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23 **ABSTRACT**

24 As an effective adsorbent, coal-based activated carbon (CAC) was modified with iron
25 through microwave radiation to adsorb polycyclic aromatic hydrocarbons (PAHs) from
26 aqueous solutions. The effects of iron nitrate concentration, microwave power, and
27 microwave radiation time on CAC were investigated. The optimum modification conditions
28 were as follows: iron nitrate concentration, 0.05 M; microwave power, 300 W; and
29 microwave radiation time, 5 min (designated as 0.05Fe-MCAC). CAC and 0.05Fe-MCAC
30 were characterized using scanning electron microscopy, nitrogen adsorption–desorption,
31 surface acidity and basicity tests, and Fourier transform infrared spectroscopy. The
32 adsorption capacities of PAHs were also determined. After modification the following
33 phenomena occurred: pore structures developed; BET surface area increased from 686.06 to
34 1079.67 m²/g; the number of oxygen-containing groups decreased; and basicity was
35 enhanced. The PAHs adsorption capacity of 0.05Fe-MCAC was higher than that of CAC.
36 The altered texture and chemical properties of 0.05Fe-MCAC played an important role in
37 PAHs adsorption. The pseudo-second-order models of CAC and 0.05Fe-MCAC fitted well.
38 The PAHs adsorption of 0.05Fe-MCAC owned lower activation energy and greater stability
39 than that of CAC. Results indicated that iron-modified CAC via microwave radiation is a
40 promising and efficient adsorbent of PAHs from aqueous solutions.

41

42 **Keywords** Coal-based activated carbon · Microwave radiation · Iron modification · PAHs
43 adsorption

44

45 **1. Introduction**

46 Polycyclic aromatic hydrocarbons (PAHs) commonly refer to a large class of dangerous
47 and harmful ecosystem pollutants. They are generated during the incomplete combustion of
48 hydrocarbons and other organic compounds, such as coal, petroleum, and biomass [1, 2].
49 PAHs can be transported in long distances in water but cannot be easily biodegraded because
50 of their chemical persistence and semi-volatile nature [3]. In addition their toxic, mutagenic,
51 and carcinogenic properties, they are considered as priority pollutants [4]. PAHs are
52 effectively removed from aqueous solutions through adsorption [5, 6]. Nevertheless,
53 economical and applicable absorbents should be developed to remove PAHs efficiently.

54 Activated carbon (AC) is characterized by a wide surface area and developed porosity;
55 as such, it is considered a highly promising absorbent for a wide range of technical
56 applications [6–8]. AC is also a commonly used adsorbent in wastewater treatments
57 worldwide. AC is modified to regulate its pore structure and chemical properties. This
58 process is an effective route to enhance the removal efficiency of AC as an adsorbent of
59 various pollutants. Liu et al. [9] modified bamboo-based AC and found that the modified AC
60 can effectively adsorb methylene blue. Shaarani et al. [10] demonstrated that
61 ammonia-modified AC for adsorption of 2, 4-dichlorophenol was superior to the AC. Yin et
62 al. [11] also modified AC-enhanced contaminant uptake from aqueous solutions. However,
63 coal-based AC (CAC) has been rarely developed as an absorbent of PAHs from aqueous
64 solutions [12–14]. Other materials are also more commonly used than CAC. Organic
65 compound adsorption by AC is generally influenced by various properties, such as pore size,
66 pore diameter distribution, surface properties, and surface functional groups [15, 16].

67 Therefore, structure and surface functional groups should be appropriately controlled to
68 improve the adsorption of PAHs from aqueous solutions.

69 Metal-modified AC may provide an enhanced porosity structure and can vary in terms
70 of pore structure and surface functional groups; thus, adsorption properties are altered [17].
71 Various metal oxides, such as manganese, mercury, and iron, have been added to AC to
72 improve their adsorption performance [18–20]. However, iron-modified CAC used for the
73 adsorption of PAHs from aqueous solutions has yet to be reported. Microwave is currently
74 used in various fields to heat dielectric materials because this technique requires a
75 considerably short treatment time and consumes low energy. In our previous study,
76 microwave radiation can change the physical properties of AC [14]. Thus, iron-modified
77 CAC via microwave radiation should be investigated to enhance the adsorption of PAHs.

78 This study aimed to modify CAC with iron via microwave radiation and to investigate
79 the properties of the modified CAC and its adsorption capacities for PAHs from aqueous
80 solutions. CAC and 0.05Fe-MCAC were characterized through scanning electron
81 microscopy (SEM), nitrogen adsorption-desorption, surface acidity and basicity, and Fourier
82 transform infrared spectroscopy (FTIR) methods. The adsorption capacity of naphthalene on
83 0.05Fe-MCAC was also examined, and the adsorption kinetics of PAHs on CAC and
84 0.05Fe-MCAC were systematically analyzed. PAHs adsorption on CAC and 0.05Fe-MCAC
85 were compared, and the correlation of this property with their structures was determined.
86 This work could evaluate the effectiveness of 0.05Fe-MCAC in the removal of PAHs from
87 aqueous solutions and could enhance our understanding of the adsorption behavior of PAHs
88 onto 0.05Fe-MCAC.

89 **2. Materials and methods**

90 *2.1. Preparation of CAC*

91 Coal-based activated carbon (CAC) was prepared according to our previous study [21],
92 where the used coal (Xinjiang Tebian Electric Apparatus Stock Co., Ltd, China) was
93 activated using potassium hydroxide under microwave radiation. Microwave radiation was
94 conducted in a 2.45 GHz microwave oven (MM823LA6-NS, Midea). The preparation
95 conditions of CAC were as follows: hydroxide potassium-to-coal ratio (w/w), 1:1;
96 microwave power, 700 W; and radiation time, 10 min. The obtained products were in an
97 air-dried oven at 110 °C for 4 h and marked as CAC. All of the chemicals and reagents used
98 in this study were of analytical grade.

