00 ± 0.58	16.08 ± 1.39
32	77.76 ± 0.04	62.68 ± 0.82	54.53 ± 0.34	46.36 ± 0.79	38.49 ± 0.75	33.79 ± 1.28	31.10 ± 1.11
64	154.18 ± 1.00	115.40 ± 1.37	107.33 ± 0.89	89.09 ± 2.04	73.35 ± 0.24	66.82 ± 1.17	58.94 ± 0.79
120	286.21 ± 0.65	206.64 ± 0.77	191.16 ± 3.20	158.04 ± 2.51	136.08 ± 4.28	120.60 ± 2.72	105.48 ± 1.38
250	558.87 ± 0.61	414.74 ± 5.29	380.24 ± 4.49	313.49 ± 13.56	250.49 ± 11.45	223.50 ± 11.14	109.84 ± 5.76

^aThe soybean stalk-based biochar concentration was 0.01 g/30 mL, and contact time was 24 h.

sorption of Hg(II) $Q_{m,T}$ and the parameter $Q_{m,T}K_T$ decreased as the initial PHE concentration increased. When the concentration of PHE in solution increases, there is a decrease in both the sorption capability and the sorption affinity of low concentration Hg(II) onto prepared biochar.

Discussion of Cosorption Mechanism. Based on our results, PHE sorption was suppressed by Hg(II) in dual-component solution. Also, PHE inhibited the sorption of Hg(II) from the prepared biochar. When the soybean stalk-based biochar concentration was 0.01 g/30 mL, and the contact time was 24 h, the amounts of PHE and Hg(II) (in dual-component solution) sorbed onto soybean stalk-based biochars were as listed in Table 5. We found that when the initial PHE concentration remained constant, the amount of sorbed PHE decreased as the concentration of Hg(II) increased. Similarly, when the initial concentration of Hg(II) remained constant, sorbed Hg(II) decreased with increasing

concentrations of PHE. This suggests that there may be direct competitive sorption between PHE and Hg(II).

In the sorption system, biochar characteristics such as pore size and structure, specific surface area, and surface chemistry greatly affect the sorption of PHE and Hg(II). In addition to the biochar characteristics, the sorbate properties influence sorption performance. Since PHE is a nonpolar compound, sorption is governed mainly by hydrophobic interactions.³² Xia and Ball³³ and Chiou et al.³⁴ discussed that surface adsorption and partitioning are the main mechanisms for the sorption of hydrophobic organic chemicals, including PHE, on carbonaceous materials. At low concentrations (i.e., below 1% of its solubility), surface adsorption is likely the dominant mechanism.³⁵ However, partitioning would increase as the concentration of sorbate increases,³⁵ and at a higher concentration partitioning is the dominant mechanism. This study suggests that partitioning is the dominant mechanism of PHE sorption. Nevertheless, surface adsorption mechanisms

would coexist with partitioning, and therefore, the PHE sorption from solution was also influenced by a surface adsorption mechanism. The Hg(II) was bound to the sorbent surface mainly by ion exchange and physicochemical adsorption.³⁶ Also, precipitation and reduction reactions were two important mechanisms for Hg(II) sorption from solution. Knocke and Hamphil³⁷ have attributed mercury sorption onto carbon to the presence of Hg(OH)₂. Lloyd-Jones et al.³⁸ concluded that, in the presence of chloride ions, Hg(II) could be reduced to Hg₂Cl₂ precipitate during sorption. During PHE sorption from the dual-component solution onto biochar, when Hg(II) was present, mercury ions should easily out-compete water molecules for functional groups on the biochar surface, forming strong inner-sphere complexes. Moreover, because cation hydration reactions are very strong, the complexed mercury ions likely host one or more dense water hydration shells. The coordinated “hard” water may bind adjacent biochar surfaces and compete for surface area with PHE, leading to local thermodynamic inhibition of PHE sorption around the metal-complexed moieties.³⁹ Besides, the soluble Hg(II) could form Hg(OH)₂ or Hg₂Cl₂ precipitates on the surface of the biochar through precipitation and reduction reactions. The complexation, precipitation, and reduction reaction not only modified the surface chemistry and pore structure of the biochar but also produced compounds that could result in biochar pore blockage. Thus, the effective biochar surface area for PHE sorption would be reduced, resulting in a decrease in sorbed PHE. Higher initial concentrations of Hg(II) had greater effects on PHE removal efficiencies. Similarly, during sorption of Hg(II) from the dual-component solution onto the biochar, in the presence of PHE, the PHE could compete with Hg(II) for sorption sites on the prepared biochar surface, resulting in decreased sorption of Hg(II). Moreover, when removing PHE from solution, surface adsorption contributed less as the PHE concentration increased. At low PHE concentrations, PHE sorption strongly competed with Hg(II) sorption, and PHE in the dual-component solution had a significant effect on Hg(II) removal efficiency. At high concentrations, when surface adsorption played only a minor role, Hg(II) removal efficiency was not affected by PHE.

In conclusion, our investigation indicated that the prepared biochar could efficiently remove PHE and Hg(II) from aqueous solution. In monocomponent solutions, PHE removal efficiencies reached 99.5% when its initial concentration was 1 mg L⁻¹, and Hg(II) removal efficiency was 86.4% when its initial concentration was 2 μg L⁻¹. PHE and Hg(II) exhibited direct competitive sorption when they coexisted in aqueous solution, suppressing one another.

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ABBREVIATIONS USED

PHE, phenanthrene; PAHs, polycyclic aromatic hydrocarbons; SEM, scanning electron microscope; HPLC, high-performance liquid chromatography

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