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1     **Preparation of activated carbon from Xinjiang region coal by microwave**  
2     **activation and its application in naphthalene, phenanthrene, and pyrene**  
3                     **adsorption**

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23 **Abstract:**

24 Coal-based activated carbons (CAC) were prepared from coal in Xinjiang China by  
25 microwave-assisted activation. The effects of preparation conditions on adsorption capabilities of  
26 CAC for methylene blue (MB) and iodine were investigated. The microwave activation was carried  
27 out with coal alkali ratio (CAR) of 1:3 for 12 min at 700 W of power, the adsorption capacities of the  
28 prepared CAC achieved the maximal values of 312 and 1048.19 mg/g for MB and iodine. The  
29 increasing of CAR, activation time, and microwave power reduced the surface functional groups and  
30 improved the  $pH_{PZC}$  of CAC. The BET surface area and total pore volume of CAC prepared were  
31 identified as 1770.49 m<sup>2</sup>/g and 0.99 cm<sup>3</sup>/g, respectively. Hence, the work demonstrates that the use  
32 of microwave heating for preparing CAC is more rapid, cheaper and efficient. The adsorption  
33 behaviors of typical polycyclic aromatic hydrocarbons (PAHs) in ethanol aqueous solution on CAC  
34 were also explored. Equilibrium data were favorably described by the Langmuir and Freundlich  
35 isotherms, and adsorption kinetics was fitted to the pseudo-second-order model well. The  
36 equilibrium adsorption amounts were 117.17 mg/g for pyrene, 111.39 mg/g for phenanthrene, and  
37 78.18 mg/g for naphthalene. Thus, CAC prepared by microwave activation could have a very  
38 effective application in removal of these PAHs.

39 **Key words:** Coal-based activated carbon; Microwave activation; PAHs; Adsorption

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## 45 **1. Introduction**

46 Activated carbons (AC) are porous material with extremely high surface areas; they have been  
47 widely used in a variety of industrial applications such as separation/purification of liquids and gases,  
48 removal of toxic substances, catalysts and catalyst support, super capacitors, electrodes and gas  
49 storage [1]. AC is usually prepared from different sources of raw materials utilizing different  
50 processing methods. Major raw materials for the preparation of AC are coal, petroleum, peat, wood  
51 and agricultural wastes. Among which, coal is the most commonly used precursor for AC production  
52 due to the advantage of its low cost of production and abundant resources as well as specific  
53 beneficial properties [2]. Furthermore, coal-based activated carbon (CAC) is greater demand since it  
54 has greater density, corrosion endurance, hardness and more durable than other AC [3]. Coal is an  
55 abundant resource with geological reserves exceeding 2.19 million tons. China accounts for 40% of  
56 the total reserves. Xinjiang Province in Northwest China has become a large-scale coal production  
57 base. The high quality of coals is characterized as low ash yields, low S contents, and low mineral  
58 contents [4]. Providing abundant and high quality raw materials is thus important for the  
59 development of high value-added coal chemical products. For this reason, coal is selected as a stable  
60 alternative for the preparation of AC in Xinjiang.

61 Generally, two methods are used for the preparation of ACs via physical and chemical activation.  
62 During physical activation, the raw material is carbonized first at high temperature and then it is  
63 activated by CO<sub>2</sub> or steam under pressure to increase porosity and surface area of ACs. In chemical  
64 activation both carbonization and activation takes place simultaneously, in which raw material is first  
65 impregnated with activating chemical and then carbonized at desired temperature that varies  
66 according to activating chemical used [5]. Conventional heating method is usually transferred from

67 surface into the interior of the material by thermal conduction using the tubular furnace at relatively  
68 high temperature and long time; as a result, the process of heating was slow, high energy  
69 consumption and non-uniform with the surfaces [6]. In recent years, microwave irradiation has been  
70 widely investigated due to the tremendous thermal gradient from the interior of the char particle to  
71 its cool surface allows the microwave-induced reaction to proceed more quickly and effectively at a  
72 lower bulk temperature [7]. Moreover, microwave radiation supply energy directly to carbon  
73 skeleton at molecular level. Thus, microwave heating provides additional advantages such as energy  
74 savings and shortening the processing time, possibility of selective heating, precise control of  
75 temperature, small equipment size and reduced waste comparing with traditional heating techniques  
76 [8, 9, 10, 11, 12, 13].

77 In microwave irradiation chemical activation, the raw material is first impregnated by activating  
78 agents such as  $\text{H}_3\text{PO}_4$ ,  $\text{KOH}$  or  $\text{ZnCl}_2$ , followed by thermal activation to create the pore structure.  
79 The microwave induced chemical activation usually has higher carbon yield and better developed  
80 pore structure than the physical activation [14, 15, 16, 17]. Liu *et al.* [9] develop a microwave  
81 induced activation process for the preparation of high surface area bamboo-based AC. The optimal  
82 activation conditions were determined as: microwave power 350 W, radiation time 20 min and  
83 phosphoric acid/carbon ratio 1:1, under which a surface area of  $1432 \text{ m}^2/\text{g}$  could be reached. Li *et al.*  
84 [7] prepared relatively well developed porosity AC from tobacco stems by chemical activation with  
85  $\text{K}_2\text{CO}_3$  using microwave radiation. The optimum conditions were as follow: microwave power 700  
86 W, microwave radiation time 30 min,  $\text{K}_2\text{CO}_3/\text{C}$  ratio 1.5:1. Wang *et al.* [10] has been successfully  
87 used to prepare AC from wood via microwave-induced  $\text{ZnCl}_2$  activation. However, relatively few  
88 studies have focused on the preparation of CAC from anthracite by microwave activation. Revealing

89 the correlation between the microwave process conditions of preparing CAC and its adsorption  
90 performance is also necessary.

91 Polycyclic aromatic hydrocarbons (PAHs) are a class of compounds that have more than two  
92 aromatic rings in their molecules. PAHs can transport long distance in air and water, and some PAHs  
93 are capable of interacting with DNA to promote mutagenic and carcinogenic responses [18, 19].  
94 Because of their stability and difficult degradation by microorganisms, it is difficult to remove PAHs  
95 using only biological treatment processes. Additionally, PAHs are not efficiently removed by  
96 conventional physicochemical methods such as coagulation, flocculation, sedimentation, filtration,  
97 or ozonation. AC is the most commonly used porous media for the removal of PAHs from solution  
98 [20-22]. Yuan *et al.* [23] reported that porous carbons were prepared from petroleum coke by KOH  
99 chemical activation and used as adsorbents for effective adsorbing naphthalene, fluorene,  
100 phenanthrene, pyrene and fluoranthene from aqueous solutions, at an initial concentration of  
101 3250–6250 ng/mL, over 90% of PAHs are removed from the solution within 30 min. Kong *et al.* [20]  
102 reported that the performance of sesame stalk-based AC by potassium hydroxide in the efficient  
103 removal of phenanthrene from an aqueous solution, at a carbon concentration of 10 mg/32mL and a  
104 carbonization temperature of 700 °C, the removal efficiency of phenanthrene approached 100%,  
105 which was comparable to that by the commercial carbon. Cabal *et al.* [21] studied the preparation of  
106 AC from bean pods waste by chemical activation was investigated as adsorbents for the adsorption  
107 of naphthalene from water solutions at low concentration. Moreover, a number of studies have  
108 shown that AC prepared from different materials has significant differences in the adsorption of  
109 PAHs. The adsorption behavior of different PAHs on AC has some differences [24, 25, 26]. These  
110 three typical PAHs (naphthalene, phenanthrene, pyrene) were selected owing to their common

111 presence in the environment and their troublesome properties. These are taken as representatives of  
112 two-, three- and four-ringed PAHs. It can be seen that these substances have low solubility in water,  
113 which tends to be even lower when the number of aromatic rings is increased. Therefore, exploring  
114 CAC prepared using microwave activation for the adsorption features of typical PAHs in 30%  
115 ethanol aqueous solution is considerably interesting and informative.