99 *2.2. Modification of iron nitrate via microwave radiation*

100 In this study, 0.2 g of CAC absorbent was added to a 150 mL conical flask with 15 mL
101 of different concentrations (0.05–1 M) of $\text{Fe}(\text{NO}_3)_3$ solution, and ultrasound was conducted
102 for 2 h. The mixture was heated in a microwave oven (MCR-3, Shanghai Keli) at microwave
103 power of 100–700 W and microwave radiation times of 1–8 min. After modification
104 treatment, the mixture was filtered and extensively washed with double distilled water and
105 dried in an oven at 110 °C for 4 h. These samples were named as Fe-MCAC and 0.05 M of
106 $\text{Fe}(\text{NO}_3)_3$ -modified sample was designated as 0.05 Fe-MCAC.

107 *2.3. Characterization of CAC and 0.05Fe-MCAC*

108 *2.3.1. SEM*

109 The morphologies of carbon samples were observed on scanning electron microscopy
110 (SEM, JEOL, JSM-6490LV, Japan) with an acceleration voltage of 15 kV. Prior to analysis,

111 the samples were dried at 383 K and stored in a desiccator overnight.

112 2.3.2. *Fourier transform infrared (FTIR) spectrometer*

113 For FTIR measurements, the CAC and 0.05Fe-MCAC samples were blended with KBr
114 to form pellets; the spectra were obtained on a PHI5700 ESCA spectrophotometer in the
115 range of 4000-400 cm^{-1} at 4 cm^{-1} resolution.

116 2.3.3. *BET surface area and pore structure analysis*

117 The Brunauer-Emmett-Teller (BET) surface area and porous properties of the CAC and
118 0.05Fe-MCAC samples were determined from the N_2 adsorption at 77 K using a surface
119 area analyzer (SI/MP, Quantachrome, USA).

120 2.3.4. *Surface acidity and basicity*

121 The amphoteric characteristics of the CAC and 0.05Fe-MCAC samples were
122 characterized by measuring the amount of the surface functional groups using the acid-base
123 titration method proposed by Boehm [22]. According to this method and our reported
124 studies [14, 22], 200 mg of each sample was added to 25 mL solutions of 0.05 M: sodium
125 hydroxide, sodium carbonate, sodium bicarbonate and hydrochloric acid, respectively. The
126 mixture was oscillated for 24 h in constant temperature vibrator at 25 °C, and the resulting
127 suspensions were filtered for estimating the residual base/acid.

128 2.4. *Adsorption test*

129 2.4.1. *Adsorption of PAHs from aqueous solution*

130 Naphthalene, phenanthrene, pyrene were selected as the typical compounds, which are
131 commonly exist in wastewater/soil mediums. 15 mg of the carbon samples were added into
132 flask containing 100 mL, 30.0 mg/L of naphthalene, phenanthrene, and pyrene solution at

133 20 °C, respectively. After agitation for 60 min, the mixture solution was filtered, and
134 naphthalene, phenanthrene, and pyrene concentrations were measured using a UV-75N
135 spectrophotometer at 218 nm, 248 nm and 237 nm, respectively. The amounts of naphthalene,
136 phenanthrene, and pyrene on samples were calculated using the average of the three data.

137 2.4.2. Adsorption kinetic

138 Naphthalene, phenanthrene, and pyrene adsorption kinetics were evaluated at 10, 20, 30,
139 and 40 °C, respectively. The initial concentration was set as 30 mg/L, and the samples were
140 reacted at different contacting time intervals. The mixture was separated through filtration.
141 Naphthalene, phenanthrene, and pyrene concentrations were determined using a UV-75N
142 spectrophotometer. The amounts of naphthalene, phenanthrene, and pyrene at time t (min), q_t
143 (mg/g), can be calculated according to Eq. (1),

$$144 \quad q_t = \frac{(C_0 - C_t) \times V}{m} \quad (1)$$

145 where C_t (mg/L) is the liquid-phase concentration of naphthalene, phenanthrene, and pyrene
146 at any time t, respectively.

147 2.5. Regeneration of spent carbon

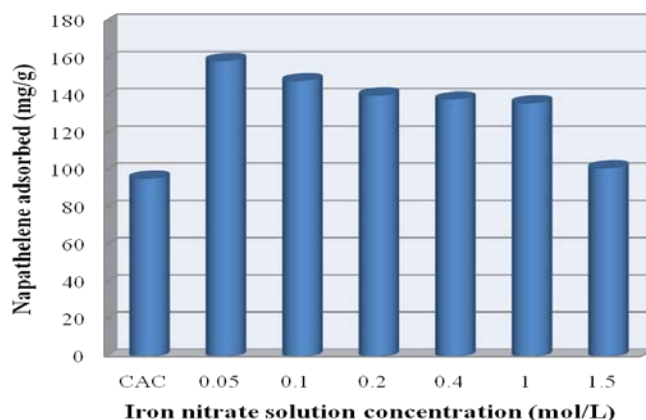
148 The 0.05Fe-MCAC adsorbed pyrene sample was desorbed and immersed in 100 mL
149 absolute ethanol for 90 min. The carbon sample was removed and dried in vacuum at 110 °C
150 for 24 h. The regeneration of carbon was determined, and the pyrene adsorption capacity was
151 calculated repeatedly by using the described adsorption method. Desorption experiments
152 were conducted again using the same adsorption method, and the cycle was repeated thrice.

