

AperTO - Archivio Istituzionale Open Access dell'Università di Torino

**Enhanced PAHs adsorption using iron-modified coal-based activated carbon via microwave radiation**

**This is the author's manuscript**

*Original Citation:*

*Availability:*

This version is available <http://hdl.handle.net/2318/1637317> since 2017-07-13T17:54:08Z

*Published version:*

DOI:10.1016/j.jtice.2016.03.050

*Terms of use:*

Open Access

Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use of all other works requires consent of the right holder (author or publisher) if not exempted from copyright protection by the applicable law.

(Article begins on next page)

This Accepted Author Manuscript (AAM) is copyrighted and published by Elsevier. It is posted here by agreement between Elsevier and the University of Turin. Changes resulting from the publishing process - such as editing, corrections, structural formatting, and other quality control mechanisms - may not be reflected in this version of the text. The definitive version of the text was subsequently published in JOURNAL OF THE TAIWAN INSTITUTE OF CHEMICAL ENGINEERS, 64, 2016, 10.1016/j.jtice.2016.03.050.

You may download, copy and otherwise use the AAM for non-commercial purposes provided that your license is limited by the following restrictions:

- (1) You may use this AAM for non-commercial purposes only under the terms of the CC-BY-NC-ND license.
- (2) The integrity of the work and identification of the author, copyright owner, and publisher must be preserved in any copy.
- (3) You must attribute this AAM in the following format: Creative Commons BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/deed.en>), 10.1016/j.jtice.2016.03.050

The publisher's version is available at:

<http://linkinghub.elsevier.com/retrieve/pii/S187610701630044X>

When citing, please refer to the published version.

Link to this full text:

<http://hdl.handle.net/2318/1637317>

1           **Enhanced PAHs adsorption using iron-modified coal-based**  
2                           **activated carbon via microwave radiation**

3   **Xinyu Ge<sup>a</sup>, Zhansheng Wu<sup>a,b\*</sup>, Zhilin Wu<sup>b</sup>, Yujun Yan<sup>a</sup>, Giancarlo Cravotto<sup>b</sup>, Bang-Ce**

4                                   **Ye<sup>a</sup>**

5   *<sup>a</sup>School of Chemistry and Chemical Engineering, Shihezi University, Shihezi 832003, P.R.*  
6   *China*

7   *<sup>b</sup>Dipartimento di Scienza e Tecnologia del Farmaco, University of Turin, Torino 10125, Italy*

8   Corresponding author: Zhansheng Wu, Shihezi University, Shihezi 832003, P.R. China.

9   Tel: 86993-2055015, Fax: 86993-2057270, E-mail address: [wuzhans@126.com](mailto:wuzhans@126.com).

10

11

12

13

14

15

16

17

18

19

20

21

22

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 m<sup>2</sup>/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  $\text{cm}^{-1}$  at 4  $\text{cm}^{-1}$  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  $\text{N}_2$  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

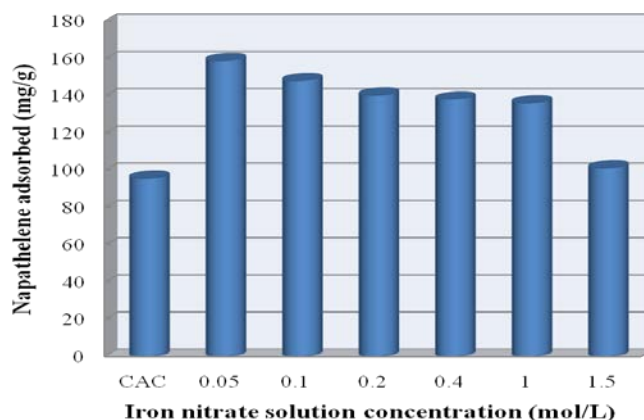
148 The 0.05Fe-MCAC adsorbed pyrene sample was desorbed and immersed in 100 mL  
149 absolute ethanol for 90 min. The carbon sample was removed and dried in vacuum at 110 °C  
150 for 24 h. The regeneration of carbon was determined, and the pyrene adsorption capacity was  
151 calculated repeatedly by 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