116 The main purpose of the present study is to use rich anthracite from Xinjiang as raw material to  
117 develop a microwave-induced activation process for the preparation of CAC with high surface area  
118 and high adsorption performance to PAHs. The effects of activator types, coal alkali ratio (CAR),  
119 activation time, and microwave power on the adsorption capabilities of CAC for MB and iodine  
120 were investigated. CAC was characterized by using the Boehm method, point of zero charge,  
121 nitrogen adsorption isotherm, and scanning electron microscopy (SEM). The adsorption features,  
122 isotherm, and kinetics of typical PAHs such as naphthalene, phenanthrene, and pyrene were also  
123 explored. The results were used to evaluate the potential application of CAC prepared by  
124 microwave-induced activation for the removal of PAHs.

## 125 **2. Materials and methods**

### 126 **2.1. Materials**

127 This raw anthracite coal was purchased from TBEA, Changji, Xinjiang Uygur Autonomous  
128 Region, China. The coal was passed through a 100 mesh sieve, washed with distilled water to  
129 remove carbon and fines, and dried in an air oven at 110 °C for 4 h. The resultant coal powder was  
130 used to prepare the CAC. The selected physio-chemical properties of naphthalene, phenanthrene and  
131 pyrene are shown in **Table 1**. Naphthalene, phenanthrene and pyrene (>98%; Aladdin, Shanghai,  
132 China) were used to prepare the stock solutions by dissolving an appropriate amount in 30% ethanol

133 aqueous solution.

134 **Table 1 should be positioned here.**

## 135 **2.2. Preparation of CAC**

136 CAC was prepared within a microwave oven (MM823LA6-NS, Midea) at a frequency of 2.45  
137 GHz. The oven was equipped with a power controller (100, 300, 500, 700, and 900 W) and a time  
138 controller (4, 8, 12, 16, and 20 min). The mixture of 10 g with various ratios (1:1, 1:2, 1:3, 1:4, and  
139 1:5) of the dried coal powder to activator (KOH, ZnCl<sub>2</sub> and H<sub>3</sub>PO<sub>4</sub>) was placed in a quartzose tube  
140 of a microwave reactor to activate under vacuum atmosphere at the given power and time. The  
141 resultant products were washed with 10% hydrochloric acid and then with distilled water until the  
142 filtrate reached neutral. The remaining solid was dried in an oven at 110 °C for 4 h and stored in  
143 sealed glass bottles for the adsorption experiments.

144 The amount of MB adsorption is often regarded as a measure of its performance for high  
145 molar-mass species and was determined according to GB/T12496.10-1999 (Detection standard of  
146 activated carbon in China) [20]. On the other hand, the adsorption performance of activated carbons  
147 for low-molar mass species is generally indicated by the iodine number, which was determined at  
148 303 K based on the Standard Detection Method (ASTM Designation: D4607-86) [20].

## 149 **2.3. Characterization methods**

150 The textural properties of the CAC were evaluated by measuring nitrogen adsorption isotherm at  
151 77 K with ASAP 2020C surface area and porosity analyzer (Micromeritics Instrument Corp., USA).  
152 The S<sub>BET</sub> was calculated using the BET equation. The total pore volume (V<sub>t</sub>) was calculated by  
153 converting the adsorption amount at P/P<sub>0</sub> = 0.95 to a volume of liquid adsorbate. The micropore area  
154 (A<sub>m</sub>) and volume (V<sub>m</sub>) were obtained using the t-plot method. The external volume (V<sub>e</sub>) was the



155 deduction of  $V_m$  from  $V_t$  and the external area ( $A_a$ ) was the deduction of  $A_m$  from  $S_{BET}$ . The surface  
156 morphology of the CAC was examined using scanning electron microscopy (SEM) (JSM-6490LV,  
157 Japan Electron Optics Laboratory Ltd. Corp., Japan) at accelerating voltages of 15 kV. Before  
158 observation, the samples were coated with gold in E-1010 Ion sputter. X-ray diffraction (XRD) was  
159 carried out on a Rigaku D/MAX-YA diffractometer with Ni-filtered Cu Ka radiation as the X-ray  
160 source.

161 The “Boehm titration” is a commonly used technique to determine the acidic oxygen surface  
162 functional groups on carbon samples whereby bases of various strengths ( $\text{NaHCO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaOH}$ )  
163 neutralize different acidic oxygen surface functionalities [19]. The weakest base,  $\text{NaHCO}_3$ ,  
164 neutralizes only the strongest acidic carbon surface functionalities (CSFs) which are carboxylic  
165 groups, while  $\text{Na}_2\text{CO}_3$  neutralizes carboxylic and lactonic groups. The strongest base typically used,  
166  $\text{NaOH}$ , neutralizes carboxylic, lactonic and phenolic groups. The number of each type of CSF can be  
167 determined by difference between the uptake of each reaction base [19]. A mixture of 1.5 g CAC and  
168 25.00 mL of one of the three 0.05 M reaction bases,  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{NaOH}$  was filtered and  
169 wash with distilled water adequately after stirring for 24 h, then all the filtrate collected was added  
170 0.05 M HCl to completely neutralize and end with methyl red indicator.

171 The point of zero charge ( $\text{pH}_{PZC}$ ) is defined as the pH of the mixtures at which surface charge  
172 density on the adsorbent is zero. The  $\text{pH}_{PZC}$  values were determined by a mass titration method  
173 proposed by Franz [14]. Activated carbon (0.1 g) was added to 20 mL NaCl solutions, and then the  
174 initial pH had been adjusted with  $\text{NaOH}$  or  $\text{HCl}$ . The flasks were sealed and placed on a shaker for  
175 24 h. The  $\text{pH}_{PZC}$  occurred when there was no change in the pH after contact with the carbon.

#### 176 **2.4. Adsorption experiments of PAHs**

177 2.4.1. Adsorption performance analysis

178 Naphthalene, phenanthrene and pyrene were initially solved into ethanol aqueous solution (30  
179 vol%) to prepare the 300 mg/L stock solutions, respectively. The concentrations of various adsorbate  
180 solutions were measured after adsorption by a UV-vis spectrophotometer (UV-752N, Shanghai  
181 Metash Instruments Co., Ltd, China). The concentration of naphthalene, phenanthrene and pyrene  
182 were calculated based on the following calibration equations, respectively: (1) at 218 nm, (2) at 249  
183 nm, (3) at 237 nm.  $C = 1.7319A_{218} - 0.2309$  (1), and  $R^2$  was equal to 0.9995.  $C = 3.4483A_{249} +$   
184  $0.0103$  (2), and  $R^2$  was equal to 0.9998.  $C = 3.4483A_{237} - 0.0469$  (3), and  $R^2$  was equal to 0.9998.