153 3. Results and discussion

154 3.1. Adsorption capacity of Fe-MCAC for naphthalene

155 3.1.1. Effects of iron nitrate solution concentrations

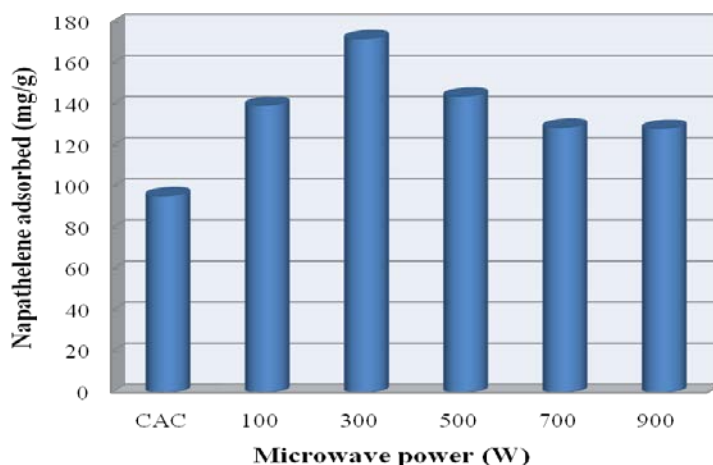
156 We investigated the effects of the concentration of iron nitrate solution on the
157 preparation of Fe-MCAC for naphthalene adsorption under the same microwave radiation
158 conditions (Fig. 1). As the concentration of iron nitrate solution increased, the amount of
159 naphthalene adsorbed on Fe-MCAC gradually decreased. The 0.05Fe-MCAC sample
160 modified with 0.05 M iron nitrate solution yielded a maximum adsorption capacity of 159.00
161 mg/g, which was significantly higher than the adsorption capacity of the CAC sample (95.74
162 mg/g). The Fe³⁺ modification influenced the adsorption capacity of the adsorbent possibly
163 because of the change in texture and chemical properties on the surface of the CAC sample.
164 Iron modification could enrich the pore structure of the Fe-MCAC sample, which enhanced
165 the adsorption capacity of Fe-MCAC for naphthalene [17]. However, a high iron nitrate
166 concentration was disadvantageous for the modified CAC for naphthalene adsorption in this
167 study because excessive amounts of iron could be blocked pore of Fe-MCAC; as a
168 consequence, a small pore volume is obtained, and the adsorption efficiency is decreased
169 [20]. Considering that low concentration can save resources and enhance adsorption capacity,
170 we selected 0.05 M iron nitrate solution as the suitable modification concentration.



171
172 **Fig. 1.** Effects of iron nitrate solution concentrations on Fe-MCAC for naphthalene
173 adsorption capacity (microwave power: 300 W, microwave radiation time: 5 min)

174 *3.1.2. Effects of microwave power*

175 The effects of microwave power on the Fe-MCAC samples are presented in Fig. 2. The
176 increased amounts of naphthalene adsorbed on the Fe-MCAC sample were higher than those
177 on the CAC sample. As radiation power was enhanced to 300 W, the amounts of naphthalene
178 on the Fe-MCAC sample were maximized possibly because the pore structure on the surface
179 of the Fe-MCAC sample was greatly developed at a radiation power of up to 300 W.
180 However, the adsorption capacity decreased from 172.18 mg/g to 128.48 mg/g as power was
181 increased from 300 W to 900 W. This result was due to the fierce reaction at high microwave
182 power that reduces the surface area and porosity of the Fe-MCAC sample; as a consequence,
183 the adsorption capacities of naphthalene were progressively decreased [23]. Hence, high
184 microwave power is disadvantageous for the modified CAC. A microwave power of 300 W
185 was the optimum modification condition.

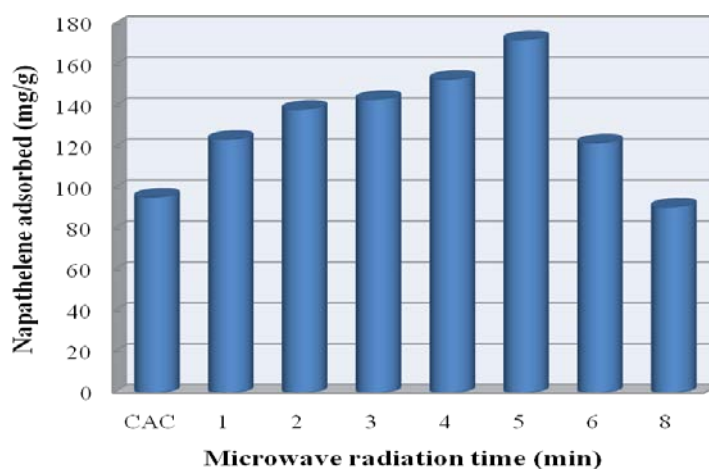


186 **Fig. 2.** Effects of microwave power on Fe-MCAC for naphthalene adsorption capacity (iron
187 nitrate: 0.05 M, microwave radiation time: 5 min)

189 *3.1.3. Effects of microwave radiation time*

190 The effect of microwave time on the preparation of Fe-MCAC can be observed by
191 increasing radiation time from 1 min to 5 min, which showed an enhancement of

192 naphthalene capacity from 124.03 mg/g to 172.80 mg/g. Beyond the value of 5 min, the
193 modified CAC obtained a lower naphthalene capacity (Fig. 3). A prominent drop was
194 observed at 6 min probably as a result of a longer radiation time effect, which largely
195 destroyed the pore walls between adjacent pores [24]. The results present that 5 min is the
196 suitable period of time for modification because it provided the maximum naphthalene
197 capacity with a value of 172.80 mg/g.



198

199 **Fig. 3.** Effects of microwave radiation time on Fe-MCAC for naphthalene adsorption
200 capacity (iron nitrate: 0.05M, microwave power: 300W)

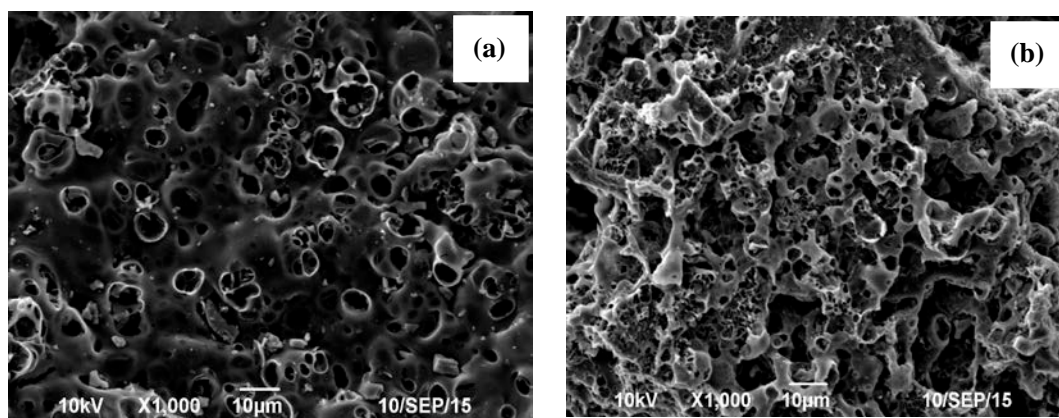
201 From the discussion above, both iron nitrate solution concentration and microwave
202 power had significant effects on the modified CAC for adsorption of naphthalene. The
203 optimum conditions obtained were as follows: iron nitrate solution concentration 0.05 M,
204 microwave power 300 W, and microwave time 5 min.

