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Original Citation:

Availability:

This version is available <http://hdl.handle.net/2318/1576958> since 2016-06-30T22:24:31Z

Published version:

DOI:10.1007/s11814-014-0317-7

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(Article begins on next page)

This is the author's final version of the contribution published as:

Xiao, Xuemin; Tian, Fei; Yan, Yujun; Wu, Zhilin; Wu, Zhansheng; Cravotto, Giancarlo. Adsorption behavior of phenanthrene onto coal-based activated carbon prepared by microwave activation. *THE KOREAN JOURNAL OF CHEMICAL ENGINEERING*. 32 (6) pp: 1129-1136.
DOI: 10.1007/s11814-014-0317-7

The publisher's version is available at:

<http://link.springer.com/content/pdf/10.1007/s11814-014-0317-7>

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1 **Adsorption behavior of phenanthrene onto coal-based activated carbon prepared** 2 **by microwave activation**

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6 **Abstract:**

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

X M Xiao & F Tian contributed equally to this work, and are co-first author.

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20 **Key words:**

21 Coal-based activated carbon; Microwave activation; Phenanthrene; Adsorption; Kinetics and
22 thermodynamics

23 **1. Introduction**

24 Polycyclic aromatic hydrocarbons (PAHs) can transport long distance in air and water, and are
25 difficult to biodegrade, due to their chemical persistence and semi-volatile nature. Some PAHs are
26 capable of interacting with DNA to promote mutagenic and carcinogenic responses. Sixteen PAHs
27 are on the US-EPA's priority pollutants list [1]. As one of PAHs, phenanthrene is a widespread
28 environmental pollutant and has been widely concerned due to its toxic property [2, 3]. However,
29 phenanthrene is not efficiently removed by conventional physicochemical methods, such as
30 coagulation, flocculation, sedimentation, filtration, or ozonation [4]. Now extensive research has
31 been conducted using adsorption method by various sorbents to removal phenanthrene in
32 contaminated water [5-13]. Tang et al. [9] found that the sorption performance of PAHs on fibric
33 peat could be improved through modification by hexadecyltrimethylammonium bromide, and its
34 equilibrium sorption capacity for phenanthrene was 854 mg/g at the phenanthrene concentration of
35 890 mg/L and sorbent concentration of 30 mg/50 ml. Li et al. [10] reported a phenanthrene removal
36 efficiency of 89.41-91.16% from aqueous solution by hydrolyzed pink bark. Yuan et al. [11] reported
37 a phenanthrene removal efficiency of 95.20% for petroleum coke-derived porous carbon. Kong et al.
38 [14] reported that the removal efficiency of phenanthrene approached 100% at a carbon
39 concentration of 10 mg/32 ml and a carbonization temperature of 700 °C. Furthermore, with the
40 presence of acenaphthene and naphthalene as co-contaminants, the removal efficiency of

41 phenanthrene by the prepared carbon was 99.60 %, which was comparable to that by the commercial
42 carbon.

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

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

56 The CACs usually were prepared by traditional heating method by thermal conduction
57 transferring from surface into interior of the material using the tubular furnace at relatively high
58 temperature and long time; as a result, the process of heating was slow, high energy consumption
59 and non-uniform with the surfaces [21]. In recent years, microwave irradiation has been widely
60 investigated because that microwave radiation supply directly energy to carbon skeleton at molecular
61 level from interior of the char particle to its surface to promote activation reaction more quickly and
62 effectively at a lower bulk temperature [22]. Thus, microwave heating provides additional

63 advantages such as energy savings, shortening the processing time, precise control of temperature,
64 and reduced waste comparing with traditional heating techniques. So coal-based activated carbon
65 would be prepared by microwave activation was considerably informative and significant. And
66 exploring the adsorption behavior of phenanthrene onto CAC obtained by microwave activation
67 from 30% ethanol aqueous solution is quite interesting and innovative. In addition, 30 vol. % ethanol
68 was added to the solution for enhancing the water solubility of phenanthrene.

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

75 **2. Materials and methods**

76 **2.1. Materials**

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

81 **2.2. Preparation and analyses of CAC**

82 CAC was prepared with a microwave oven (MM823LA6-NS, Midea) at a frequency of 2.45
83 GHz. The oven was equipped with a power controller and a timer controller. The solid KOH (15 g)
84 and dried coal mixture with a ratio of 1:3 was placed in a quartzose tube of a microwave reactor to

85 activate under vacuum atmosphere at a 693 W for 10 min. The AC samples obtained repeatedly was
86 washed with 10 % hydrochloric acid and then with distilled water until the filtrate reached neutral.
87 The remaining solid was dried in an oven at 110 °C for 4 h and stored in sealed glass bottles for the
88 adsorption experiments.