185 For each adsorption kinetics experiment, 40 mL of 300 mg/L adsorbate solution was placed in a  
186 100 mL conical flask with a cover. The solution was shaken at 25 °C and 60 rpm. After preheating  
187 for 5 min, 100 mg of CAC prepared was added to the solution. Then, the samples were taken  
188 periodically and filtrated immediately by suction. The supernatant solution was analyzed for the  
189 remaining concentration of adsorbate by a UV-vis spectrophotometer.

190 For each adsorption isotherm experiment, approximately 40 mL of different adsorbate solution of  
191 various concentrations was placed in a 100 mL conical flask with cover. To establish the thermal  
192 equilibrium before adsorption, the solution was shaken at 25 °C and a stirring rate of 60 rpm. After  
193 preheating for 5 min, 150 mg of CAC prepared was added to the solution. Then, the samples were  
194 taken after 50 min and filtrated immediately by suction. The supernatant solution was analyzed for  
195 the remaining concentration of adsorbate by a UV-vis spectrophotometer. The amount of adsorbate  
196 ( $Q_e$ ) was calculated as follow:

197 
$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

198 where  $C_0$  (mg/L) and  $C_e$  (mg/L) are liquid-phase concentrations of adsorbate at initial and

199 equilibrium, respectively.  $V$  (mL) represents the volume of the solution and  $m$  (g) stands for the mass  
200 of CAC used.

#### 201 2.4.2. Adsorption isotherm

202 The Langmuir adsorption Eq. (2), predicts the existence of monolayer coverage of the adsorbate  
203 at the outer surface of the adsorbent [9].

$$204 \quad \frac{C_e}{Q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (2)$$

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

207 The Freundlich isotherm [9] is an empirical equation employed to describe heterogeneous  
208 systems, and is expressed by the following Eq. (3):

$$209 \quad \log Q_e = \frac{1}{n} \log C_e + \log K_F \quad (3)$$

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

#### 212 2.4.3. Adsorption kinetics

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

216 The pseudo-first-order kinetic rate equation is expressed as [15]:

$$217 \quad \frac{1}{Q_t} = \frac{1}{Q_e} + \frac{k_1}{Q_e t} \quad (4)$$

218 where  $k_1$  is the rate constant of pseudo-first-order sorption (min), which can be determined from the  
219 slope of the linearized pseudo-first-order rate equation.

220 The pseudo-second-order kinetic rate equation is expressed as [15]:

$$221 \quad \frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (5)$$

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

224 In the intraparticle diffusion model, the relationship between the adsorption capacity at time  $t$ ,  
225  $Q_t$  and  $t^{1/2}$  could be written as [27]:

$$226 \quad Q_t = K_p t^{1/2} + C \quad (6)$$

227 where  $K_p$  is the intraparticle diffusion constant (mg/g/min<sup>1/2</sup>) and  $C$  is the intercept of the line, which  
228 is proportional to the boundary layer thickness.

### 229 **3. Results and discussion**

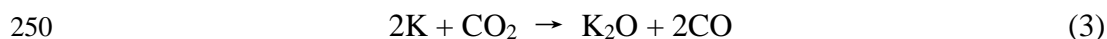
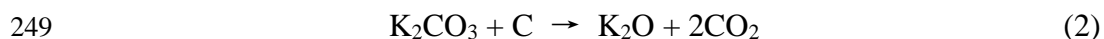
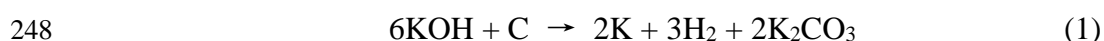
#### 230 **3.1 Preparation of CAC**

##### 231 3.1.1. Effects of activator

232 MB molecule has been estimated that the minimum pore size it can enter is 1.3 nm [28] and can  
233 be used to indicate the capacity of a carbon for sorption of medium-sized molecules. The iodine  
234 molecule provides information about the surface area that is contributed by pores larger than 1 nm  
235 [29], and the iodine number provides a good indication of the capacity of a carbon for sorption of  
236 small molecules [30]. The average pore width of KOH-activated CAC was approximately 2.8 nm in  
237 **Table 2**, which was a sufficiently large pore width to allow MB and iodine molecules to pass through  
238 for a large amount of adsorption.

239 According to the preliminary experiment, the ratio for ZnCl<sub>2</sub> or H<sub>3</sub>PO<sub>4</sub> was also 1:3, whose is  
240 optimum conditions are the same as KOH. The influences of activator types on the adsorption  
241 amounts of MB and iodine on CAC prepared at a coal activator ratio of 1:3, activation time of 12

242 min, and microwave power of 700 W are shown in Fig. 1. In the chemical activation, the adsorption  
243 property of CAC prepared with various activating agents showed a significant difference. The  
244 adsorption amounts of MB and iodine on CAC prepared with KOH reached the maximum. Alkaline  
245 hydroxide activation involves the redox reduction and carbon oxidation to generate porosity. During  
246 the reactions, the evolution of CO, CO<sub>2</sub> and H<sub>2</sub> constituents, and additional reactions [11] between  
247 the active intermediates with the carbon surface are possible (Eqs. (1) - (3)).



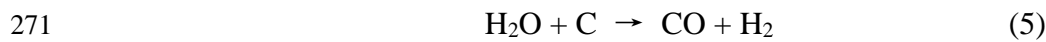
251 The produced alkaline is intercalated to the carbon matrix responsible for both stabilization and  
252 widening of the spaces between the carbon atomic layers. Thus, KOH activated samples exhibited  
253 the best adsorption capacity. Metallic potassium formed during the redox reaction can be intercalated  
254 into the carbon walls independently of the structural order responsible for separation and degradation  
255 of graphitic layers thus develop the microporosity and mesoporosity. The resulting CAC by the  
256 activation agents of ZnCl<sub>2</sub> and H<sub>3</sub>PO<sub>4</sub> had very low adsorption amounts of MB and iodine  
257 (particularly the adsorption amounts of MB), which may be due to the activation of ZnCl<sub>2</sub> and  
258 H<sub>3</sub>PO<sub>4</sub> producing a lower specific surface area and smaller pore size on CAC, which is showed in  
259 Table 2. The activation agents of ZnCl<sub>2</sub> and H<sub>3</sub>PO<sub>4</sub> could be widely used to prepare AC from  
260 lignocellulosic products [31]. So KOH was selected as appropriate activator in this investigation.

261 **Table 2 should be positioned here.**

262 **Fig. 1 should be positioned here.**

263 3.1.2. Effects of coal to KOH ratio (CAR)

264 **Table 3** presents the influences of the CAR on the adsorption amounts of MB and iodine on CAC  
265 prepared at microwave power of 700 W for 8 min. The activation reaction was strengthened and a  
266 large number of pores were formed with the rising ratio, enhancing the CAC adsorption capacity.  
267 When CAR reached 1:3, the carbons on the active sites could be reacted completely, and the  
268 adsorption capacity reached the maximum [7]. When CAR was larger than 1:3, the pores were  
269 widened. Besides, excessive KOH molecules might decompose following the reactions:



272 Therefore, the catalytic oxidation entailed the widening of mesoporous structures and carbon  
273 burn off, so the adsorption capacity of AC was decreased.