205 3.2. Characterization

206 3.2.1. SEM

207 The morphologies of the CAC and 0.05Fe-MCAC samples were carried out by SEM.
208 The pore size distribution of the CAC sample with high magnifying power ($\times 1000$) is
209 uneven and exhibits less pores (Fig. 4). After iron modification treatment under microwave

210 irradiation, the surface of the 0.05Fe-MCAC sample was more porous than that of CAC (Fig.
211 4). Iron ion has high activity and easily enters the pore of 0.05Fe-MCAC. Several studies
212 also showed that microwave radiation treatment effectively developed pores on the surface
213 of the CAC and AC, which greatly enlarged the surface area and porous structure of the
214 carbons [14, 25]. Therefore, the developed porous structure could benefit the adsorption of
215 PAHs from aqueous solutions. In addition, 0.05Fe-MCAC can provide a large surface area
216 for iron loading; and iron surface has stronger activity and can better combine with the
217 adsorbate, which may promote 0.05Fe-MCAC adsorption [14, 26]. Chen et al. showed that
218 iron-impregnated AC was highly effective in arsenic removal [20]. Considering these factors,
219 the regulation of the pore structure of CAC and Fe³⁺ loading are great of significance for
220 PAHs adsorption.

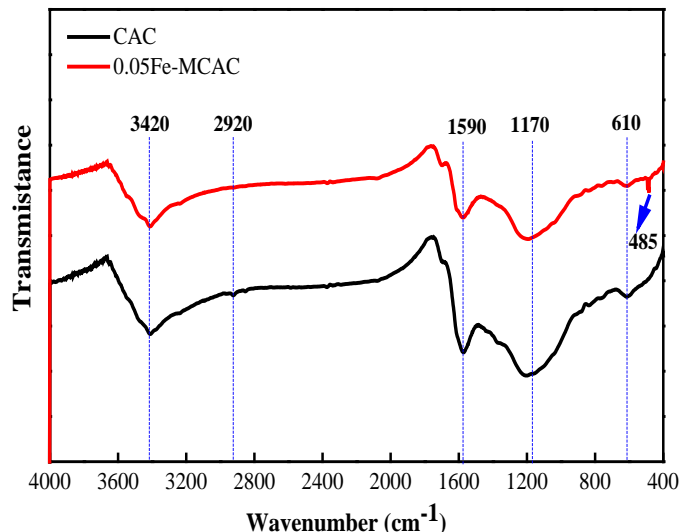


221 **Fig. 4.** Scanning electron microscope (SEM) micrograph: CAC (a); and 0.05Fe-MCAC (b)

222 3.2.2. Fourier transform infrared (FTIR) spectrometer

223 FTIR analysis permitted the spectrophotometric observation of the adsorbent surface in
224 the range of 400–4000 cm⁻¹ and served as a direct means for identifying the organic
225 functional groups on the surface (Fig. 5). Insignificant changes, such as broadening of some
226 bands and spectral shifts, were observed in the FTIR spectrum of the 0.05Fe-MCAC

227 compared with the FTIR spectrum of the CAC. The FTIR spectra of the CAC and
228 0.05Fe-MCAC presented a characteristic band at 3420 cm^{-1} , which could be attributed to the
229 -OH stretching vibration [17, 20]. The band at approximately 2920 cm^{-1} resulted from the
230 symmetric and asymmetric C–H stretching vibrations [25]. The difference in the intensity of
231 the 1590 cm^{-1} between the two samples indicated that the modification process caused C=O
232 groups to decrease [25]. The peaks at approximately 1170 cm^{-1} represented the C–O
233 vibrations of various oxygen-containing groups. After iron modification, the
234 oxygen-containing functional group had a certain decrease. The most interesting changes in
235 the corresponding band were found at 485 cm^{-1} , which could be attributed to the O-Fe
236 vibration. Rivera-Utrilla et al. also found this special band. This finding suggested that a
237 certain quantity of iron was loaded on the 0.05Fe-MCAC [27].



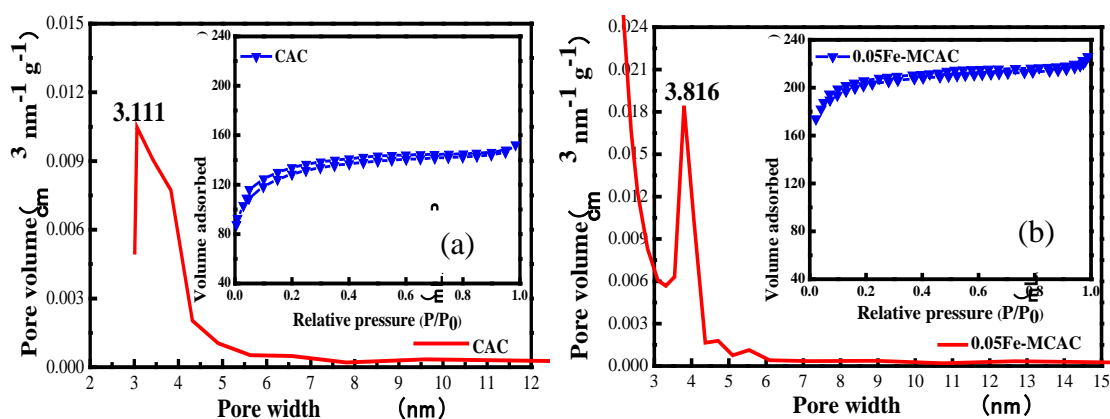
238 **Fig. 5.** FTIR analysis of the CAC and 0.05Fe-MCAC samples

240 3.2.3. Brunauer–Emmett–Teller (BET) surface area and pore structure analysis

241 The isotherms of the adsorption–desorption of N_2 at 77 K were determined, as shown in

242 Fig. 6, to investigate the influence on the textural properties of the surfaces of the CAC and

243 0.05Fe-MCAC samples. According to IUPAC classification, the N₂ adsorption isotherms of
 244 the CAC and 0.05Fe-MCAC samples were of type IV with a type-H₄ hysteresis loop. This
 245 phenomenon has been reported in the scientific literature [14, 22]. These findings revealed a
 246 high portion of pores with indefinite pore size and shape in the 0.05Fe-MCAC particles [28].
 247 The saturated adsorption amount of N₂ was as follows: 0.05Fe-MCAC > CAC. Hence, the
 248 fixing of iron to 0.05Fe-MCAC modified its textural characteristics. From the pore size
 249 analysis (Fig. 6), the two samples were essentially mesoporous because a vast majority of the
 250 pores ranged between 2 and 10 nm. After iron modification, the average pore size of the
 251 0.05Fe-MCAC sample was higher at 3.816 nm than that of the CAC (Fig. 6b). Thus, a large
 252 0.05Fe-MCAC size would be conducive to PAHs adsorption.