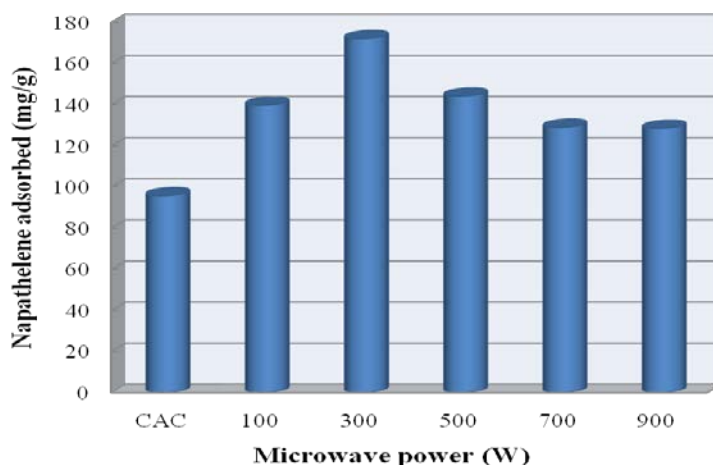
156 We investigated the effects of the concentration of iron nitrate solution on the  
157 preparation of Fe-MCAC for naphthalene adsorption under the same microwave radiation  
158 conditions (Fig. 1). As the concentration of iron nitrate solution increased, the amount of  
159 naphthalene adsorbed 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 Fe<sup>3+</sup> 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.

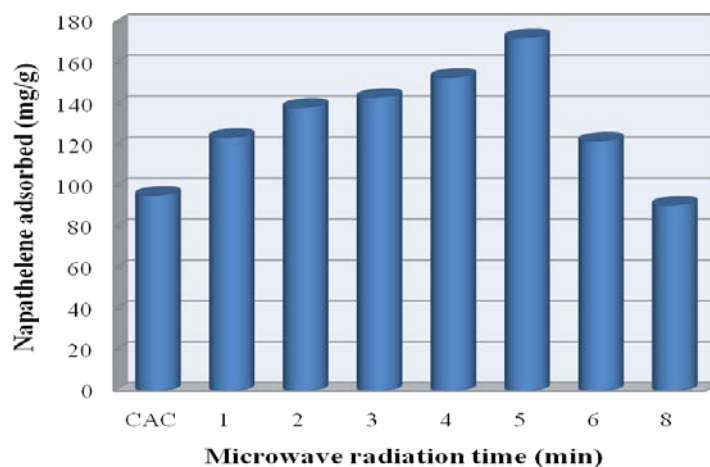


186 **Fig. 2.** Effects of microwave power on Fe-MCAC for naphthalene adsorption capacity (iron  
187 nitrate: 0.05 M, microwave radiation time: 5 min)

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)**

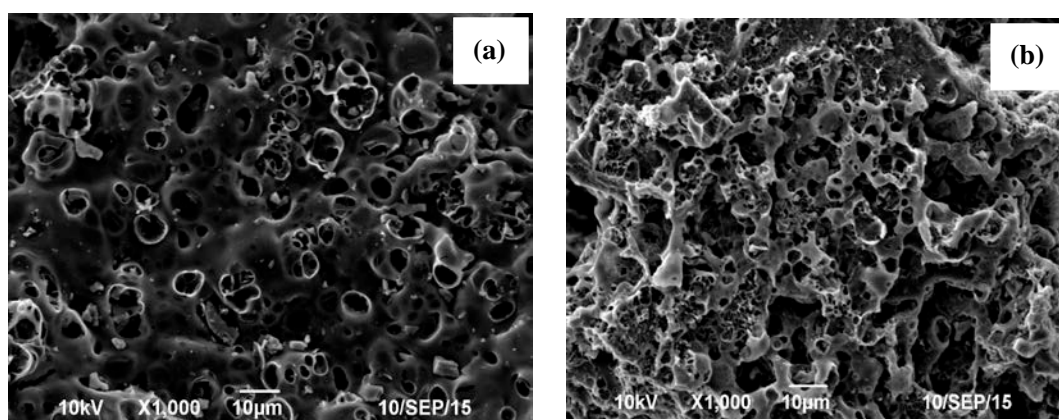
201 From the discussion above, both iron nitrate solution concentration and microwave  
202 power had significant effects on the modified CAC for adsorption of naphthalene. The  
203 optimum conditions obtained were as follows: iron nitrate solution concentration 0.05 M,  
204 microwave power 300 W, 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 Fe<sup>3+</sup> loading are great of significance for  
220 PAHs adsorption.

