

Adsorption behavior of phenanthrene onto coal-based activated carbon prepared by microwave activation

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Abstract—Coal-based activated carbon (CAC) was prepared from coal produced in Xinjiang of China by microwave activation. CAC was characterized and used as an adsorbent for phenanthrene adsorption. The effects of temperature, adsorption time, CAC amount, initial concentration and pH value of solution on phenanthrene adsorption were studied. The adsorption rate of phenanthrene onto CAC was obtained nearly 100% with initial concentration of 100 mg/L and CAC dosage of 0.3 g at 25 °C. Phenanthrene adsorption was well described with the Langmuir isotherm. The pseudo-second-order model was found to more effectively explain the adsorption kinetics of phenanthrene. The lower temperature was favorable to the adsorption rate and equilibrium adsorption capacity of phenanthrene onto CAC. The thermodynamic parameters ΔH° , ΔS° and ΔG° computed for phenanthrene adsorption onto CAC demonstrate the process was spontaneous, radiative, and entropically driven. Thus, CAC prepared by microwave activation could be effective for removing phenanthrene.

Keywords: Coal-based Activated Carbon, Microwave Activation, Phenanthrene, Adsorption, Kinetics and Thermodynamics

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) can transport long distance in air and water, and are difficult to biodegrade, due to their chemical persistence and semi-volatile nature. Some PAHs are capable of interacting with DNA to promote mutagenic and carcinogenic responses. Sixteen PAHs are on the US-EPA's priority pollutants list [1]. As one of the PAHs, phenanthrene is a widespread environmental pollutant that has been widely of concern due to its toxic property [2,3]. However, phenanthrene is not efficiently removed by conventional physicochemical methods, such as coagulation, flocculation, sedimentation, filtration, or ozonation [4]. Now extensive research has been conducted using adsorption method by various sorbents to removal phenanthrene in contaminated water [5-13]. Tang et al. [9] found that the sorption performance of PAHs on fibric peat could be improved through modification by hexadecyltrimethylammonium bromide, and its equilibrium sorption capacity for phenanthrene was 854 mg/g at the phenanthrene concentration of 890 mg/L and sorbent concentration of 30 mg/50 ml. Li et al. [10] reported a phenanthrene removal efficiency of 89.41-91.16% from aqueous solution by hydrolyzed pink bark. Yuan et al. [11] reported a phenanthrene removal efficiency of 95.20% for petroleum coke-derived porous carbon. Kong et al. [14] reported that the removal efficiency of phenanthrene approached 100% at a car-

bon concentration of 10 mg/32 ml and a carbonization temperature of 700 °C. Furthermore, with the presence of acenaphthene and naphthalene as co-contaminants, the removal efficiency of phenanthrene by the prepared carbon was 99.60%, which was comparable to that by the commercial carbon.

Activated carbon (AC) is one of the most commonly used adsorbents, which adsorption process is effective for the removal of persistent organic pollutants [15-18]. Activated carbons are porous material with extremely high surface area; they have been widely used in a variety of industrial applications such as separation/purification of liquids and gases, removal of toxic substances, catalysts and catalyst support, supercapacitors, electrodes and gas storage [19]. Major raw materials for the preparation of AC are coal, petroleum, peat, wood and agricultural wastes. Among which, coal is the most commonly used precursor for AC production due to the advantage of its availability and cost [19].

There is abundant resource of coal with geological coal reserves exceeding 2.19 million tons accounting for 40% of China in Xinjiang (Autonomous Region, China), which has been become the large-scale coal production base [20]. Providing abundant raw materials is important for the development of high-value-added coal chemical products. For this reason, coal is selected as a stable alternative for the preparation of activated carbon in Xinjiang.

The CACs usually were prepared by traditional heating method by thermal conduction transferred from surface into interior of the material using the tubular furnace at relatively high temperature and long time; as a result, the process of heating was slow, high energy consumption and non-uniform with the surfaces [21]. In recent years, microwave irradiation has been widely investigated because that microwave radiation supply directly energy to carbon skele-

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ton at molecular level from interior of the char particle to its surface to promote activation reaction more quickly and effectively at a lower bulk temperature [22]. Thus, microwave heating provides additional advantages such as energy savings, shortening the processing time, precise control of temperature, and reduced waste comparing with traditional heating techniques. So coal-based activated carbon would be prepared by microwave activation was considerably informative and significant. And exploring the adsorption behavior of phenanthrene onto CAC obtained by microwave activation from 30% ethanol aqueous solution is quite interesting and innovative. In addition, 30 vol% ethanol was added to the solution for enhancing the water solubility of phenanthrene.

This paper studies the sorption characteristics of phenanthrene on CAC by changing temperature, time, CAC amount, initial concentration and pH of phenanthrene solution. To better understand these adsorption processes, equilibrium adsorption data were used in kinetics and mass transfer models in this study. These models were proposed to predict the adsorption behavior and the mechanisms, providing a foundation for developing CAC products as potential adsorbent to remove PAHs in the environment.