253
 254 **Fig. 6.** Pore size distributions of CAC (a); and 0.05Fe-MCAC (b)

255 The pore characteristics of the CAC and 0.05Fe-MCAC samples based on the N₂
 256 adsorption–desorption isotherms are shown in Table 1. The BET surface area, mesopore
 257 surface area, external specific surface area, total pore volume, and mesoporous pore volume
 258 increased after modification with iron nitrate solution, which could enhance the adsorption
 259 efficiency for PAHs adsorption. Moreno-Piraján et al. [17] found that the AC from bamboo
 260 waste modified with iron increased the BET surface area from 985.00 to 1357.00 m²/g

261 enhanced the adsorption for arsenite and arsenate. Ponvel et al. [28] showed that the metal
 262 ion modification of AC developed pore properties, and the removal of 2, 4-dichlorophenol
 263 from aqueous solutions became more effective. Therefore, the loading of iron via microwave
 264 radiation could enlarge pores and consequently form mesopores [29]. We
 265 accordingly speculated that the formed mesopores and developed pore properties could
 266 benefit PAHs adsorption.

267 **Table 1**

268 BET analysis for CAC and 0.05Fe-MCAC

Physical parameters	CAC	0.05Fe-MCAC
BET specific surface area (m ² /g)	686.06	1079.67
Lamgmuir surface area (m ² /g)	1042.56	1689.73
Mesopore surface area (m ² /g)	290.63	491.38
Total pore volume (cm ³ /g)	0.39	0.64
Mesoporous pore volume (cm ³ /g)	0.22	0.48

269 *3.2.4 Surface acidity and basicity of CAC and 0.05Fe-MCAC*

270 The total acidity and basicity of the CAC and 0.05Fe-MCAC samples are summarized
 271 in Table 2. The Fe-MCAC sample was more basic than those on its surface.
 272 One likely reason was that Fe³⁺ was loaded onto the surface of 0.05Fe-MCAC, and oxygen
 273 was removed; thus, the basicity properties were enhanced. The study by Rivera-Utrilla et al.
 274 [27] showed that the increase in the basicity of AC surface favored the adsorption of organic
 275 compounds. Strong basic properties of the 0.05Fe-MCAC sample were generally conducive
 276 to PAHs adsorption from aqueous solutions. The amount of iron loading on the
 277 0.05Fe-MCAC sample was 0.135 mmol/g (Table 2), which could be attributed to the changes
 278 in the surface chemistry properties and increased the pore structure of the 0.05Fe-MCAC

279 sample [17]. Consequently, the loading of Fe^{3+} ions on the CAC surface increased the
280 adsorption capacity for PAHs.

281 **Table 2**

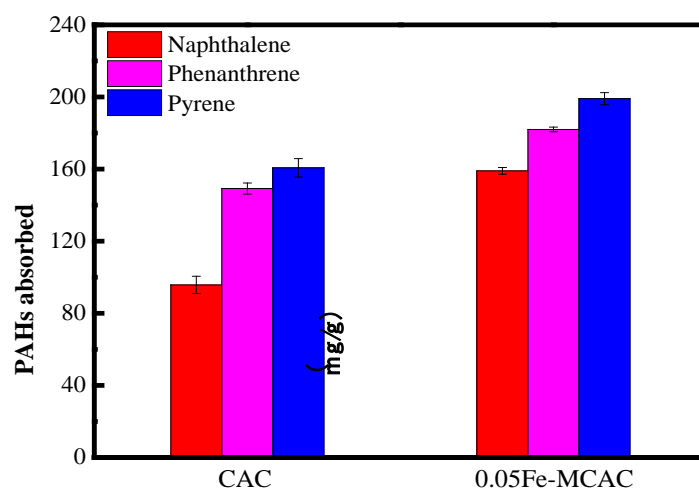
282 Total acidic and total basicity of CAC and 0.05Fe-MCAC

Sample	Total acidity (mmol/g)	Total basicity (mmol/g)	Fe loading (mmol/g)
CAC	1.19	0.14	—
0.05Fe-MCAC	0.54	3.59	0.135

283 *3.3. Adsorption of PAHs on CAC and 0.05Fe-MCAC*

284 **Fig. 7** shows that the CAC and 0.05Fe-MCAC samples for the adsorption of
285 naphthalene, phenanthrene, and pyrene solutions at 20 °C had a similar result. After
286 modification was performed, the 0.05Fe-MCAC sample yielded a higher adsorption capacity
287 for naphthalene, phenanthrene, and pyrene solutions than the CAC sample. The enhanced
288 adsorption capacity on the 0.05Fe-MCAC sample for naphthalene adsorption was the most
289 evident; in this finding, the adsorption capacity increased by 66.07% (**Fig. 7**). In the same
290 adsorption condition, the total adsorption capacity for PAHs on CAC and 0.05Fe-MCAC
291 samples followed this order: pyrene > phenanthrene > naphthalene. Using
292 petroleum-coke-derived porous carbon adsorption of PAHs from aqueous solutions, Yuan et
293 al. [3] found that the adsorption capacity followed the same order in terms of adsorption
294 capacity. A similar behavior was reported for the CAC adsorption for naphthalene,
295 phenanthrene, and pyrene by Xiao et al [29]. Therefore, increasing the number of aromatic
296 rings (or π -electrons) in the PAH compound could increase the adsorption capacity for PAHs
297 from aqueous solutions. This phenomenon could be attributed to the fact that molecules with
298 more aromatic rings show significantly higher adsorptive affinity than the aromatics with

299 less rings [30]. Moreover, PAHs and benzene molecules can form π - π complex between the
300 π -electrons of benzene rings and active sites on an AC surface [25, 29, 30]. In addition, the
301 affinity of 0.05Fe-MCAC to PAHs solution was greater than that of the other samples
302 because of iron modification. However, given that the high-activity iron-modified CAC via
303 microwave radiation provided the 0.05Fe-MCAC sample with a developed pore structure
304 and an enlarged pore size, we concluded that small-molecule PAHs could be easily adsorbed.
305 Thus, the 0.05Fe-MCAC sample had higher adsorption capacity of PAHs from aqueous
306 solutions. Compared with the CAC, the 0.05Fe-MCAC sample is a promising adsorbent for
307 PAHs from aqueous solution.