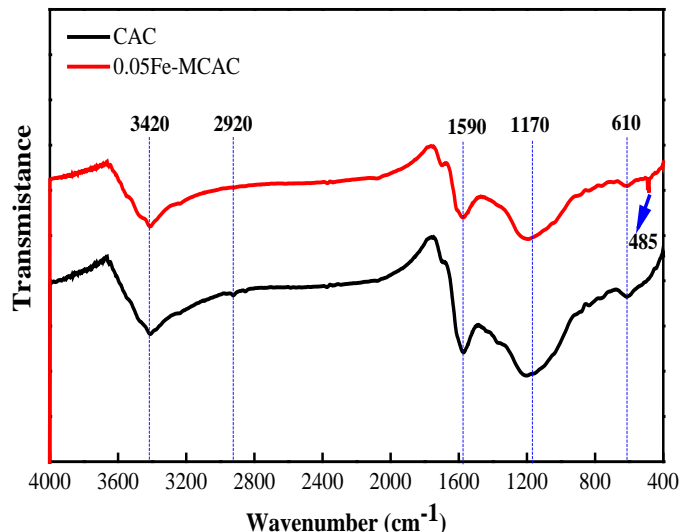


221 **Fig. 4.** Scanning electron microscope (SEM) micrograph: CAC (a); and 0.05Fe-MCAC (b)

### 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<sup>-1</sup> 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  $3420\text{ cm}^{-1}$ , which could be attributed to the  
229  $\text{-OH}$  stretching vibration [17, 20]. The band at approximately  $2920\text{ cm}^{-1}$  resulted from the  
230 symmetric and asymmetric C–H stretching vibrations [25]. The difference in the intensity of  
231 the  $1590\text{ cm}^{-1}$  between the two samples indicated that the modification process caused C=O  
232 groups to decrease [25]. The peaks at approximately  $1170\text{ cm}^{-1}$  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  $485\text{ cm}^{-1}$ , 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