MATERIALS AND METHODS

1. Materials

The raw anthracite coal was purchased from TBEA, Changji, Xinjiang Uygur Autonomous Region, China. The resultant coal sample passed through a 100 mesh sieve was used to prepare the CAC. Phenanthrene (>97%; Aladdin, Shanghai, China) was used to prepare the stock solutions by dissolving an appropriate amount in ethanol aqueous solution.

2. Preparation and Analyses of CAC

CAC was prepared with a microwave oven (MM823LA6-NS, Midea) at a frequency of 2.45 GHz. The oven was equipped with a power controller and a timer controller. The solid KOH (15 g) and dried coal mixture with a ratio of 1:3 was placed in a quartzose tube of a microwave reactor to activate under vacuum atmosphere at a 693 W for 10 min. The AC sample obtained repeatedly was washed with 10% hydrochloric acid and then with distilled water until the filtrate reached neutral. The remaining solid was dried in an oven at 110 °C for 4 h and stored in sealed glass bottles for the adsorption experiments.

Elemental analysis of CAC was by elemental analyzer (VARIO ELIII, Elementar Analysensysteme GmbH). The pore structure of CAC was evaluated by measuring nitrogen adsorption isotherm at 77 K with ASAP 2020C surface area and porosity analyzer (Micromeritics Instrument Corp, USA). The S_{BET} was calculated using the BET equation.

The study of surface acidity of CAC was implemented by mixing 0.20 g of CAC with 25.00 ml of 0.05 M NaOH and agitating for 48 h at 30±1 °C; then the suspension containing remained NaOH was titrated with 0.05 M HCl. The surface basicity of CAC was measured by titration with 0.05 M NaOH after shaking mixture which contained 0.20 g of CAC and 25.00 ml of 0.05 M HCl.

The point of zero charge (pH_{PZC}) of porous carbon was determined according to the procedure described by Noh and Schwartz [23]. The determination process was repeated for initial pH values

between 2 and 12. The final pH value was plotted against the initial pH value. The point where the pH_{final} vs. $pH_{initial}$ curve crosses the $pH_{final}=pH_{initial}$ line is the pH_{PZC} .

'Boehm titration' is commonly used to determine the acidic oxygen surface functional groups on carbon samples whereby bases of various strengths ($NaHCO_3$, Na_2CO_3 , NaOH) neutralize different acidic oxygen surface functionalities [24]. The weakest base, $NaHCO_3$, neutralizes only the strongest acidic carbon surface functionalities (CSFs) which are carboxylic groups, while Na_2CO_3 neutralizes carboxylic and lactonic groups. The strongest base typically used, NaOH, neutralizes carboxylic, lactonic and phenolic groups. The number of each type of CSF can be determined by difference between the adsorption of each reaction base [24]. A mixture of 1.5 g CAC and 25.00 ml of one of the three 0.05 M reaction bases, $NaHCO_3$, Na_2CO_3 and NaOH was filtered and washed with distilled water adequately after stirring for 24 h; then all the filtrate collected was added 0.05 M HCl to completely neutralize and end with methyl red indicator.

3. Preparation and Determination of Phenanthrene Stock Solution

Phenanthrene was initially solved into 30 vol% ethanol aqueous solutions to prepare the stock solutions of the given concentrations. Five initial solutions ranging from 100 to 900 mg/L were prepared. The concentrations of various phenanthrene solutions were measured after adsorption by a UV-vis spectrophotometer (UV-752N, Shanghai Metash Instruments Co., Ltd., China). The phenanthrene absorbance at 249 nm could be converted to phenanthrene concentration using the calibration curve, $C=3.4483A_{249}+0.0103$, and R^2 was equal to 0.9998.

4. Adsorption Experiments

4-1. Adsorption Performance Analysis

For each experiment, 40 ml of phenanthrene solution of known initial concentration was placed in a 100 ml conical flask with cover. To establish thermal equilibrium before adsorption, the solution was periodically shaken at a certain speed and constant temperature. After preheating for 5 min, 100 mg of CAC (size ≤100 mesh) was added to the solution. Then, the samples were periodically withdrawn and filtered immediately with suction for solid-liquid separation. The supernatant solution was analyzed for the remaining concentration of phenanthrene by a UV-vis spectrophotometer.

The amount of phenanthrene (Q_e) was calculated as follows:

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

The adsorption rate of phenanthrene (η) was calculated as follows:

$$\eta = \frac{C_0 - C_e}{C_0} \times 100\% \quad (2)$$

where C_0 (mg/L) and C_e (mg/L) are liquid-phase concentrations of phenanthrene at initial and equilibrium, respectively. V (ml) represents the volume of the solution and m (g) stands for the mass of CAC used.

4-2. Adsorption Isotherm

The Langmuir adsorption Eq. (3), predicts the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent [25].

$$\frac{C_e}{Q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (3)$$

where C_e and Q_e are as defined in Eq. (1), q_m is adsorption maximum (mg/g); K_L is sorption equilibrium constant (L/mg).