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

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

97 The point of zero charge (pH_{PZC}) of porous carbon was determined according to the procedure
98 described by Noh and Schwartz [23]. The determination process was repeated for initial pH values
99 between 2 and 12. The final pH value was plotted against the initial pH value. The point where the
100 pH_{final} vs. $pH_{initial}$ curve crosses the $pH_{final} = pH_{initial}$ line is the pH_{PZC} .

101 The “Boehm titration” is a commonly used technique to determine the acidic oxygen surface
102 functional groups on carbon samples whereby bases of various strengths ($NaHCO_3$, Na_2CO_3 , NaOH)
103 neutralize different acidic oxygen surface functionalities [24]. The weakest base, $NaHCO_3$,
104 neutralizes only the strongest acidic carbon surface functionalities (CSFs) which are carboxylic
105 groups, while Na_2CO_3 neutralizes carboxylic and lactonic groups. The strongest base typically used,
106 NaOH, neutralizes carboxylic, lactonic and phenolic groups. The number of each type of CSF can be

107 determined by difference between the adsorption of each reaction base [24]. A mixture of 1.5 g CAC
108 and 25.00 ml of one of the three 0.05 M reaction bases, NaHCO₃, Na₂CO₃ and NaOH was filtered
109 and wash with distilled water adequately after stirring for 24 h, then all the filtrate collected was
110 added 0.05 M HCl to completely neutralize and end with methyl red indicator.

111 **2.3. Preparation and determination of phenanthrene stock solution**

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

118 **2.4. Adsorption experiments**

119 2.4.1. Adsorption performance analysis

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

127 The amount of phenanthrene (Q_e) was calculated as follow:

$$128 \quad Q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

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

$$130 \quad \eta = \frac{C_0 - C_e}{C_0} \times 100\% \quad (2)$$

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

134 2.4.2. Adsorption isotherm

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

$$137 \quad \frac{C_e}{Q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (3)$$

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

140 The Freundlich isotherm [25] is an empirical equation employed to describe heterogeneous
141 systems, and is expressed by the following Eq. (4):

$$142 \quad \log Q_e = \frac{1}{n} \log C_e + \log K_F \quad (4)$$

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

145 2.4.3. Adsorption kinetics

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

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

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

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

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

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

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

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

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

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

162 2.4.4. Thermodynamic parameters

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

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

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

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

171
$$K_d = K_F = X \quad (9)$$

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

174
$$\Delta G^\circ = -RT \ln K_F \quad (10)$$

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

177
$$\ln K_F = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (11)$$

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

179 **3. Results and discussion**

180 **3.1. Characterization of coal and CAC**

181 The results of the analytical function of coal were as follows: 60.97% of C, 3.70% of H, 0.61%
182 of N, and 1.53% of S, 27.51% of O, 5.68% of other element. **Table 1** shows the properties of CAC.
183 The BET surface area, total pore volume, and average pore size of CAC were 1770.49 m²/g, 0.99
184 cm³/g, and 2.820 nm, respectively. The CAC was suggested to have considerable surface area and
185 total pore volume, which can make an important contribution to the adsorption capability. As listed
186 in **Table 1**, microwave heating technique has shown better effect in terms of porous structure,
187 relatively greater surface area than conventional heating method. In addition, the treatment time and
188 the consumption of gases used in the microwave heating treatment can be considerably reduced,
189 which resulted in a reduction in the energy consumption, compared with conventional surface
190 heating treatment. Hence, the work clearly demonstrates that the use of microwave heating for
191 preparation CAC is important in aspects of economic and performance. Surface acidity and basicity
192 was a major criterion describing the surface chemistry of an adsorbent. Data analysis showed that

193 CAC exhibited an alkali character with surface acidity and basicity of 0.75 and 1.50 mmol/g,
194 respectively. The alkali nature of CAC is attributed to KOH as activation agent for the CAC
195 preparation. However, the surface acidity was associated with a low content because of the presence
196 of oxygen-containing groups on the carbon surface, such as carboxylic groups, lactonic groups, and
197 phenolic groups. In addition the pH_{PZC} of CAC was 8.06. The surface total acidic groups, carboxylic
198 groups, and phenolic groups of CAC obtained by Boehm titration were 0.17, 0.07, and 0.10 mmol/g,
199 respectively. These results also proved that CAC exhibited an alkali character.