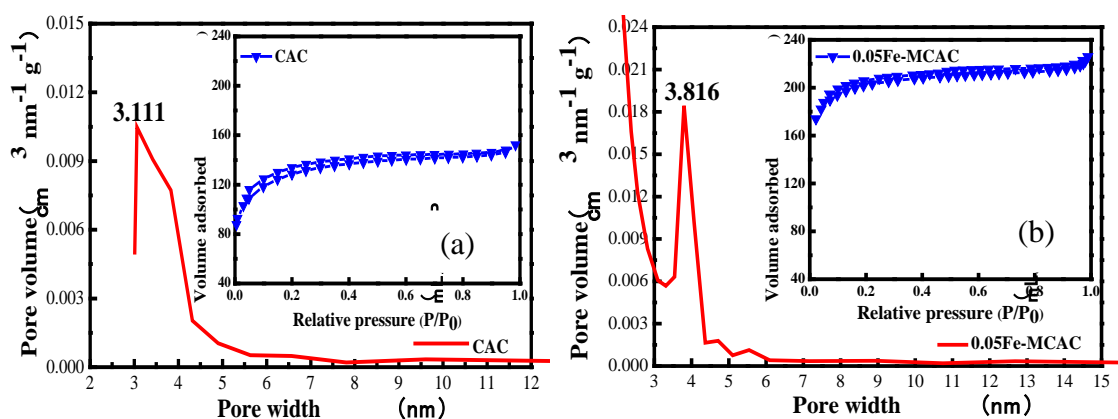
239

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

241 The isotherms of the adsorption–desorption of  $\text{N}_2$  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 N<sub>2</sub> adsorption isotherms of  
 244 the CAC and 0.05Fe-MCAC samples were of type IV with a type-H<sub>4</sub> 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 N<sub>2</sub> 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 N<sub>2</sub>  
 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 m<sup>2</sup>/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 <sup>2</sup> /g)	686.06	1079.67
Lamgmuir surface area (m <sup>2</sup> /g)	1042.56	1689.73
Mesopore surface area (m <sup>2</sup> /g)	290.63	491.38
Total pore volume (cm <sup>3</sup> /g)	0.39	0.64
Mesoporous pore volume (cm <sup>3</sup> /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 Fe<sup>3+</sup> 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  $\text{Fe}^{3+}$  ions on the CAC surface increased the  
280 adsorption capacity for PAHs.

281 **Table 2**

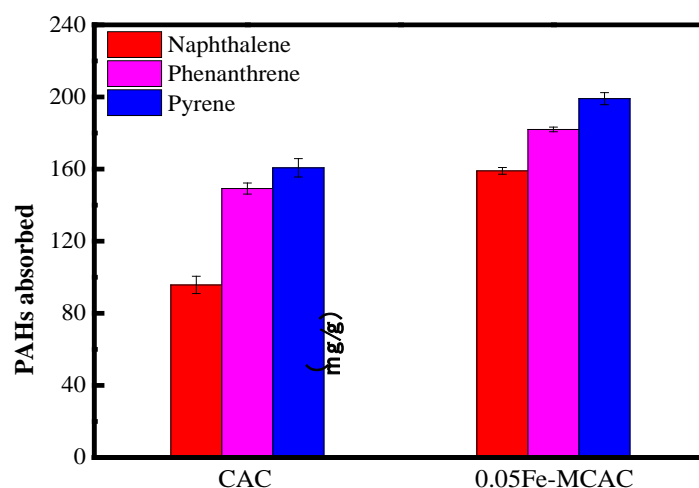
282 Total acidic and total basicity of CAC and 0.05Fe-MCAC

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  $\pi$ -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  $\pi$ - $\pi$  complex between the  
300  $\pi$ -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.



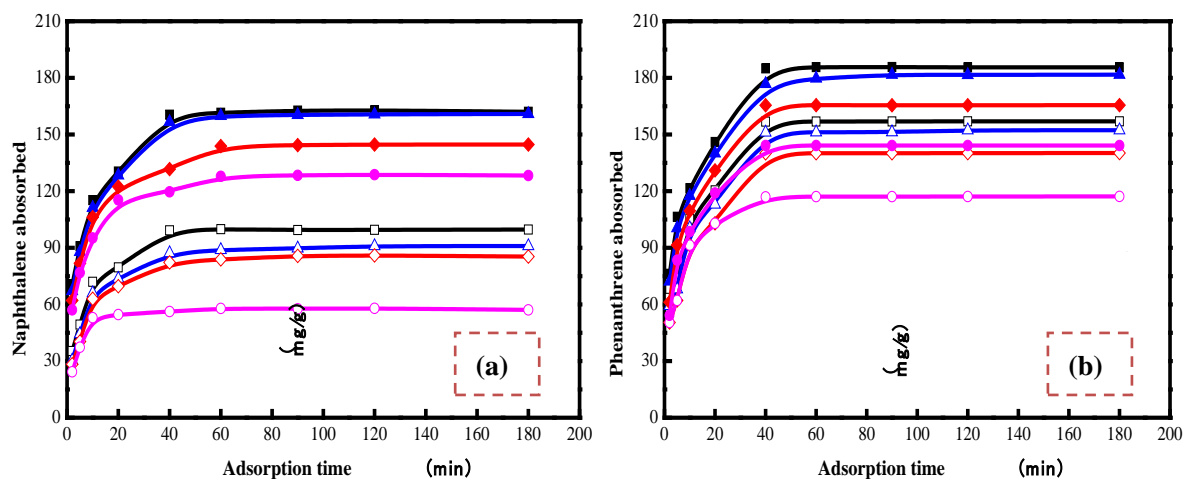
308 **Fig. 7.** Adsorption of PAHs on CAC and 0.05Fe-MCAC at 20 °C