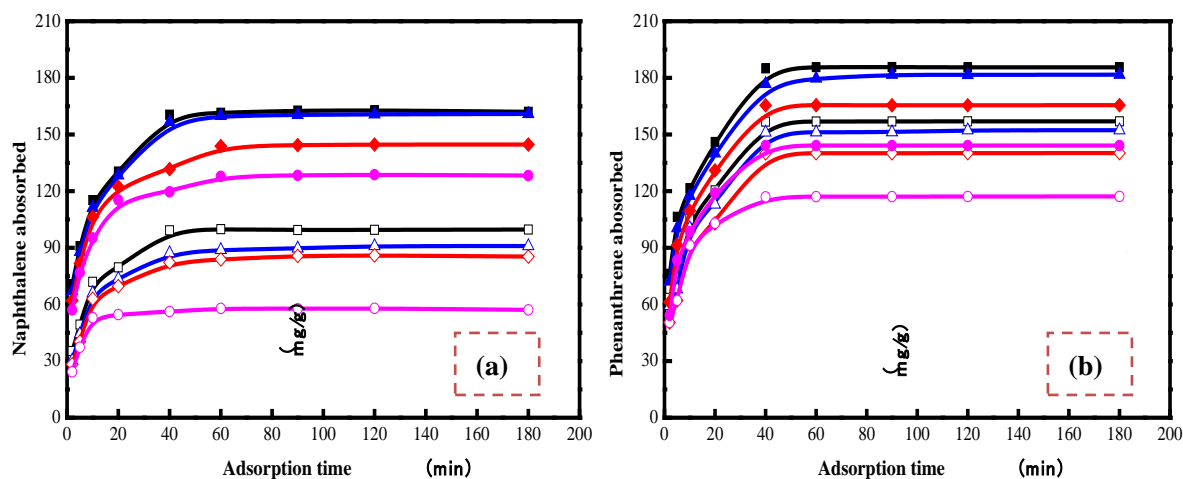
308 **Fig. 7.** Adsorption of PAHs on CAC and 0.05Fe-MCAC at 20 °C

310 3.4. Adsorption kinetics

311 The adsorption mechanism (adsorbed physically, e.g., by a dispersive force) associated
312 with the removal of PAHs on the surfaces of the CAC and 0.05Fe-MCAC samples was
313 explained [31]. The adsorption kinetics results showed that the increase in temperature
314 reduced the adsorption capacity of naphthalene, phenanthrene, and pyrene adsorbed onto
315 CAC and 0.05Fe-MCAC (Figs. 8a-c). This result indicated that low temperature favored the

316 adsorption of naphthalene, phenanthrene, and pyrene from aqueous solutions.

317 **Fig. 8** shows that the adsorption of all PAHs appeared to have similar kinetic behavior
318 from 10 °C to 40 °C. Adsorption involves two distinguished periods, namely, an initial
319 period of rapid adsorption and a period of slow adsorption [14, 32]. The initial adsorption
320 stage was short in the first 10 min; a gradual process occurred until equilibrium was attained
321 after a 40 min contact time; this finding indicated that the maximum sorption of naphthalene,
322 phenanthrene, and pyrene occurred for approximately 40 min (**Fig. 8**). The 0.05Fe-MCAC
323 sample adsorbed naphthalene, phenanthrene, and pyrene solutions to a greater extent than the
324 CAC sample. The adsorption process of PAHs on the 0.05Fe-MCAC sample was faster than
325 that on other materials [12, 33]. A 2 mg modified periodic mesoporous organosilica (PMO)
326 reached adsorption equilibrium for the adsorption of PAHs aqueous solutions (8 mg/L, 5 mL)
327 for 24 h [12]. Using 0.5 g of an immature coal (leonardite) removed 100 µg/L of PAHs from
328 aqueous solutions, and equilibrium time was reached at 24 h [33]. Moreover, the economical
329 dosage of absorbents is a symbol to evaluate the adsorption efficiency. The dosage of the
330 0.05Fe-MCAC sample was 15 mg in our study, which showed higher adsorption capacity
331 and faster adsorption than those in previous studies [12, 33].



332

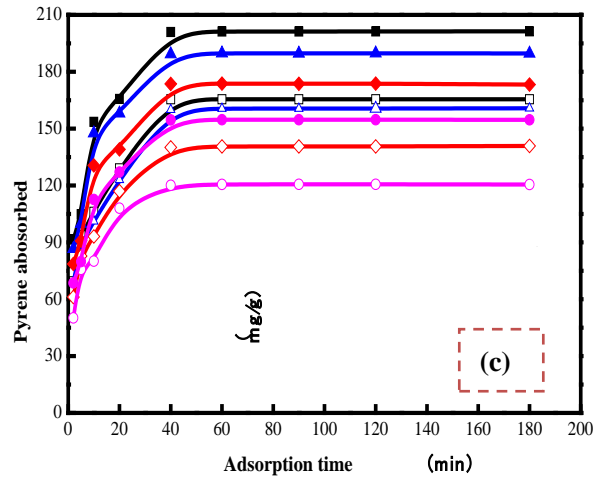


Fig. 8. Naphthalene (a), phenanthrene (b), and pyrene (c) on the CAC and 0.05Fe-MCAC kinetic curves at different temperature

(Conditions: Vacant points: CAC, Filled points: 0.05Fe-MCAC; ■/□ 10 °C, ▲/△ 20 °C, ◆/◇ 30 °C, ●/○ 40 °C)

In order to evaluate the adsorption kinetics of naphthalene, phenanthrene, and pyrene on the CAC and 0.05Fe-MCAC samples, the pseudo first order and the pseudo second order kinetic models were applied to the experimental data.