274 Surface functional groups such as phenolic group (-OH), lactonic group (-COOCO-), and  
275 carboxylic group (-COOH) were determined by Boehm titration. The results of these surface  
276 functional groups for CAC with various CARs are shown in **Table 3**. The CAR apparently had a  
277 destructive influence on the functional groups of CAC. With increased CAR, the amount of lactonic  
278 groups, phenolic and carboxylic groups decreased, and phenolic and carboxylic groups are fairly low.  
279 A possible explanation for this could be that the alkali activator affected the number of surface acidic  
280 functional groups. The results of  $\text{pH}_{\text{PZC}}$  titrations for CAC under various CARs can also be seen in  
281 **Table 3**.  $\text{pH}_{\text{PZC}}$  increased with increased CAR. Previous research has indicated that the existence of  
282 surface functional groups, such as carboxyl, carbonyl, and phenol, constitutes the source of surface  
283 acidity [9, 12, 32] and the opposite is observed for alkali treatment. Considering the results of the  
284 adsorption capacity of CAC, CAR was set at 1:3 for this study.

285 3.1.3. Effects of activation time

286 **Table 3** demonstrates the effects of activation time on the adsorption amounts of MB and iodine  
287 on CAC prepared with CAR of 1:3 at microwave power of 700 W. The MB adsorption amounts of  
288 CAC increased from approximately 234 to 312 mg/g with increased activation time from 4 to 12 min,  
289 and then decreased to 238.5 mg/g for 20 min activation. Similarly, the iodine number of the CAC  
290 increased gradually from approximately 962.12 to 1048.19 mg/g with increased time from 4 to 12  
291 min, and then slightly decreased to 1045.87 mg/g for 20 min activation. However, when the  
292 activation time reached a certain value, the carbon pores were burnt off by microwave heating,  
293 thereby lowering the CAC adsorption capacity. A similar tendency was observed in the preparation  
294 of AC from rice husk [17].

295 The results of the surface functional content and  $pH_{PZC}$  titrations for CAC under various  
296 activation times can be seen in **Table 3**. With increased activation time from 4 to 20 min, the number  
297 of surface functional groups decreased.  $pH_{PZC}$  generally showed the opposite trend. The  
298 phenomenon implied that increasing activation time promoted an acceleration of energy, leading to a  
299 destruct of surface functional groups and developed the rudimentary of the pore structure [11].  
300 Considering the results of the CAC adsorption capacity, the activation time was set at 12 min in this  
301 study.

#### 302 3.1.4. Effects of microwave power

303 The effects of microwave power on the adsorption amounts of MB and iodine of CAC prepared  
304 by KOH activator with CAR of 1:3 for 12 min, as shown in **Table 3**. The adsorption amounts of MB  
305 rose from 54 to 312 mg/g with increased power from 100 to 700 W and then decreased. The  
306 adsorption amounts of iodine increased from 769.02 to 1048.19 mg/g with increased power from 100  
307 to 700 W and then decreased. More carbon molecules were activated along with the higher

308 microwave power participate in the activation reaction, and lead to the development of pore structure  
309 adequately. However, the exceeded of a certain power may lead to excessive destruction of pore  
310 structure [11].

311 The results of the surface functional content and  $\text{pH}_{\text{PZC}}$  titrations for CAC under various  
312 microwave powers can be seen in Table 3. With increased microwave power from 100 to 900 W, the  
313 number of lactonic groups decreased. The surface functional content and  $\text{pH}_{\text{PZC}}$  had the opposite  
314 trend. Menéndez *et al.* [12] pointed out that microwave treatment reduced the functional group,  
315 especially those of acidic in nature, and increased the  $\text{pH}_{\text{PZC}}$  of the carbon. In this study, CAC  
316 produced directly by microwave heating agreed with the reported findings [12]. The optimum  
317 microwave power in this experiment was thus 700 W.

318 **Table 3 should be positioned here.**

## 319 **3.2. Characterization of CAC**

### 320 3.2.1. Porous structure analysis

321 The  $\text{N}_2$  adsorption isotherms of the CAC at 77 K are presented in Fig. 2. The adsorption  
322 isotherms demonstrated a sharp rise at low  $P/P_0$  range, and a gradual increase was seen at relatively  
323 high  $P/P_0$  range. According to the classification of IUPAC [33], all adsorption isotherms were of type  
324 I, indicating that the CACs were mainly microporous. The  $\text{N}_2$  adsorption isotherms on activated  
325 carbons from Zonguldak region coals using chemical activation also conformed to type I isotherm by  
326 Kopac and Toprak [3]. Moreover, the saturated adsorption amounts of  $\text{N}_2$  increased after microwave  
327 activation, implying an increase in the pore volume.

328 The textural properties obtained from the  $\text{N}_2$  adsorption isotherms are summarized in Table 2.  
329 CAC-4 had a well-developed porosity with a surface area of 1770.49  $\text{m}^2/\text{g}$ , which was primarily



330 microporous under optimal conditions. Liu *et al.* [9] reported that bamboo-based AC using  
331 microwave radiation has a maximum surface area of 1409 m<sup>2</sup>/g. Yagmur *et al.* [13] reported that the  
332 maximum BET surface area was 1157 m<sup>2</sup>/g for the AC from waste tea treated with chemical  
333 activation with microwave energy. Compared with previous works, CAC obtained a higher specific  
334 surface area. This observation suggested that coal could also form a considerable porous structure  
335 through microwave-assisted chemical activation. The specific surface area obtained by the BET  
336 equation ( $S_{\text{BET}}$ ), micropore area ( $A_{\text{m}}$ ), external surface area ( $A_{\text{e}}$ ), micropore volume ( $V_{\text{m}}$ ), and total  
337 pore volume ( $V_{\text{t}}$ ) of CAC-2 were larger than those of CAC-1, whereas the average pore width of  
338 CAC-2 was smaller than CAC-1. This result indicated that the increasing potassium hydroxide  
339 amount enhanced the pore development and created new pores of coal, resulting in further increased  
340 specific surface area and decreased average pore width. CAC-2, CAC-3, and CAC-4 were obtained  
341 using different activation times. With increased activation time from 4 min to 12 min, the  $S_{\text{BET}}$ ,  $A_{\text{e}}$ ,  
342 and  $V_{\text{t}}$  gradually increased. The  $A_{\text{m}}$  and  $V_{\text{m}}$  of CAC-2 and CAC-4 had no significant differences, and  
343 they were larger than those of CAC-3 but not significantly. The phenomenon implied that the  
344 increase in activation time promotes an acceleration of energy, which in turn increases the reaction  
345 rates, thus developed the rudimentary of the pore structure [11]. The six surface physical parameter  
346 values of CAC-5 prepared at 100 W of microwave power were small, indicating no strong reaction  
347 occurred between the coal and activation agent at low microwave power.