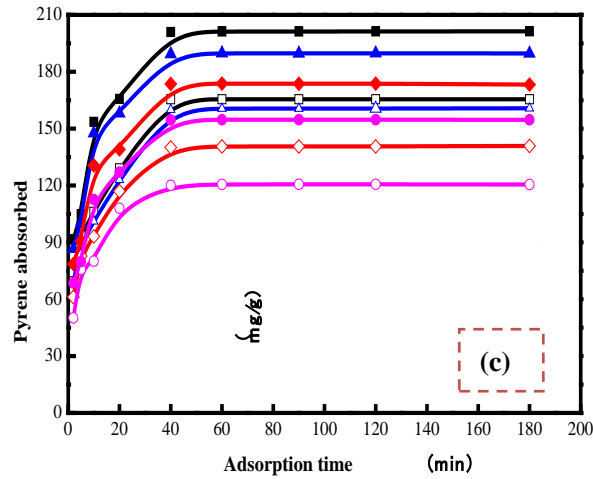
### 310 3.4. Adsorption kinetics

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].





333  
 334 **Fig. 8.** Naphthalene (a), phenanthrene (b), and pyrene (c) on the CAC and 0.05Fe-MCAC  
 335 kinetic curves at different temperature

336 (Conditions: Vacant points: CAC, Filled points: 0.05Fe-MCAC; ■/□ 10 °C, ▲/△ 20 °C,  
 337 ◆/◇ 30 °C, ●/○ 40 °C)

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

### 341 3.4.1. Pseudo-first-order kinetics

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

$$343 \frac{1}{q_t} = \frac{1}{q_e} + \frac{k_1}{q_e t} \quad (2)$$

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

347 Table 3 shows the quantity of naphthalene, phenanthrene, and pyrene adsorbed at  
 348 equilibrium for each of the CAC and 0.05Fe-MCAC samples synthesized using the  
 349 pseudo-first-order model, constant kinetics, and a factor of correlation  $R^2$  between  
 350 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  $q_{\text{exp}}$  values in the pseudo-second-order  
364 model were closer to the experimental  $q_{\text{cal}}$  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.

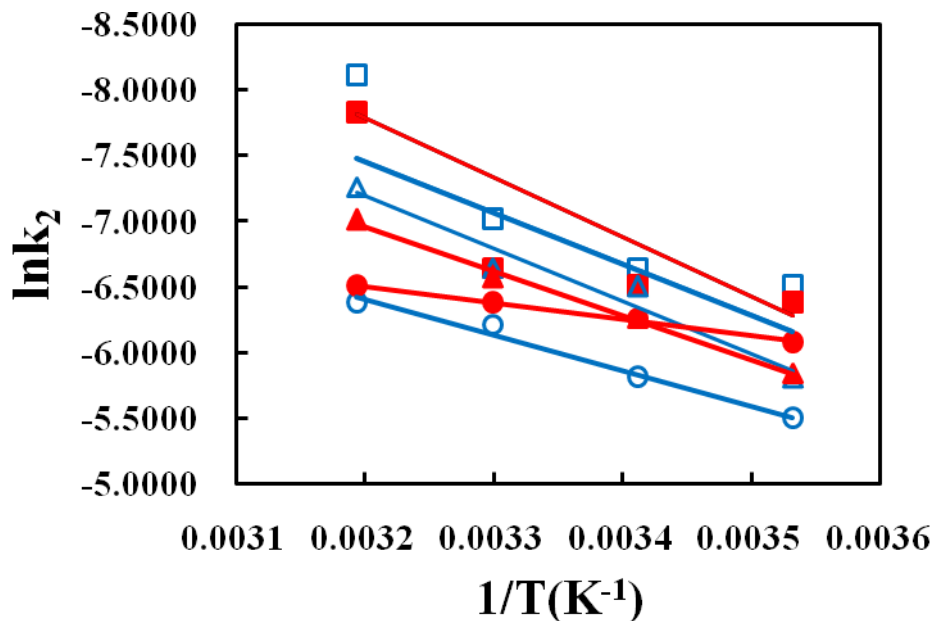
373 3.4.3 The activation energy of PAHs adsorption