3.4.1. Pseudo-first-order kinetics

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

$$\frac{1}{q_t} = \frac{1}{q_e} + \frac{k_1}{q_e t} \quad (2)$$

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.

Table 3 shows the quantity of naphthalene, phenanthrene, and pyrene adsorbed at equilibrium for each of the CAC and 0.05Fe-MCAC samples synthesized using the pseudo-first-order model, constant kinetics, and a factor of correlation R^2 between 0.8870–0.9860. These values suggest the dispersion of the experimental data and show

351 that the adsorption of naphthalene, phenanthrene, and pyrene on the CAC and
352 0.05Fe-MCAC samples are not a first-order reaction.

353 3.4.2. Pseudo-second-order kinetics

354 The pseudo-second-order kinetic rate equation is expressed as:

$$355 \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

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

359 The amounts of naphthalene, phenanthrene, and pyrene adsorbed in equilibrium at
360 different temperatures, the velocity constant of the model, and the correlation factors were
361 obtained from the linearization of the model (Table 3). The pseudo-second-order model from
362 10 °C to 40 °C all had good fit for the CAC and 0.05Fe-MCAC samples with high
363 correlation coefficients ($R^2 = 0.9992$ – 0.9997). The q_{exp} values in the pseudo-second-order
364 model were closer to the experimental q_{cal} values than the values in the pseudo-first-order
365 model. This indicated the applicability of the second-order kinetic model to describe the
366 adsorption processes of naphthalene, phenanthrene, and pyrene on the CAC and
367 0.05Fe-MCAC samples. This result also suggested that the adsorption process involved
368 chemical adsorption [14, 20]. We found that the 0.05Fe-MCAC sample had the best
369 adsorption efficiency for naphthalene adsorption. From the literature, the adsorption of
370 naphthalene on naturally and chemically modified bentonites [1] and the adsorption of PAHs
371 on the CAC and modified CAC [14, 24] were best represented by the pseudo-second-order
372 model.

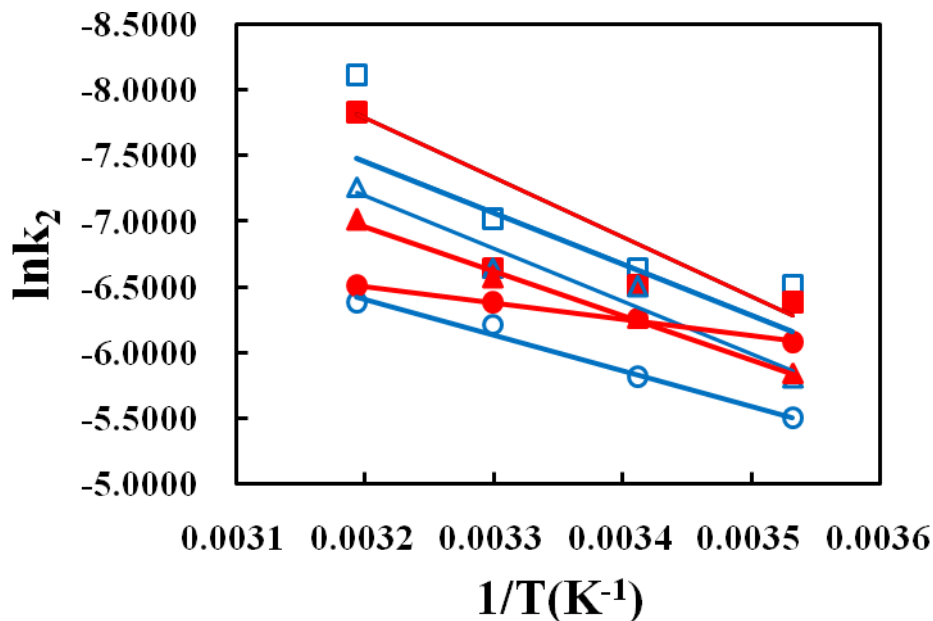
373 3.4.3 The activation energy of PAHs adsorption

374 In engineering practice, the activation energy, E_a (kJ/mol), is obtained from an
375 Arrhenius equation (4):

$$376 \ln k_2 = \ln A - \frac{E_a}{R} \left(\frac{1}{T} \right) \quad (4)$$

377 Where k_2 is the rate constant of second-order adsorption, A is the frequency factor or the
378 Arrhenius constant, R is the universal gas constant (8.314 J/K mol) and T is the absolute
379 temperature (K).

380 When $\ln k_2$ is plotted against the reciprocal of the temperature ($1/T$) as in Fig. 9, E_a
381 represents the slope shown in Table 3. We found that the modified sample had low activation
382 energy for PAH adsorption, which may have improved the adsorption of PAH. Iron had a
383 certain catalytic effect and enhanced the reaction rate. These low activation energy values of
384 E_a (≤ 40 kJ/mol) for adsorption of PAHs on the carbon adsorbents were mainly mechanisms
385 of physical adsorption [34].



386

387 **Fig. 9.** Plots of $\ln k_2/T^{-1}$ for adsorption of naphthalene, phenanthrene and pyrene on CAC and

388 0.05Fe-MCAC at different temperatures (Vacant points: CAC, Filled points: 0.05Fe-MCAC,

389 ○ / ● naphthalene, ▲ / △ phenanthrene, □ / ■ pyrene)

390 **Table 3** Kinetic models parameters for the adsorption of naphthalene, phenanthrene and