The Freundlich isotherm [25] is an empirical equation employed to describe heterogeneous systems:

$$\log Q_e = \log C_e + \log K_F \quad (4)$$

where K_F is a constant which represents a measure of the adsorption capacity of the adsorbent for specific solute, and n is a measure of intensity of adsorption.

4-3. Adsorption Kinetics

Kinetic models are used to examine the rate of the adsorption process and potential rate determining step, i.e., particle diffusion or chemical reaction. The capability of pseudo-first-order, pseudo-second-order and intraparticle diffusion, was examined in this study.

The pseudo-first-order kinetic rate equation is expressed as [26]:

$$\frac{1}{Q_t} = \frac{1}{Q_e} + \frac{k_1}{Q_e t} \quad (5)$$

where k_1 is the rate constant of pseudo-first-order sorption (min). The first-order rate constant can be determined from the slope of the linearized pseudo-first-order rate equation.

The pseudo-second-order kinetic rate equation is expressed as [27]:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (6)$$

where k_2 is the rate constant of pseudo-second-order sorption (g/mg/min). The second-order rate constant can be determined from the intercept of the linearized pseudo-second-order rate equation.

In the intraparticle diffusion model, the relationship between the adsorption capacity (Q_t) at time t , can be written as [28]:

$$Q_t = K_p t^{1/2} + C \quad (7)$$

where K_p is the intraparticle diffusion constant (mg/g/min^{1/2}) and C is the intercept of the line, which is proportional to the boundary layer thickness.

4-4. Thermodynamic Parameters

The activation energy, E_a , is obtained from an Arrhenius Eq. (8) [29]:

$$\ln(k) = \ln(A) - \frac{E_a}{R} \left(\frac{1}{T} \right) \quad (8)$$

where A the frequency factor or the Arrhenius constant, R the universal gas constant (8.314 J/K mol), T the absolute temperature, and k the rate constant, is given by the pseudo-second-order rate constant k_2 .

The data obtained from adsorption isotherm models can be conveniently used to determine such thermodynamic parameters as free energy of adsorption ΔG^θ , enthalpy change of adsorption ΔH^θ and the change in standard entropy ΔS^θ . These parameters are evaluated using the following equation:

$$K_d = K_F = X \quad (9)$$

where K_d (L/mol) is the sorption distribution coefficient. The K_d values were plugged into Eq. (9) to determine the free energy of sorption process at various temperatures [26].

$$\Delta G^\theta = -RT \ln K_F \quad (10)$$

where ΔG^θ is the free energy of sorption (kJ/mol). Enthalpy change ΔH^θ and entropy change ΔS^θ values were calculated at different temperatures by the following Eq. (10) [26]:

$$\ln K_F = \frac{\Delta S^\theta}{R} - \frac{\Delta H^\theta}{RT} \quad (11)$$

where K_F is the adsorption equilibrium constant in Eq. (4) for the phenanthrene.

Table 1. Comparison of different kinds of ACs

Sample	Carbon source	Heating methods	S_{BET} (m ² /g)	V_{total} (cm ³ /g)	pH _{PZC}	Acidity (mmol/g)	Basicity (mmol/g)	Total acidic groups (mmol/g)
CAC This work	Coal	Microwave	1770.49	0.990	8.06	0.75	1.50	0.17
Commercial AC [21]	Pitch	Convention	1403.00	0.583	-	0.36 (mmol/m ² ×10 ⁴)	-	5.84 (mmol/m ² ×10 ⁴)
Commercial AC [21]	Wood	Convention	1100.00	1.061	-	9.77 (mmol/m ² ×10 ⁴)	-	14.32 (mmol/m ² ×10 ⁴)
Lotus stalk based - AC [17]	Lotus stalk	Convention	1220.00	1.191	4.09	0.32	-	1.58
Jatropha hull based - AC [22]	Jatropha hull	Convention	748.00	0.580	-	-	-	-
Industrial waste lignin based - AC [30]	Lignin	Microwave	1172.20	0.640	-	-	-	0.138
Bamboo based - AC [31]	Bamboo	Microwave	1323.00	0.699	3.4	0.68	0.02	1.26

AC: activated carbon; CAC: coal-based activated carbon; pH_{PZC}: the point of zero charge; V_{tot} : total pore volume