348 **Fig. 2 should be positioned here.**

349 Enhancing microwave power from 100 to 700 W drastically improved textural properties,  
350 possibly ascribed to the combined effect of internal and volumetric heating responsible for the  
351 expansion of carbon structure [11]. Also, considerable changes in the surface properties were

352 achieved within a short time, which should be attributed to the distinct mechanism of microwave  
353 heating. As listed in **Table 4**, the samples obtained by microwave heating have higher BET surface  
354 area. It can be seen advantage of microwave heating is that the treatment time as well as the  
355 consumption of gases used in the treatment can be considerably reduced, which resulted in a  
356 reduction in the energy consumption, compared with conventional surface heating. In addition,  
357 microwave heating technique has overall shown better effect in terms of porous structure, relatively  
358 greater surface area than conventional heating method [3]. Hence, the work reported here clearly  
359 demonstrates that the use of microwave heating for preparation CAC is more rapid, cheaper and  
360 efficient than the use of a conventional furnace.

361 **Table 4 should be positioned here.**

### 362 3.2.2. Surface morphology analysis

363 SEM images of the coal and CAC prepared under optimum conditions (CAC-4) are shown in **Fig.**  
364 **3**. The surface of raw material (**Fig. 3(A)**) was fairly smooth without any pores except for some  
365 occasional cracks. After activation, it shows the obtained CAC has an irregular surface with pores  
366 and craters. From **Table 2**, it was also known that the pores are micro- and mesopores. As shown in  
367 **Fig. 3(B)**, the external surface of the CAC-4 demonstrated a well pronounced pore structure,  
368 indicating constitution of new matrix during the activation stage.

369 **Fig. 3 should be positioned here.**

### 370 3.2.3. Crystal structure

371 X-ray diffraction technique is a powerful tool to analyze crystalline nature of materials. **Fig. 4**  
372 shows the XRD profiles of coal and CAC-4. The coal shows an intense diffraction peaks at  $26^\circ$ . The  
373 CAC-4 prepared from coal via microwave-induced KOH activation shows an intense diffraction

374 peaks at around  $29^\circ$  and several not obvious diffraction peaks at around  $44^\circ$ , corresponding to the  
375 (002) and (100) diffraction of disordered stacking of micrographites, respectively [14].

376 **Fig. 4 should be positioned here.**

### 377 **3.3. Adsorption isotherm of selected PAHs on CAC-4**

378 **Table 5** lists the parameters of the Langmuir and Freundlich adsorption isotherm models of  
379 naphthalene, phenanthrene, and pyrene in ethanol aqueous solution onto CAC-4 at  $25^\circ\text{C}$ , along with  
380 their regression coefficients ( $R^2$ ), the adsorption capacity and sorption equilibrium constants ( $q_m$  and  
381  $K_L$ ), and intensity parameters ( $K_F$  and  $n$ ).  $R^2$  reflected the goodness of fit of each of the models to the  
382 data. For the Langmuir isotherm, the  $R^2$  values were  $>0.9934$ . The regression coefficients  $R^2$  of the  
383 Freundlich isotherm were  $>0.9809$ . Both Langmuir and Freundlich isotherm models efficiently  
384 predicted the adsorption of the three PAHs on CAC-4 with high correlation coefficients. This  
385 observation indicated that the sorption of naphthalene, phenanthrene, and pyrene onto CAC-4 may  
386 be confined to a monolayer adsorption and heterogeneous sorption. Similarly, adsorption isotherm of  
387 PAHs from vegetable oil on AC also fitted well by both isotherm models [26]. While Yuan *et al.* [22]  
388 reported that the equilibrium adsorption isotherms of PAHs from water on petroleum coke-derived  
389 porous carbon fitted the Freundlich equation well, and Kong *et al.* [20] reported that the  
390 phenanthrene removal from aqueous solution on sesame stalk-based carbon fit the Freundlich  
391 equation well.

392 With carbon, the sorption process results from molecular interactions between the carbon surface  
393 and the adsorbate, such as van der Waals attractions, electrostatic forces, and weak intermolecular  
394 association [34]. The properties of the adsorbate greatly influence the sorption process. Since PAHs  
395 are nonpolar compounds, sorption is governed mainly by hydrophobic interactions [24]. The values

396 of  $K_L$ ,  $K_F$ , and  $q_m$  followed the trend of pyrene > phenanthrene > naphthalene, which confirmed that  
397 hydrophobic interactions follow the same trend. Kong *et al.* [20] reported that the hydrophobic  
398 interactions were the key factor for phenanthrene removal from aqueous solution by the sesame  
399 stalk-based carbon. Moreover, the values of  $n$  were all greater than 1 and did not significantly change,  
400 showing that the prepared CAC favorably adsorbed the three PAHs [22].

401 **Table 5 should be positioned here.**

### 402 **3.4. Adsorption kinetics of selected PAHs on CAC-4**

403 **Fig. 5** shows the plots of the adsorption amounts of naphthalene, phenanthrene, and pyrene at  
404 different time intervals. The adsorption process consisted of two distinguished periods. In the first  
405 stage, the three PAHs were rapidly adsorbed onto easily accessible hydrophobic sites in the CAC-4  
406 matrix within 5 min. In a well-stirred, solid–liquid system, the first stage of diffusive transport of  
407 PAHs molecules from the bulk solution to the exterior surface of porous CAC particles, as well as  
408 the intraparticle diffusion of the PAHs through the interior pores of CAC, were assumed to be rapid.  
409 In the second stage, adsorption was probably limited by the slow migration of adsorbates to less  
410 accessible sites associated with micropores within the CAC-4 matrix, which could take a long time.  
411 Valderrama *et al.* [25] reported similarly that the adsorption process of PAHs onto granular AC also  
412 was the two-stage. The adsorption amount increased with increased contact time. The maximum  
413 adsorption was observed at 20 min, beyond which almost no further increase in the adsorption  
414 amount was observed.

415 The experimental data for the naphthalene, phenanthrene, and pyrene adsorption onto CAC-4  
416 were fitted by three kinetic models, the values of  $k_1$ ,  $k_2$ ,  $k_p$ , and  $Q_e$ , and the correlation coefficients  
417 are listed in **Table 6**. The experimental kinetic data followed the pseudo-second-order kinetic curves

418 for the three PAHs, which can be demonstrated by higher  $R^2$  ( $>0.9999$ ) and closer  $Q_e$  values to the  
419 experimental ones,  $q_{exp}$ . The adsorption progress of the PAHs on the CAC surface were presumably  
420 caused by the chemical interaction [14]. Cabal *et al.* [21] found the experimental data of adsorption  
421 kinetics of aqueous naphthalene on the AC were fitted to the pseudo-second kinetic model with a  
422 high correlation coefficient. While a literature showed that sorption systems of naphthalene and  
423 pyrene on AC followed a pseudo-first-order reaction model, although the pseudo-second-order  
424 reaction model provides an acceptable description of the sorption process [25]. The equilibrium  
425 adsorption amounts at 20 min were 117.17 mg/g for pyrene, 111.39 mg/g for phenanthrene, and  
426 78.18 mg/g for naphthalene, respectively, decreased as follows: pyrene > phenanthrene >  
427 naphthalene. Compared with the carbonaceous materials such as the phenanthrene adsorption  
428 amount at 24 h from aqueous solution of sesame stalk- based AC was 73.74 mg/g [20], the  
429 naphthalene adsorption amount at 60 min from aqueous solution of reed straw- based AC was 107.00  
430 mg/g [35], and the pyrene adsorption amount at 24 h from aqueous solution of rice husk- based AC  
431 was 104.50 mg/g [36], the PAHs adsorption performance of prepared carbon in this work was higher  
432 and faster. In addition, coal as a precursor is relatively cheaper. Thus, these results indicate that CAC  
433 prepared with microwave activation had excellent capability to remove PAHs from aqueous solution.