391 pyrene on CAC and 0.05Fe-MCAC

Adsorbates	Samples	T (°C)	q_{exp} (mg/g)	Pseudo-first-order			Pseudo-second-order			E_a (kJ/mol)
				q_e (mg/g)	k_1 (min ⁻¹)	R^2	q_e (mg/g)	k_2 (g/(mg·mi n))	R^2	
Naphthalene	CAC	10	105.00	99.65	3.70	0.9660	109.11	0.0041	0.9997	22.36
		20	95.74	83.45	4.60	0.9790	95.98	0.0030	0.9992	
		30	85.94	79.91	4.45	0.9710	90.91	0.0020	0.9998	
		40	57.94	52.50	3.00	0.9840	58.82	0.0017	0.9994	
	0.05Fe-MCAC	10	167.98	152.67	3.01	0.9490	169.04	0.0023	0.9993	10.23
		20	159.00	146.67	3.00	0.9490	162.67	0.0019	0.9995	
		30	144.68	132.86	2.71	0.9660	147.67	0.0017	0.9991	
		40	128.74	121.62	2.86	0.9750	132.86	0.0015	0.9995	
Phenanthrene	CAC	10	160.96	142.86	2.71	0.8870	156.98	0.0030	0.9996	33.18
		20	149.20	130.86	3.40	0.9530	150.67	0.0015	0.9993	
		30	140.85	120.67	3.50	0.9770	144.32	0.0013	0.9995	
		40	117.20	110.43	3.00	0.9350	123.00	0.0007	0.9994	
	0.05Fe-MCAC	10	190.43	157.78	3.14	0.8730	185.58	0.0029	0.9998	28.11
		20	181.99	173.47	3.71	0.9010	185.46	0.0019	0.9998	
		30	165.52	142.86	2.71	0.9450	166.67	0.0014	0.9992	
		40	144.18	126.67	3.83	0.9860	146.73	0.0009	0.9993	
Pyrene	CAC	10	172.46	165.67	2.50	0.8970	169.50	0.0015	0.9993	38.75
		20	160.72	154.65	2.83	0.9020	163.32	0.0013	0.9994	
		30	140.85	132.86	2.71	0.9450	146.67	0.0009	0.9993	
		40	120.60	115.94	3.00	0.9860	124.00	0.0003	0.9992	
	0.05Fe-MCAC	10	201.32	193.45	2.60	0.8900	206.13	0.0017	0.9995	33.56
		20	199.07	189.98	2.61	0.8990	200.32	0.0015	0.9996	
		30	173.25	163.94	3.00	0.8930	176.53	0.0013	0.9994	
		40	154.70	142.47	2.43	0.8980	156.32	0.0004	0.9993	

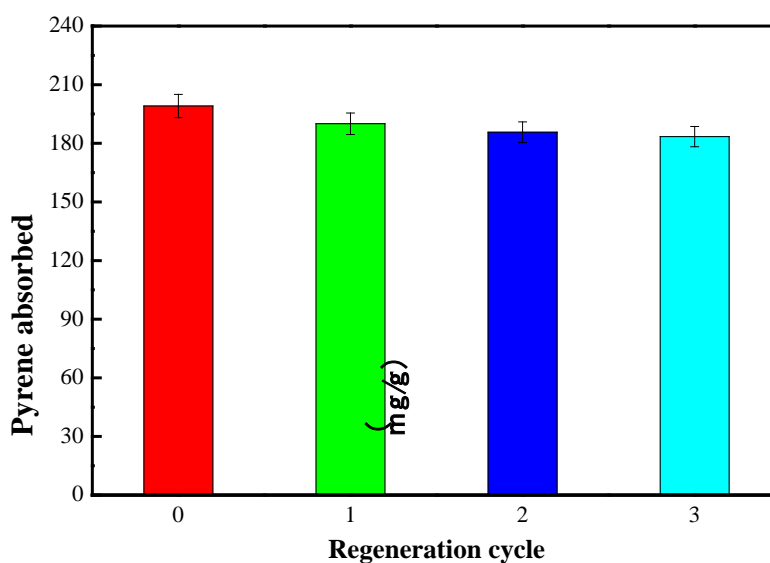
392 3.5 Regeneration of 0.05Fe-MCAC

393 The results of regeneration studies are presented in Fig. 10. The 0.05Fe-MCAC sample

394 still had a high adsorption capacity for pyrene, which reached a level of 92.14% (183.43

395 mg/g) of the initial value after three cycles. This indicated that the modified sample had good

396 stability, reusability, and adsorption effect for pyrene from aqueous solutions because the
397 iron ion could exist in the surface structure of modified CAC in a stable form. The study
398 reported by Shi et al. showed that naphthalene adsorption onto stable high-surface-area
399 carbon still had high capacity after three cycles of alcohol treatment for the regeneration of
400 the spent carbon [35].



401
402 **Fig.10.** Adsorption capacities of pyrene onto 0.05Fe-MCAC for three cycles

403 **4. Conclusions**

404 CAC was modified with iron via microwave radiation. The obtained **0.05Fe-MCAC**
405 sample was characterized through SEM, FTIR, surface acidity and basicity, and nitrogen
406 adsorption–desorption **methods**. The surface chemistry and textural properties of CAC
407 changed when it was modified by iron nitrate via microwave radiation. The developed pore
408 structure, increased surface area, improved basic properties, and reduced oxygen-containing
409 groups **avored** PAHs adsorption from aqueous solutions. The modified sample
410 (**0.05Fe-MCAC**) **yielded** a high adsorption capacity of 160.88 mg/g for naphthalene, 181.99
411 mg/g for phenanthrene, and 199.07 mg/g for pyrene. **Among our observations**, the increase

412 in the adsorption capacity of naphthalene on the 0.05Fe-MCAC sample was the most **evident**.
413 **The modified sample was greater extent and more rapid for adsorbing naphthalene with less**
414 **aromatic rings than the CAC**. Kinetic studies exhibited a faster adsorption rate of PAHs on
415 the 0.05Fe-MCAC sample **than the CAC**. The pseudo-second-order model fitted well for
416 CAC and 0.05Fe-MCAC samples. **Low temperature is favorable for the adsorption of**
417 **naphthalene, phenanthrene, and pyrene from aqueous solutions**. The modified
418 **0.05Fe-MCAC exhibited lower activation energy for the adsorption of naphthalene,**
419 **phenanthrene, and pyrene solutions than that of CAC**. The CAC modified with iron nitrate
420 via microwave radiation was an efficient adsorbent of PAHs from aqueous solutions. **The**
421 **modified sample also showed good stability and reusability for the adsorption of PAHs in**
422 **solutions**. Thus, the CAC sample modified **via a simple treatment is a very effective sorbent**.

423

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428

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