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  $E_a$  ( $\leq 40$  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 <sup>-1</sup> )	$R^2$	$q_e$ (mg/g)	$k_2$ (g/(mg·min))	$R^2$	
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	

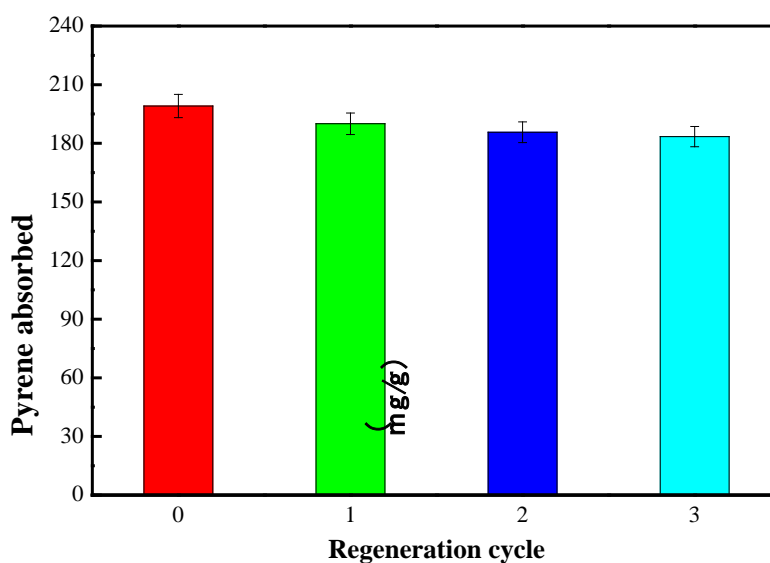
### 392 3.5 Regeneration of 0.05Fe-MCAC

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

## 424 **Acknowledgments**

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

428

## 429 **References**

- 430 [1] [Kaya EMO, Ozcan AS, Gok O, Ozcan A. Adsorption kinetics and isotherm parameters](#)  
431 [of naphthalene onto natural- and chemically modified bentonite from aqueous solutions.](#)  
432 [Adsorption 2013; 19: 879-888.](#)
- 433 [2] [Tran-Duc T, Thamwattana N, Cox BJ, Hill JM. Adsorption of polycyclic aromatic](#)  
434 [hydrocarbons on graphite surfaces. Com Mater Sci 2010; 49: 307-312.](#)
- 435 [3] [Yuan MJ, Tong ST, Zhao SQ, Jia CQ. Adsorption of polycyclic aromatic hydrocarbons](#)