RESULTS AND DISCUSSION

1. Characterization of Coal and CAC

The results of the analytical function of coal were as follows: 60.97% of C, 3.70% of H, 0.61% of N, and 1.53% of S, 27.51% of O, 5.68% of other elements. Table 1 shows the properties of CAC. The BET surface area, total pore volume, and average pore size of CAC were 1,770.49 m²/g, 0.99 cm³/g, and 2.820 nm, respectively. The CAC was suggested to have considerable surface area and total pore volume, which can make an important contribution to the adsorption capability. As listed in Table 1, microwave heating technique has shown better effect in terms of porous structure, relatively greater surface area than conventional heating method. In addition, the treatment time and the consumption of gases used in the microwave heating treatment can be considerably reduced, which results in a reduction in the energy consumption, compared with conventional surface heating treatment. Hence, the work clearly demonstrates that the use of microwave heating for preparation CAC is important in aspects of economic and performance. Surface acidity and basicity was a major criterion describing the surface chemistry of an adsorbent. Data analysis showed that CAC exhibited an alkali character with surface acidity and basicity of 0.75 and 1.50 mmol/g, respectively. The alkali nature of CAC is attributed to KOH as activation agent for the CAC preparation. However, the surface acidity was associated with a low content because of the presence of oxygen-containing groups on the carbon surface, such as carboxylic groups, lactonic groups, and phenolic groups. In addition the pH_{PZC} of CAC was 8.06. The surface total acidic groups, carboxylic groups, and phenolic groups of CAC obtained by Boehm titration were 0.17, 0.07, and 0.10 mmol/g, respectively. These results also proved that CAC exhibited an alkali character.

2. Effects of Conditions on Adsorption Behavior

2-1. Effects of Temperature on the Adsorption Rate

A series of 100 ml conical flasks with cover were set in a water

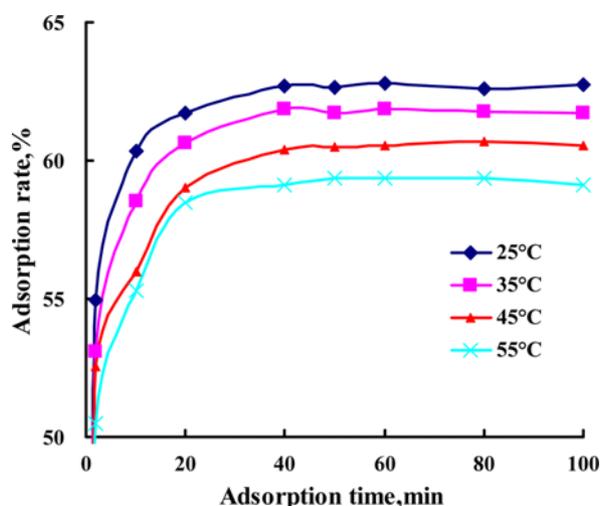


Fig. 1. Adsorption rate of phenanthrene from ethanol aqueous solution at different temperatures by CAC with various times (40 ml of 30 vol% ethanol solution; initial concentration of phenanthrene: 500 mg/L; pH: 7.0; 0.1 g of CAC; agitation speed: 90 rpm).

bath and shaken at 90 rpm at 25, 35, 45, and 55 °C, respectively. 0.1 g of CAC was added to 40 ml of phenanthrene solution with an initial concentration of 500 mg/L. The pH value of the initial solution was 7.0. The effects of temperature on the adsorption rate were studied.

Fig. 1 shows the variation of adsorption rate of phenanthrene with temperature. The equilibrium adsorption rate of phenanthrene on the CAC surface decreased slightly when the temperature increased. Low temperature is favorable to the adsorption rate of phenanthrene; the adsorption process of phenanthrene approached equilibrium gradually after 40 min, i.e., the CAC achieved saturated adsorption after 40 min at each temperature.

Fig. 1 shows the two stages of the sorption process. In the first stage, phenanthrene was rapidly adsorbed onto those easily accessible hydrophobic sites within the CAC matrix in 20 min. The adsorption process could be the chemical interaction between phenanthrene and CAC surface. In the second stage, the adsorption was probably limited by the slow migration of phenanthrene to less accessible sites associated with micropores within the CAC matrix, which could take hours. Valderrama et al. [6] reported similarly that the adsorption process of polyaromatic hydrocarbons onto granular activated carbon and Macronet hyper-cross-linked polymers (MN200) also was the two-stage. The first step of solution/solid transfer is assumed to be rapid in comparison to the intraparticle diffusion process, which is the last step of the sorption corresponding to the extraction of PAHs. And the solution film is the determining step of the mass transfer rate. Thus, 35 °C and 50 min were selected as sufficient adsorption equilibrium conditions in this experiment.

2-2. Effects of the Amount of CAC on Adsorption Rate and Amounts

Fig. 2 shows that an increase in the CAC amount resulted in an increased phenanthrene adsorption rate onto CAC. When the amount of CAC was over 0.3 g, the adsorption rate of phenanthrene slightly increased and it reached over 98% in 40 ml of solutions. This result shows that when the adsorption process is close to equilibrium, the increase of the amount of CAC has little significance. The in-