200 **3.2. Effects of conditions on adsorption behavior**

201 3.2.1. Effects of temperature on the adsorption rate

202 A series of 100 ml conical flasks with cover were set in a water bath and shaken at 90 rpm at 25,
203 35, 45, and 55 °C, respectively. 0.1 g of CAC was added to 40 ml of phenanthrene solution with an
204 initial concentration of 500 mg/L. The pH value of the initial solution was 7.0. The effects of
205 temperature on the adsorption rate were studied.

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

211 **Fig. 1** shows the two stages of sorption process. In the first stage, phenanthrene was rapidly
212 adsorbed onto those easily accessible hydrophobic sites within the CAC matrix in 20 min. The
213 adsorption process could be the chemical interaction between phenanthrene and CAC surface. In the
214 second stage, the adsorption was probably limited by the slow migration of phenanthrene to less

215 accessible sites associated with micropores within the CAC matrix, which could take hours.
216 Valderrama et al. [6] reported similarly that the adsorption process of polyaromatic hydrocarbons
217 onto granular activated carbon and Macronet hyper-cross-linked polymers (MN200) also were the
218 two-stage. The first step of solution/solid transfer is assumed to be rapid in comparison to the
219 intraparticle diffusion process, which is the last step of the sorption corresponding to the extraction
220 of PAHs. And the solution film is the determining step of the mass transfer rate. Thus, 35 °C and 50
221 min were selected as sufficient adsorption equilibrium conditions in this experiment.

222 3.2.2. Effects of the amount of CAC on adsorption rate and amounts

223 **Fig. 2** shows that an increase in the CAC amount resulted in an increased phenanthrene
224 adsorption rate onto CAC. When the amount of CAC is over 0.3 g, the adsorption rate of
225 phenanthrene slightly increase and it reached over 98% in 40 ml of solutions. This result shows that
226 when the adsorption process is close to equilibrium, the increase of the amount of CAC has little
227 significance. The increase in CAC amount results in the increase in the surface area of adsorption
228 and increase in the number of adsorption sites. Gong et al. [15], who investigated the effect of
229 activated carbon amount on PAHs removal from four oils, observed similar results and explanation.
230 An increase in the activated carbon amount was observed to result in an increased PAHs adsorption
231 rate on activated carbon. More than 90% of PAHs in 40 ml of oils was removed when the activated
232 carbon amount was >3 g for oils A-C.

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

236 3.2.3. Effects of the initial concentration of phenanthrene on adsorption rate and amounts

237 Effects of various initial phenanthrene concentrations ranging from 100 to 900 mg/L in ethanol
238 aqueous solution on adsorption were investigated at different temperatures. As show in Fig. 3A as
239 the initial concentration increased, the adsorption rates showed a downward trend at the
240 experimental temperatures. For the same initial concentration, the increase in temperature resulted in
241 the slight decline in absorption rate. Therefore, low temperature was more conducive to absorption.
242 Fig. 3B shows that an increase of adsorption amounts was observed as the initial concentration of
243 phenanthrene increased. This result is attributed to the increased number of available sorption site by
244 increasing the sorbent concentration, which allows more phenanthrene molecules to pass from the
245 bulk solution to the particle surface. [14]

246 3.2.4. Effects of pH value

247 The effect of initial pH value of solution was studied under an initial phenanthrene
248 concentration of 500 mg/L (Fig. 4). The adsorption amounts of phenanthrene with the pH values of 2,
249 4, 6, 7, 8, 10, 12 were 97.15, 93.59, 92.36, 93.80, 93.54, 93.98, 93.57%, respectively. The results
250 showed that the amounts of phenanthrene adsorbed onto CAC did not changed significantly when
251 the solution value was raised from 2 to 12. Foo et al. [24] reported an enhancement of the adsorption
252 of MB by increasing pH value from 2 to 12, and the adsorption capacity of PAC prepared via
253 microwave assisted KOH activation increased from 321.33 to 462.77 mg/g, and that of PAC
254 prepared via microwave assisted K₂CO₃ activation increased from 257.07 to 388.58 mg/g,
255 respectively. However, the effect of pH value on the adsorption of phenanthrene by CAC can't be
256 observed.