- 436 from water using petroleum coke-derived porous carbon. *J Hazard Mater* 2010; 181:  
437 1115-1120.
- 438 [4] Cai S, Syage JA, Hanold KA, Balogh MP. Ultra performance liquid  
439 chromatography-atmospheric pressure photoionization tandem mass spectrometry for  
440 high-sensitivity and high-throughput analysis of U.S. environmental protection agency  
441 16 priority pollutants polynuclear aromatic hydrocarbons. *Anal Chem* 2009; 81:  
442 2123-2128.
- 443 [5] Valderrama C, Gamisans X, De las Heras X, Farran A, Cortina JL. Sorption kinetics of  
444 polycyclic aromatic hydrocarbons removal using granular activated carbon: Intraparticle  
445 diffusion coefficients. *J Hazard Mater* 2008; 157: 386-396.
- 446 [6] Xiao XM, Tian F, Yan YJ, Wu ZS, Adsorption behavior of pyrene from onto coal-based  
447 activated carbons prepared by microwave activation. *J Shihezi Univ* 2014; 32: 485-490.
- 448 [7] Ge XY, Wu ZS, Yan YJ, Zeng YX, The ammonia modification of coal-based activated  
449 carbon and its pyrene adsorption performance in aqueous solution. *J Shihezi Univ* 2016;  
450 34: 92-99.
- 451 [8] Huang LH, Sun YY, Wang WL, Yue QY, Yang T. Comparative study on characterization  
452 of activated carbons prepared by microwave and conventional heating methods and  
453 application in removal of oxytetracycline (OTC). *Chem Eng J* 2011; 171: 1446-1453.
- 454 [9] Liu QS, Zheng T, Li N, Wang P, Abulikemu G. Modification of bamboo-based activated  
455 carbon using microwave radiation and its effects on the adsorption of methylene blue.  
456 *Appl Surf Sci* 2010; 256: 3309-3315.
- 457 [10] Shaarani FW, Hameed BH. Ammonia-modified activated carbon for the adsorption of 2,  
458 4-dichlorophenol. *Chem Eng J* 2011; 169: 180-185.
- 459 [11] Yin CY, Aroua MK, Daud WMAW. Review of modifications of activated carbon for  
460 enhancing contaminant uptakes from aqueous solutions. *Sep Purify Technol* 2007; 52:  
461 403-415.
- 462 [12] Vidal CB, Barros AL, Moura CP, De Lima ACA, Dias FS, Vasconcellos LCG, Fachine  
463 PBA, Nascimento RF. Adsorption of polycyclic aromatic hydrocarbons from aqueous  
464 solutions by modified periodic mesoporous organosilica. *J Colloid Interf Sci* 2011; 357:  
465 466-473.

- 466 [13]Chen BL, Yuan MX, Liu H. Removal of polycyclic aromatic hydrocarbons from  
467 aqueous solution using plant residue materials as a biosorbent. *J Hazard Mater* 2011;  
468 188: 436-442.
- 469 [14]Ge XY, Tian F, Wu ZL, Yan YJ, Cravotto G, Wu ZS. Adsorption of naphthalene from  
470 aqueous solution on coal-based activated carbon modified by microwave induction:  
471 microwave power effects. *Chem Eng Process* 2015; 91: 67-77.
- 472 [15]Moreno-Piraján JC, Tirano J, Salamanca B, Giraldo L. Activated carbon modified with  
473 copper for adsorption of propanethiol. *Int J Mol Sci* 2010; 11: 927-942.
- 474 [16]Bhatnagar A, Hogland W, Marques M, Sillanpää M. An overview of the modification  
475 methods of activated carbon for its water treatment applications. *Chem Eng J* 2013; 219:  
476 499-511.
- 477 [17]Moreno-Piraján JC, Giraldo L. Activated carbon from bamboo waste modified with iron  
478 and its application in the study of the adsorption of arsenite and arsenate. *Cent Eur J*  
479 *Chem* 2013; 11: 160-170.
- 480 [18]Sun ZM, Yu YC, Pang SY, Du DY. Manganese-modified activated carbon fiber  
481 (Mn-ACF): Novel efficient adsorbent for Arsenic. *App Surf Sci* 2013; 284: 100-106.
- 482 [19]De M, Azargohar R, Dalai AK, Shewchuk SR. Mercury removal by bio-char based  
483 modified activated carbons. *Fuel* 2013; 103: 570-578.
- 484 [20]Chen WF, Parette R, Zou JY, Cannon FS, Dempsey BA, Arsenic removal by  
485 iron-modified activated carbon. *Water Res* 2007; 41: 1851-1858.
- 486 [21]Xiao XM, Tian F, Yan YJ, Wu ZS, Wu ZL, Cravotto G. Adsorption behavior of  
487 phenanthrene onto coal-based activated carbon prepared by microwave activation.  
488 *Korean J Chem Eng* 2015; 32: 1129-1136.
- 489 [22]Song XL, Liu HY, Cheng L, Qu YX. Surface modification of coconut-based activated  
490 carbon by liquid-phase oxidation and its effects on lead ion adsorption. *Desalination*  
491 2010; 255: 78-83.
- 492 [23]Foo KY, Hameed BH, Microwave-assisted preparation and adsorption performance of  
493 activated carbon from biodiesel industry solid residue: Influence of operational  
494 parameters. *Bioresour Technol* 2012; 103: 398-404.
- 495 [24]Foo KY, Hameed BH, Potential of jackfruit peel as precursor for activated carbon