434 The agreement between the equilibrium adsorption values determined ( $q_{exp}$ ) and the adsorption  
435 maximum ( $q_m$ ) obtained from the Langmuir isotherm was clear and sufficient. The observed trend in  
436 adsorption amounts was generally consistent with the trend in the amount of aromatic rings and  
437 molecular weight shown in Table 2. The adsorption amounts were higher for larger molecular PAHs  
438 such as pyrene, which suggested that the PAHs were able to form a  $\pi$ - $\pi$  complex between the  
439  $\pi$ -electrons of benzene rings and active sites on the AC surface [18]. Therefore, the  $\pi$ - $\pi$  dispersive

440 interactions between the aromatic ring in PAHs and the graphene layers on CAC were the key  
441 parameters that determined the adsorptive affinity of those molecules with a polycyclic aromatic  
442 skeleton structure [19]. This phenomenon can explain why molecules with more aromatic rings  
443 showed a significantly higher adsorptive affinity than aromatics with fewer rings. The electron  
444 donor–acceptor mechanism could involve lactonic groups that predominated on the basic carbon  
445 surface. Lactonic groups acted as electron donors. The aromatic rings in the adsorbate accepted  
446 electrons [21], consistent with the number of lactonic groups and  $pH_{PZC}$  CAC-4 prepared at 0.35  
447 mmol/g and 8.35, respectively.

448 **Fig. 5 should be positioned here.**

449 **Table 6 should be positioned here.**

#### 450 **4. Conclusions**

- 451 1. The optimum conditions for CAC preparation were identified to be KOH activator, CAR of 1:3,  
452 activation time of 12 min, and microwave power of 700 W. Under the optimum conditions  
453 adsorption amounts of MB and iodine on CAC was 312 and 1048.19 mg/g, respectively.
- 454 2. The CAR, activation time, and microwave power destructed surface functional groups and  
455 raised the  $pH_{PZC}$  of CAC. The BET surface area and pore volume of the optimal CAC were  
456 evaluated as 1770.49 m<sup>2</sup>/g and 0.99 cm<sup>3</sup>/g, which was primarily microporous. The SEM image  
457 of the optimal CAC showed that the external surface of CAC had a well-pronounced and almost  
458 uniform pore structure. Hence, the work clearly demonstrates that the use of microwave heating  
459 for preparing CAC is more rapid, cheaper and efficient.
- 460 3. The adsorption equilibrium of naphthalene, phenanthrene, and pyrene on CAC-4 was  
461 satisfactorily represented by both the Langmuir and Freundlich isotherm models with high

462 correlation coefficients. The prepared CAC favorably adsorbed naphthalene, phenanthrene, and  
463 pyrene. The experimental kinetic data followed the pseudo-second-order kinetic curves for  
464 naphthalene, phenanthrene, and pyrene, presuming that the adsorption progress is affected by  
465 chemical interactions. The equilibrium adsorption amounts were 117.17 mg/g for pyrene, 111.39  
466 mg/g for phenanthrene, and 78.18 mg/g for naphthalene. Overall, CAC from Xinjiang region  
467 coal prepared by microwave activation could be effectively applied in liquid-phase adsorption  
468 involving PAHs.

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575 **Figure captions:**

576 **Fig. 1** Adsorption amounts of MB and iodine by CAC with various activator types (preparation  
577 conditions: activation time = 12 min; microwave power = 700 W; CAR= 1:3).

578 **Fig. 2** Nitrogen adsorption isotherm for the prepared CACs (CAC-1: activation time = 8 min;  
579 microwave power = 700 W; CAR= 1:1, CAC-2: activation time = 8 min; microwave power = 700 W;  
580 CAR= 1:3, CAC-3: activation time = 4 min; microwave power = 700 W; CAR= 1:3, CAC-4:  
581 activation time = 12 min; microwave power = 700 W; CAR= 1:3, CAC-5: activation time = 12 min;  
582 microwave power = 100 W; CAR= 1:3).

583 **Fig. 3** SEM micrographs of the selected samples at 5000× magnification: (A) coal, (B) CAC-4  
584 (preparation conditions: activation time = 12 min; microwave power = 700 W; CAR= 1:3).

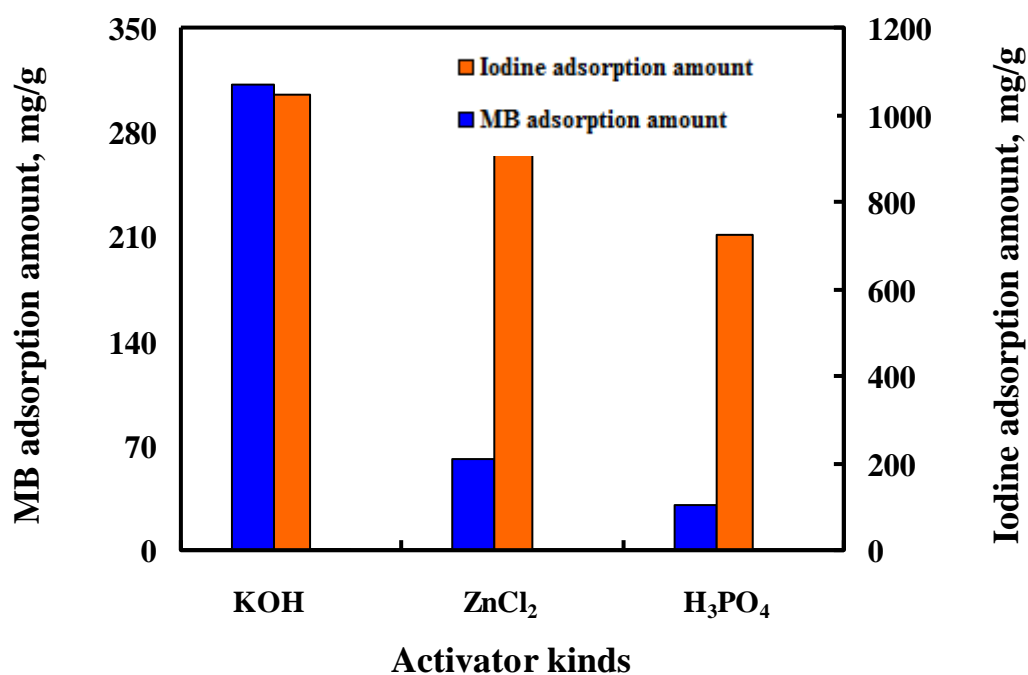
585 **Fig. 4** XRD profiles of coal and CAC-4 (preparation conditions: activation time = 12 min;  
586 microwave power = 700 W; CAR= 1:3).