257 3.3. Adsorption isotherm

258 The adsorption rate of phenanthrene as a function of concentration at equilibrium at various

259 temperatures as seen in Fig. 5. And the analysis of the isotherm data could be important and useful in
260 the design of adsorption process equipment. Thus, the equilibrium data for adsorption of
261 phenanthrene onto CAC were analyzed using two isotherm equations, namely, Langmuir and
262 Freundlich. The isotherm data were fitted to the non-linearized Langmuir and linearized Freundlich
263 models to determine the adsorption capacity (mg/g) and sorption equilibrium constants (L/mg ; q_m
264 and K_L) and intensity parameters (K_F and n). Table 2 shows that the Langmuir model yielded a better
265 fit than the Freundlich model of phenanthrene adsorption with various temperatures, and these
266 correlation coefficients (R^2) were >0.9940 , which could be due to phenanthrene monolayer adsorb
267 onto CAC. These correlation coefficients (R^2) obtained from the Freundlich model of phenanthrene
268 adsorption were >0.9477 . Existing studies reported that some PAHs sorption to heterogeneous
269 carbonaceous matters gave linear isotherms. Yuan et al. [11] found that phenanthrene adsorption
270 onto all four carbons follows the Freundlich equation to some degree, with all correlation
271 coefficients being greater than 0.94. Gong et al. [15] also found that adsorption equilibrium of PAHs
272 onto activated carbon from vegetable oil was successfully evaluated by the Freundlich isotherms,
273 with all coefficients being greater than 0.93.

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

279 3.4. Adsorption kinetics

280 Fig. 6 shows the variation of adsorption amounts of phenanthrene with time and temperatures at

281 the initial concentration of 500 mg/L of phenanthrene. The results showed that the increase in
282 temperature resulted in the change in the equilibrium time of phenanthrene in the solution adsorbed
283 onto CAC. The enhancement of the adsorption amount was favored slightly at lower temperature.
284 The adsorption process consisted of two distinguished periods, which agrees well with that of the
285 aforementioned finding.

286 The phenanthrene adsorption onto CAC was fitted by three kinetic models, and values of k_1 , k_2 ,
287 k_p , and Q_e as well as correlation coefficients are listed in [Table 3](#). The results showed that the
288 correlation coefficient for the first-order kinetic model was lower than the second-order kinetic, but
289 the theoretical Q_e values found in this model were reasonable from 25 °C to 55 °C. The experimental
290 date of the pseudo-second-order kinetic model of phenanthrene indicated extremely high correlation
291 coefficient ($R^2 > 0.9998$) at all experimental temperatures. The theoretical Q_e values computed from
292 this model were consistent with the experimental q_{exp} values, which suggest that the adsorption
293 process could involve physical adsorption and a chemical interaction of valency forces by sharing of
294 or exchange with proton between phenanthrene and CAC. The adsorption mechanism and the
295 potential rate-determining steps could be involved in mass transport and chemical reaction processes
296 [\[32\]](#).

297 In addition, the correlation coefficient R^2 of intraparticle diffusion kinetic models was decreased
298 up to 0.7097. Weber and Morris [\[29\]](#) reported that if intraparticle diffusion is involved in the sorption
299 process, a plot of the square root of time versus adsorption would result in a linear relationship, and
300 the particle diffusion would be the determining step if this line passes through the origin. In this
301 study, the Q_t versus $t^{0.5}$ graph is initially linear, indicating that intraparticle diffusion could be
302 involved in the sorption process of phenanthrene on CAC. However, it was not the only

303 rate-determining step.

304 **3.5. Adsorption thermodynamic properties**

305 When $\ln k$ is plotted versus the reciprocal of the temperature ($1/T$), the slope is E_a (Fig. 7).
306 Activation energy for the phenanthrene sorption on CAC was 23.77 kJ/mol which indicates that the
307 main adsorption process is physical adsorption. Subsequently, $\ln K_F$ is plotted against temperature
308 ($1/T$), as show in Fig. 8, the results of the thermodynamic parameters were evaluated for the sorption
309 system of phenanthrene at 25, 35, 45, and 55 °C (Table 4). The negative value of ΔG° indicates the
310 spontaneous phenanthrene adsorption onto CAC. The ΔG° values decreased lightly with increasing
311 the temperature, indicating that the affinity between phenanthrene and CAC surface weakened with
312 increasing temperature. This result shows that the removal process was favored at lower temperature.
313 The negative value of ΔH° indicates an exothermal adsorption process, which is in agreement with
314 the aforementioned result, i.e., the phenanthrene amount decreased with increasing temperature.
315 Phenanthrene adsorption onto CAC was clearly entropically driven. The positive values of ΔS°
316 suggest increased randomness at the solution interface during the phenanthrene adsorption processes
317 [26].

318 **4. Conclusions**

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

324 Phenanthrene adsorption was described well by the Langmuir model, and the correlation

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

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

333 This paper lays the foundation on developing CAC products with specific performance and using
334 CAC to remove PAHs in the environment. Overall, CAC from Xinjiang region coal prepared by
335 microwave activation could be effectively applied in liquid-phase adsorption involving PAHs.

336

337 **Acknowledgements**

338 This work was supported financially by funding from the National Natural Science Foundation
339 of China (51262025) and International scientific and technological cooperation project of Xinjiang
340 Bingtuan (2013BC002).

341

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