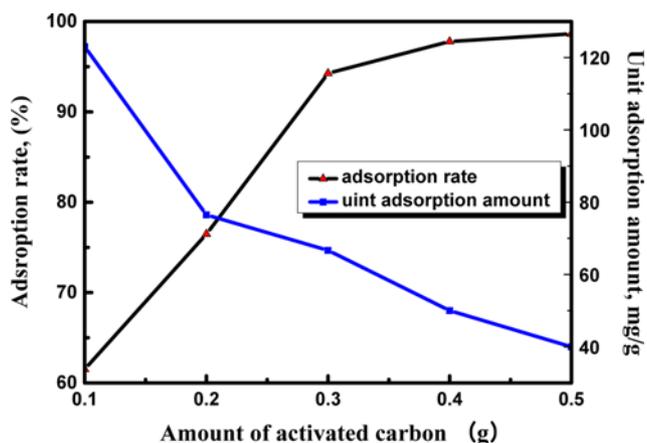


Fig. 2. Adsorption rate and amount of phenanthrene from ethanol aqueous solution by CAC with various CAC amounts (40 ml of 30 vol% ethanol solution; initial concentration: 500 mg/L of phenanthrene; pH: 7.0; adsorption time: 50 min; adsorption temperature: 35 °C; agitation speed: 90 rpm).

crease in CAC amount results in the increase in the surface area of adsorption and increase in the number of adsorption sites. Gong et al. [15], who investigated the effect of activated carbon amount on PAHs removal from four oils, observed similar results and explanation. An increase in the activated carbon amount was observed to result in an increased PAHs adsorption rate on activated carbon. More than 90% of PAHs in 40 ml of oils was removed when the activated carbon amount was >3 g for oils A-C.

Unit adsorption amount decreased and the utilization of CAC reduced with the increase of the amount of CAC could be seen in Fig. 2. Given the adsorption efficiency and cost, 0.3 g was selected as the amount of CAC in this experiment.

2-3. Effects of the Initial Concentration of Phenanthrene on Adsorption Rate and Amounts

Effects of various initial phenanthrene concentrations ranging from 100 to 900 mg/L in ethanol aqueous solution on adsorption were investigated at different temperatures. As shown in Fig. 3(a)

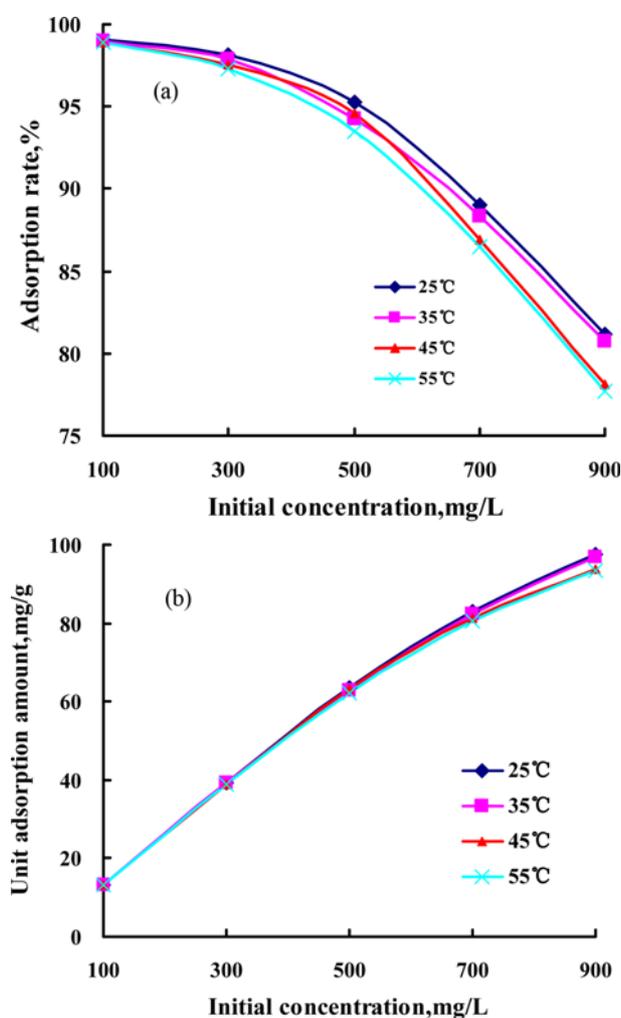


Fig. 3. Adsorption rate and amount of phenanthrene from ethanol aqueous solution by CAC with various initial concentrations at various temperatures: (a) adsorption rates and (b) unit adsorption amounts (40 ml 30 vol% ethanol solution; pH: 7.0; 0.3 g of CAC; adsorption time: 50 min; adsorption temperature: 35 °C; agitation speed: 90 rpm).

as the initial concentration increased, the adsorption rates showed a downward trend at the experimental temperatures. For the same initial concentration, the increase in temperature resulted in a slight decline in absorption rate. Therefore, low temperature was more conducive to absorption. Fig. 3(b) shows that an increase of adsorption amounts was observed as the initial concentration of phenanthrene increased. This result is attributed to the increased number of available sorption sites by increasing the sorbent concentration, which allows more phenanthrene molecules to pass from the bulk solution to the particle surface [14].