- 496 prepared by microwave induced NaOH activation. *Bioresource Technol* 2012; 112:  
497 143–150.
- 498 [25] Ge XY, Ma XF, Wu ZS, Xiao XM, Yan YJ. Modification of coal-based activated carbon  
499 with nitric acid using microwave radiation for adsorption of phenanthrene and  
500 naphthalene. *Res Chem Intermediat* 2014; 41: 7327-7347.
- 501 [26] Liu QS, Zheng T, Li N, Wang P, Abulikemu G. Modification of bamboo-based activated  
502 carbon using microwave radiation and its effects on the adsorption of methylene blue.  
503 *Appl Surf Sci* 2010; 256: 3309-3315.
- 504 [27] Rivera-Utrilla J, Sánchez-Polo M, Gómez-Serrano V, Álvarez PM, Alvim-Ferraz MCM,  
505 Dias JM. Activated carbon modifications to enhance its water treatment applications. An  
506 overview. *J Hazard Mater* 2011; 187: 1-23.
- 507 [28] Ponvel KM, Kavitha D, Kim KM, Lee CH. Adsorption of 2, 4-dichlorophenol on  
508 metal-nitrate modified activated carbon. *Korean J Chem Eng* 2009; 26: 1379-1382.
- 509 [29] Xiao XM, Liu DD, Yan YJ, Wu ZL, Wu ZS, Cravotto G. Preparation of activated carbon  
510 from Xinjiang region coal by microwave activation and its application in naphthalene,  
511 phenanthrene, and pyrene adsorption. *J Taiwan Inst Chem Eng* 2015; 53: 160-167.
- 512 [30] Dowaidar AM, EI-Shahawi MS, Ashour I. Adsorption of polycyclic aromatic  
513 hydrocarbons onto activated carbon from non-aqueous media: the influence of the  
514 organic solvent polarity. *Sep Sci Technol* 2007; 42: 3609-3622.
- 515 [31] Valderrama C, Cortina JL, Farran A, Gamisans X, Lao CJ. Kinetics of sorption of  
516 polyaromatic hydrocarbons onto granular activated carbon and macronet  
517 hyper-cross-linked polymers (MN200). *Colloid Inter Sci* 2007; 310: 35-46.
- 518 [32] Ania CO, Cabal B, Pevida C, Arenillas A, Parra JB, Rubiera F, Pis JJ. Removal of  
519 naphthalene from aqueous solution on chemically modified activated carbons. *Water*  
520 *Res* 2007; 41: 333-340.
- 521 [33] Zeledon-Toruno ZC, Lao-Luque C, De las Heras FXC, Sole-Sardans M. Removal of  
522 PAHs from water using an immature coal (leonardite). *Chemosphere* 2007; 67: 505-512.
- 523 [34] Chen Y, Jiang WJ, Jiang L, Ji XJ. Adsorption behavior of activated carbon derived from  
524 pyrolusite-modified sewage sludge: equilibrium modeling, kinetic and thermodynamic

- 525 studies, *Water Sci Technol* 2011; 64: 661-669.
- 526 [35] Shi QQ, Li AM, Zhu ZL, Liu B. Adsorption of naphthalene onto a high-surface-area
- 527 carbon from waste ion exchange resin. *J Environ Sci China* 2013; 25: 188-194.