587 **Fig. 5** Adsorption amounts of naphthalene, phenanthrene and pyrene in ethanol aqueous solution on  
588 CAC-4 (preparation conditions: activation time = 12 min; microwave power = 700 W; CAR= 1:3) at  
589 various times and at 25 °C.

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594 **Fig. 1** Adsorption amounts of MB and iodine by CAC with various activator types (preparation

595 conditions: activation time = 12 min; microwave power = 700 W; CAR= 1:3).

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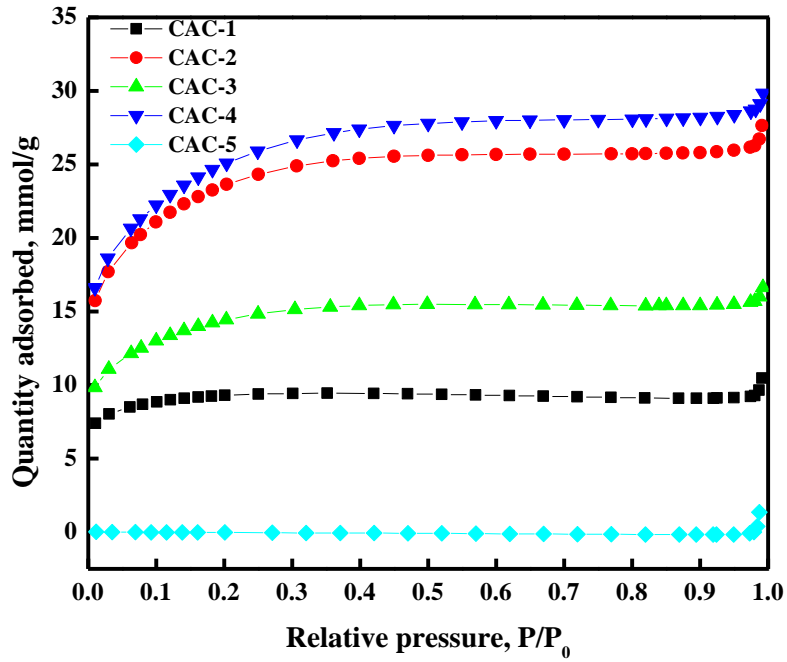
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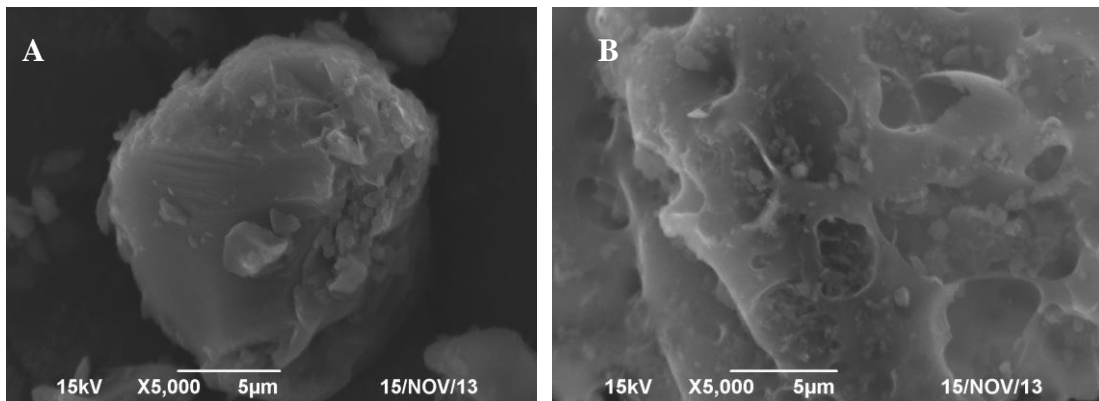


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605 **Fig. 2** Nitrogen adsorption isotherm for the prepared CACs (CAC-1: activation time = 8 min;  
 606 microwave power = 700 W; CAR= 1:1, CAC-2: activation time = 8 min; microwave power = 700 W;  
 607 CAR= 1:3, CAC-3: activation time = 4 min; microwave power = 700 W; CAR= 1:3, CAC-4:  
 608 activation time = 12 min; microwave power = 700 W; CAR= 1:3, CAC-5: activation time = 12 min;  
 609 microwave power = 100 W; CAR= 1:3).

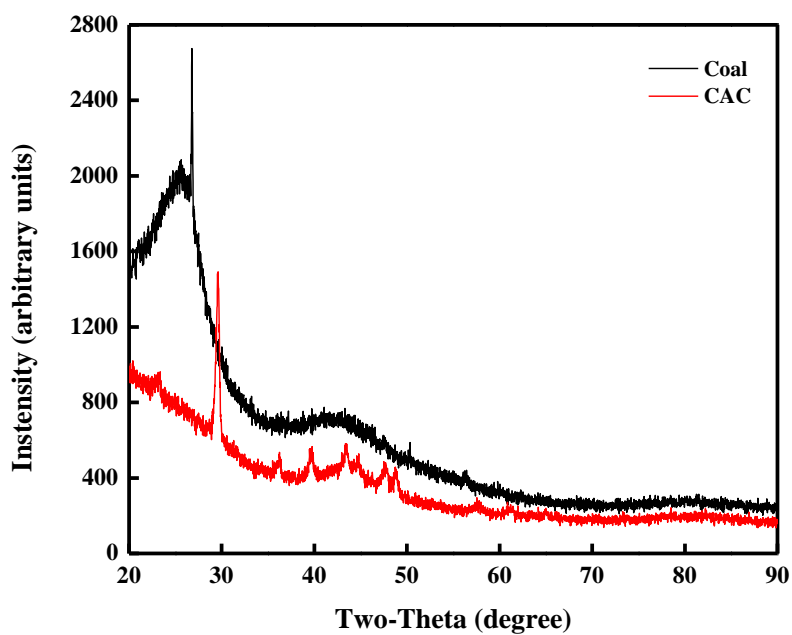
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613 **Fig. 3** SEM micrographs of the selected samples at 5000× magnification: (A) coal, (B) CAC-4  
 614 (preparation conditions: activation time = 12 min; microwave power = 700 W; CAR= 1:3).



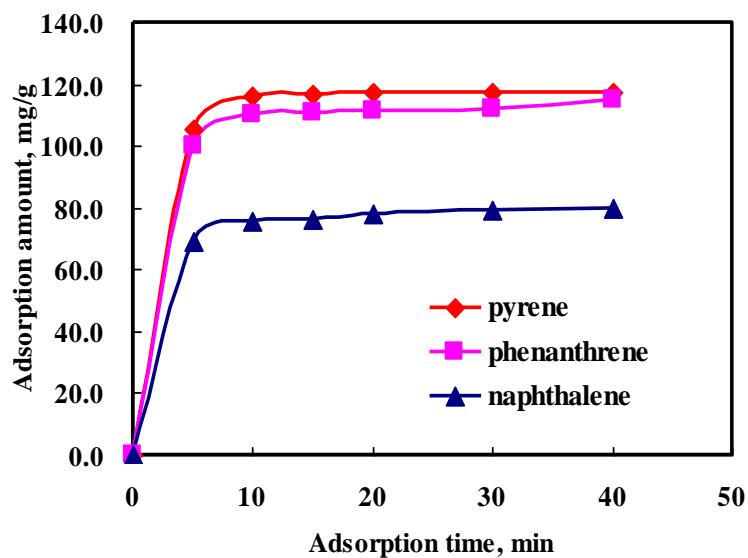
615

616 **Fig. 4** XRD profiles of coal and CAC-4 (preparation conditions: activation time = 12 min;

617 microwave power = 700 W; CAR= 1:3).