2-4. Effects of pH Value

The effect of initial pH value of solution was studied under an initial phenanthrene concentration of 500 mg/L (Fig. 4). The adsorption amounts of phenanthrene with the pH values of 2, 4, 6, 7,

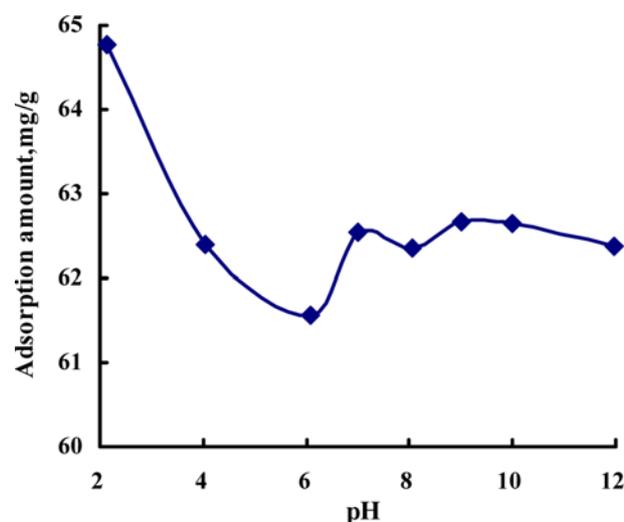


Fig. 4. Adsorption amount of phenanthrene from ethanol aqueous solution by CAC with various initial pH (40 ml solution; initial concentration: 500 mg/L; 0.3 g of CAC; adsorption time: 50 min; adsorption temperature: 35 °C; agitation speed: 90 rpm).

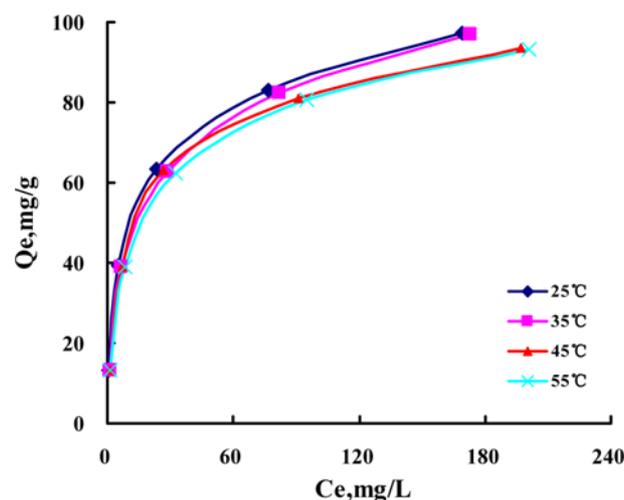


Fig. 5. Adsorption isotherm of phenanthrene in 30 vol% ethanol solution on CAC.

Table 2. Isotherm constants for adsorption of phenanthrene in ethanol aqueous solution onto CAC

T (K)	Langmuir			Freundlich		
	K_L (L/mg)	q_m (mg/g)	R^2	K_F	n	R^2
298.15	0.09	102.04	0.9954	16.71	2.68	0.9489
308.15	0.08	102.04	0.9940	15.60	2.62	0.9584
318.15	0.08	98.03	0.9969	15.35	2.68	0.9477
328.15	0.07	98.03	0.9955	14.74	2.66	0.9612

K_L : sorption equilibrium constants; q_m : adsorption maximum; R^2 : regression coefficients; s, n, K_F : intensity parameters

8, 10, 12 were 97.15, 93.59, 92.36, 93.80, 93.54, 93.98, 93.57%, respectively. The results showed that the amounts of phenanthrene adsorbed onto CAC did not change significantly when the solution value was raised from 2 to 12. Foo et al. [24] reported an enhancement of the adsorption of MB by increasing pH value from 2 to 12, and the adsorption capacity of PAC prepared via microwave assisted KOH activation increased from 321.33 to 462.77 mg/g, and that of PAC prepared via microwave assisted K_2CO_3 activation increased from 257.07 to 388.58 mg/g, respectively. However, the effect of pH value on the adsorption of phenanthrene by CAC cannot be observed.

3. Adsorption Isotherm

The adsorption rate of phenanthrene as a function of concentration at equilibrium at various temperatures as seen in Fig. 5. And the analysis of the isotherm data could be important and useful in the design of adsorption process equipment. Thus, the equilibrium data for adsorption of phenanthrene onto CAC were analyzed by using two isotherm equations, namely, Langmuir and Freundlich. The isotherm data were fitted to the non-linearized Langmuir and linearized Freundlich models to determine the adsorption capacity (mg/g) and sorption equilibrium constants (L/mg; q_m and K_L) and intensity parameters (K_F and n). Table 2 shows that the Langmuir model yielded a better fit than the Freundlich model of phenanthrene adsorption with various temperatures, and these correlation coefficients (R^2) were >0.9940, which could be due to phenanthrene monolayer adsorb onto CAC. These correlation coefficients (R^2) obtained from the Freundlich model of phenanthrene adsorption were >0.9477. Existing studies reported that some PAHs sorption to heterogeneous carbonaceous matters gave linear isotherms. Yuan et al. [11] found that phenanthrene adsorption onto all four carbons follows the Freundlich equation to some degree, with all

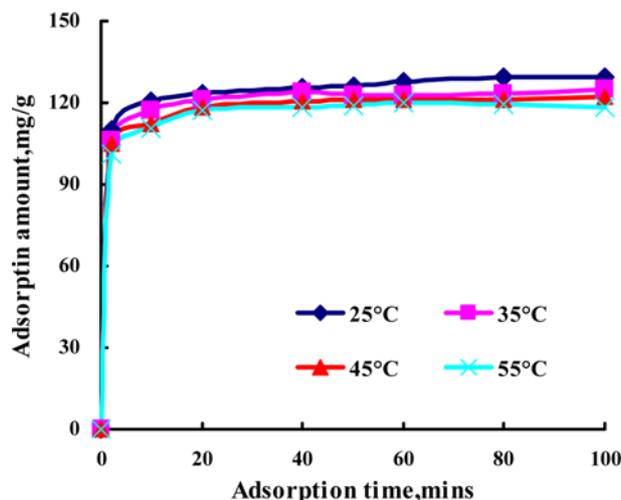


Fig. 6. Adsorption amounts of phenanthrene in 30 vol% ethanol aqueous solution on CAC at various times with different temperatures.

correlation coefficients being greater than 0.94. Gong et al. [15] also found that adsorption equilibrium of PAHs onto activated carbon from vegetable oil was successfully evaluated by the Freundlich isotherms, with all coefficients being greater than 0.93.

As shown in Table 2, q_m and K_L of phenanthrene on CAC decreased with increasing temperature, indicating the lower temperature is favorable to create more adsorption sites onto CAC. The maximum q_m was 102.04 mg/g at 25 °C. The observed decrease in K_F value with increasing temperature, also implying the above-mentioned viewpoint. The values of n did not significantly change among the four temperatures due to the same carbon.

4. Adsorption Kinetics

Fig. 6 shows the variation of adsorption amounts of phenanthrene with time and temperatures at the initial concentration of 500 mg/L of phenanthrene. The results showed that the increase in temperature resulted in the change in the equilibrium time of phenanthrene in the solution adsorbed onto CAC. The enhancement of the adsorption amount was favored slightly at lower temperature. The adsorption process consisted of two distinguishing periods, which agrees well with that of the aforementioned finding.

The phenanthrene adsorption onto CAC was fitted by three kinetic models, and values of k_1 , k_2 , k_p and Q_e as well as correlation coefficients are listed in Table 3. The results show that the correlation coefficient for the first-order kinetic model was lower than the second-order kinetic, but the theoretical Q_e values found in this

Table 3. Kinetics constants for adsorption of phenanthrene in ethanol aqueous solution onto CAC

T (K)	q_{exp} (mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model			Intraparticle diffusion model	
		k_1 (min^{-1})	Q_e (mg/g)	R^2	k_2 (g/mg min)	Q_e (mg/g)	R^2	k_p (mg/g/min ^{1/2})	R^2
298.15	125.93	0.33	126.58	0.9281	0.01	129.87	0.9998	2.01	0.8522
308.15	123.72	0.33	123.46	0.9633	0.01	125.00	0.9998	1.81	0.7356
318.15	120.97	0.31	120.48	0.8732	0.01	123.46	0.9999	1.89	0.8272
328.15	118.76	0.37	119.05	0.9372	0.02	119.05	0.9999	1.86	0.7097

q_{exp} : experimental equilibrium adsorption value; $k_{1,2,p}$: constant; Q_e : fitting equilibrium adsorption value

model were reasonable from 25 °C to 55 °C. The experimental date of the pseudo-second-order kinetic model of phenanthrene indicated extremely high correlation coefficient ($R^2 > 0.9998$) at all experimental temperatures. The theoretical Q_e values computed from this model were consistent with the experimental q_{exp} values, which suggests that the adsorption process could involve physical adsorption and a chemical interaction of valency forces by sharing of or exchange with proton between phenanthrene and CAC. The adsorption mechanism and the potential rate-determining steps could be involved in mass transport and chemical reaction processes [32].

In addition, the correlation coefficient R^2 of intraparticle diffusion kinetic models was decreased up to 0.7097. Weber and Morris [29] reported that if intraparticle diffusion is involved in the sorption process, a plot of the square root of time versus adsorption would result in a linear relationship, and the particle diffusion would be the determining step if this line passes through the origin. In this study, the Q_t versus $t^{0.5}$ graph is initially linear, indicating that

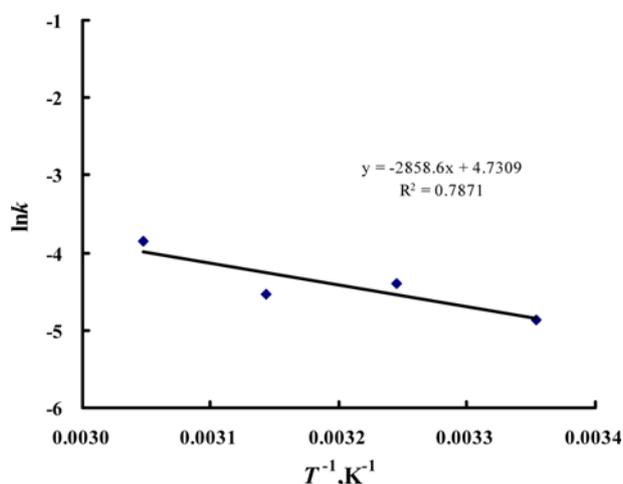


Fig. 7. Plots of $\ln k$ vs. T^{-1} for adsorption of phenanthrene in 30 vol% ethanol solution on CAC at different temperatures.