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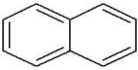
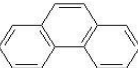

621 **Fig. 5** Adsorption amounts of naphthalene, phenanthrene and pyrene in ethanol aqueous solution on

622 CAC-4 (preparation conditions: activation time = 12 min; microwave power = 700 W; CAR= 1:3) at

623 various times and at 25 °C.

624

625 **Table 1** Selected properties of PAHs used [22]

PAHs	Structure	Formula	Molecular weight (g/mol)	Molecular dimension (nm×nm×nm)	Molar volume (cm <sup>3</sup> /mol)	Water solubility (ng/g)	logKow
Naphthalene		C <sub>10</sub> H <sub>8</sub>	128.17	0.91×0.73×0.38	148	30800	3.30
Phenanthrene		C <sub>14</sub> H <sub>10</sub>	178.22	1.17×0.80×0.34	199	1283	4.57
Pyrene		C <sub>16</sub> H <sub>10</sub>	202.25	0.92	214	135	5.18

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633 **Table 2** Activation conditions and surface characteristics of the prepared CACs.

Sample	Activation conditions			S <sub>BET</sub>	A <sub>m</sub>	A <sub>e</sub>	V <sub>m</sub>	V <sub>t</sub>	V <sub>m</sub> /V <sub>t</sub>	Average pore width
	Microwave time min	Microwave power W	Coal activator ratio	m <sup>2</sup> /g	M <sup>2</sup> /g	M <sup>2</sup> /g	cm <sup>3</sup> /g	cm <sup>3</sup> /g	%	nm
CAC-1	8	700	1:1	623.84	417.31	206.53	0.23	0.32	71.88	3.25
CAC-2	8	700	1:3	1651.50	543.09	1108.40	0.33	0.91	36.26	2.86
CAC-3	4	700	1:3	1007.27	379.35	627.92	0.22	0.54	40.74	2.86
CAC-4	12	700	1:3	1770.49	508.87	1261.62	0.61	0.99	61.62	2.82
CAC-5	12	100	1:3	0.21	0.00	0.00	0.00	0.00	0.00	0.00
CAC-6	12	700	1:3	934.54	425.64	534.22	0.37	0.49	75.51	1.95
CAC-7	12	700	1:3	843.56	384.34	423.55	0.31	0.42	73.81	1.88

634 S<sub>BET</sub>: specific surface area obtained by BET equation, A<sub>m</sub>, A<sub>e</sub>: micropore area, external surface area,635 V<sub>m</sub>, V<sub>t</sub>: micropore volume, total pore volume.

636 Activator: The CAC-1, CAC-2, CAC-3, CAC-4, CAC-4 and CAC-5 with KOH; the CAC-6 with

637 ZnCl<sub>2</sub>; the CAC-7 with H<sub>3</sub>PO<sub>4</sub>.

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644 **Table 3** Adsorption performance and surface properties of CAC prepared with various CAR,  
 645 activation time and microwave power.

Treatments		MB adsorption amount (mg/g)	Iodine adsorption amount (mg/g)	Lactonic group ( mmol/g)	Carboxylic groups ( mmol/g)	Phenolic groups ( mmol/g)	pH <sub>PZC</sub>
CAR	1:1	77.7	999.38	0.5667	0.0333	0.0812	8.10
	1:2	268.5	1034.24	0.4933	0.0167	0.0530	8.20
	1:3	291.0	1038.90	0.4700	0.0063	0.0233	8.30
	1:4	270.0	1034.23	0.3500	0.0056	0.0100	8.35
	1:5	256.5	1017.95	0.2333	0.0028	0.0067	8.30
Activation time (min)	4	234.0	962.12	0.5267	0.0900	0.0267	8.10
	8	282.0	1033.54	0.4700	0.0733	0.0190	8.30
	12	312.0	1048.19	0.3500	0.0700	0.0058	8.35
	16	238.5	1045.87	0.2267	0.0333	0.0047	8.32
	20	241.5	1045.87	0.1833	0.0083	0.0033	8.31
Microwave power (W)	100	54.0	769.02	0.5733	0.0933	0.0562	7.50
	300	180.0	1003.99	0.4567	0.0267	0.0333	7.60
	500	210.0	1031.91	0.4133	0.0133	0.0193	7.90
	700	312.0	1048.19	0.3500	0.0093	0.0097	8.35
	900	219.0	1043.54	0.3333	0.0045	0.0033	8.30

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656 **Table 4** Comparison of different kinds of ACs.

Sample	Carbon source	Heating methods	S <sub>BET</sub> (m <sup>2</sup> /g)	V <sub>total</sub> (cm <sup>3</sup> /g)	Data sources
Commercial AC	Pitch	Convention	1403.00	0.583	[19]
Commercial AC	Wood	Convention	1100.00	1.061	[19]
Lotus stalk based - AC	Lotus stalk	Convention	1220.00	1.191	[14]
Jatropha hull based - AC	Jatropha hull	Convention	748.00	0.580	[2]
CAC	Coal	Convention	830.5m <sup>2</sup> /g	0.250	[3]
Rice husk based - AC	Rice husk	Microwave	752.00	0.640	[37]
Cotton stalk based - AC	Cotton stalk	Microwave	729.33.00	0.380	[38]
CAC	Coal	Microwave	1770.49	0.990	This work

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679 **Table 5** Isotherm constants for the adsorption of naphthalene, phenanthrene, and pyrene in ethanol  
 680 aqueous solution onto CAC-4 at 25 °C.

PAHs	Langmuir			Freundlich		
	$K_L$ (L/mg)	$q_m$ (mg/g)	$R^2$	$K_F$ (L/mg)	$n$	$R^2$
Naphthalene	0.03	89.29	0.9934	5.50	1.71	0.9921
Phenanthrene	0.28	116.28	0.9990	24.62	1.60	0.9848
Pyrene	0.90	117.65	0.9991	52.16	1.61	0.9809

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692 **Table 6** Kinetics constants for the adsorption of naphthalene, phenanthrene, and pyrene in ethanol  
 693 aqueous solution onto CAC-4.

PAHs	$q_{exp}$ (mg/g)	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model			Intraparticle diffusion model	
		$k_1$	$Q_e$	$R^2$	$k_2$	$Q_e$	$R^2$	$k_p$	$R^2$
		( $\text{min}^{-1}$ )	(mg/g)		(g/mg min)	(mg/g)		(mg/g/ $\text{min}^{1/2}$ )	
Naphthalene	78.18	0.61	80.65	0.9615	0.02	81.30	0.9999	1.84	0.9125
Phenanthrene	111.39	0.25	112.36	0.9970	0.04	112.36	1.0000	0.76	0.9124
Pyrene	117.17	0.13	117.65	0.9644	0.06	117.65	1.0000	0.61	0.9049

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