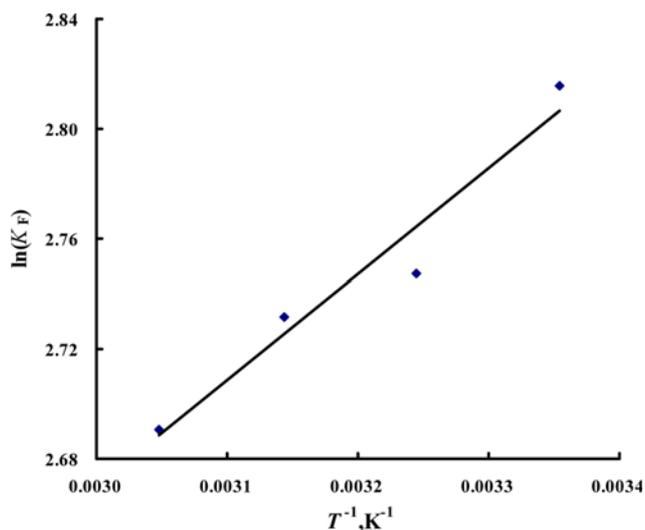


Fig. 8. Plots of $\ln(K_F)$ vs. T^{-1} for adsorption of phenanthrene in 30 vol% ethanol solution on CAC at different temperatures.

Table 4. Thermodynamic parameters for adsorption of phenanthrene in ethanol aqueous solution onto CAC

T (K)	K_F	E_a (kJ/mol)	ΔH^θ (kJ/mol)	ΔS^θ (J/K mol)	ΔG^θ (kJ/mol)
298.15	16.71				-6.98
308.15	15.60	23.77	-3.20	12.60	-7.04
318.15	15.35				-7.22
328.15	14.74				-7.34

intraparticle diffusion could be involved in the sorption process of phenanthrene on CAC. However, it was not the only rate-determining step.

5. Adsorption Thermodynamic Properties

When $\ln k$ is plotted versus the reciprocal of the temperature ($1/T$), the slope is E_a (Fig. 7). Activation energy for the phenanthrene sorption on CAC was 23.77 kJ/mol, which indicates that the main adsorption process is physical adsorption. Subsequently, $\ln K_F$ is plotted against temperature ($1/T$); as shown in Fig. 8, the results of the thermodynamic parameters were evaluated for the sorption system of phenanthrene at 25, 35, 45, and 55 °C (Table 4). The negative value of ΔG^θ indicates the spontaneous phenanthrene adsorption onto CAC. The ΔG^θ values decreased lightly with increasing the temperature, indicating that the affinity between phenanthrene and CAC surface weakened with increasing temperature. This result shows that the removal process was favored at lower temperature. The negative value of ΔH^θ indicates an exothermal adsorption process, which is in agreement with the aforementioned result: the phenanthrene amount decreased with increasing temperature. Phenanthrene adsorption onto CAC was clearly entropically driven. The positive values of ΔS^θ suggest increased randomness at the solution interface during the phenanthrene adsorption processes [26].

CONCLUSIONS

The CAC prepared by microwave activation can substantially remove phenanthrene from 30 vol% ethanol aqueous solution. The increase of the amount of activated carbon resulted in the increase in the adsorption rate and decrease in unit adsorption amount. The adsorption rate decreases and adsorption amount increases as the initial concentration increases. The pH value of solution does not affect the adsorption rate and amount of phenanthrene on CAC.

Phenanthrene adsorption was described well by the Langmuir model, and the correlation coefficients (R^2) were > 0.9954 . The lower temperature is favorable to phenanthrene adsorption onto CAC was favored at lower temperature. The kinetic of phenanthrene adsorption was described by the pseudo-second-order equation with extremely high correlation coefficient ($R^2 > 0.9998$) and suggested that the adsorption involved chemical interaction. Phenanthrene adsorption onto CAC was a two-stage process.

The activation energy values indicated that the overall adsorption process of phenanthrene was physical adsorption. The thermodynamic parameters ΔH^θ , ΔS^θ , and ΔG^θ were computed. The phenanthrene sorption on CAC was spontaneous, radiative, and entropically driven.

This paper lays the foundation on developing CAC products

with specific performance and using CAC to remove PAHs in the environment. Overall, CAC from Xinjiang region coal prepared by microwave activation could be effectively applied in liquid-phase adsorption involving PAHs.

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