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1 **Adsorption of naphthalene from aqueous solution on coal-based**
2 **activated carbon modified by microwave induction: microwave**
3 **power effects**

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25 **Abstract:** To remove polycyclic aromatic hydrocarbons effectively, coal-based activated
26 carbon (CAC) was produced by various microwave power modification. Original and
27 modified CAC (MCACs) were characterized by N₂ adsorption method, scanning electron
28 microscopy, X-ray photoelectron spectroscopy, Boehm method, and point of zero charge
29 determination. Their adsorption behavior of naphthalene was also investigated. Adsorption
30 equilibrium isotherms, adsorption kinetics, and thermodynamics of naphthalene adsorption
31 on CAC and MCACs were generated. Microwave modification enhanced the basic surface
32 groups of MCACs, extended their Brunauer–Emmett–Teller surface area and pore volume,
33 and varied their distribution of surface oxygen groups. Surface area, pore volume, and
34 functional groups of MCACs were positively related to their naphthalene-adsorption capacity.
35 The adsorption equilibrium of naphthalene on CAC and MCACs needed only 40 min, and
36 this adsorption was fast. Adsorption isotherms revealed that the Freundlich model was
37 applicable to the adsorption process. The adsorption kinetics of naphthalene onto adsorbents
38 was described by pseudo-second-order kinetic model. Naphthalene adsorption was found to a
39 spontaneous and exothermal adsorption process. All these results showed that microwave
40 radiation was an efficient and rapid method of modifying activated carbons. Moreover,
41 MCACs was a promising low-cost and fast adsorbent that can be used to remove naphthalene
42 from aqueous solutions.

43 **Keywords:** Coal-based activated carbon; microwave; modification; adsorption; naphthalene

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50 **1. Introduction**

51 The increasing concern over pollution of water courses arising from different
52 anthropogenic activities has resulted in growing demand of activated carbons. They have
53 proved to be effective for the removal of a wide variety of organic and inorganic pollutants
54 dissolved in aqueous media or from gaseous environments [1]. However, activated carbon is
55 expensive, which limits its large-scale application [2]. Abundant reserves of coal resources
56 exist in Xinjiang, which has unique advantages in raw materials and has attracted an
57 increasing research interest [3, 4].

58 The excellent performances of activated carbons is well known to be closely related to
59 the well developed porous structures, large surface area and a wide spectrum of surface
60 functional groups. It is an established fact that the activated carbon surface can display acidic,
61 basic and/or neutral characteristics depending on the presence of surface functional groups [5].
62 Thus, recently focus has been given on how to modify as well as to characterize the surface
63 functional groups of carbon materials in order to improve or enhance their affinities towards
64 certain contaminants [2, 6, 7].

65 Polycyclic aromatic hydrocarbons (PAHs) belong to a class of chemicals that contain two
66 or more fused benzene rings. Polycyclic aromatic hydrocarbons are priority pollutants due to
67 their carcinogenic, mutagenic, and toxic properties [8, 9]. PAHs are generally produced as
68 by-products during incomplete combustion of fuel, coal, oil, garbage, wood, organic
69 substances, polymers, etc. Because of their chemical persistence and semi-volatile nature,
70 PAHs can travel long distance in air and water, and are difficult to biodegrade. Once inside the
71 human body, PAHs can easily pass through cell membranes and are readily absorbed into the

72 cells as they are rich in carbon and are hydrophobic. Some PAHs are capable of interacting
73 with DNA, stimulating mutagenic and carcinogenic responses [10]. The U.S. Environmental
74 Protection Agency lists 16 polycyclic aromatic hydrocarbons (PAHs) as priority pollutants
75 [11]. Thus, developing a suitable and effective modification method for removing PAHs from
76 water is necessary.

77 In recent years, various techniques have been employed for the removal of PAHs from
78 wastewaters [12-14]. Among them, adsorption processes may be effective for the removal of
79 persistent organic pollutants, in particular, activated carbons have been widely used [9, 10,13].
80 The advantages of the adsorption process are simplicity in operation, inexpensive compared
81 to other separation methods and insensitivity to toxic substances.

82 Surface modification is frequently applied on ordinary sorbent through incorporating
83 special functional groups onto the sorbent matrix by heating to obtain great sorption capacity
84 and high selectivity for a specific organic compound. Compared with conventional thermal,
85 microwave modification has the advantages of rapid temperature rise, effective effect of
86 surface functionalities and saving of energy method [15]. Menendez et al. [16] found that
87 microwave heating has been used to remove oxygen functionalities and produce a
88 highly-basic activated carbon in just a few minutes, basic properties lasting upon air exposure.
89 Moreover, Nabais et al. [17] and Zhang et al. [18] reported on the surface chemistry
90 modification of carbon materials by means of microwave heating was very effective.
91 Moreover, activated carbon is known to be a good microwave absorber, and modification of
92 activated carbons using microwave radiation is very interesting and valuable.

93 For these reasons, this work investigated the feasibility of naphthalene adsorption by

94 microwave radiation modification of coal-based activated carbon (CAC). Surface properties
95 of coal-based activated carbon before and after modification (MCACs) were characterized
96 by means of scanning electron micrograph (SEM), nitrogen adsorption-desorption, Boehm
97 method, point of zero charge (pH_{PZC}) and XPS. The equilibrium and kinetic data of the
98 adsorption process were then analyzed to study the adsorption isotherms, kinetics,
99 thermodynamics and mechanism of naphthalene from aqueous solution on the CAC and
100 MCACs. An optimal treatment condition was obtained on the basis of the relationship
101 between the physical and chemical properties of the surface and the adsorption capacities of
102 naphthalene. This study developed a modification method for effectively removing
103 hazardous PAHs, particularly naphthalene, and provided a good research idea.

104 **2. Materials and Methods**

105 *2.1. Preparation of CAC*

106 The raw material used in this study was anthracite, which was purchased from TBEA,
107 Xinjiang Uygur Autonomous Region, China. The coal was crushed and sieved to 100 meshes.
108 The resultant coal was washed four times with distilled water to remove dust and dried in an
109 air oven at 110 °C for 4 h. CAC was prepared by potassium hydroxide activation in a
110 microwave oven under N_2 atmosphere. The ration of hydroxide potassium/coal (w/w) was 1:1,
111 microwave power was 700 W, and radiation time was 10 min. After microwave activation, the
112 samples were cooled to room temperature, and washed with 10% hydrochloric acid and then
113 with distilled water repeatedly with distilled water until pH 7 was reached in the residual
114 liquid, dried at 110 °C for 12 h and stored in a desiccator for further use and marked as CAC.
115 All chemicals and reagents used were of analytical grade.

116 *2.2. Microwave modification of CAC*

117 Microwave radiation with frequency 2.45 GHz was conducted in microwave reactor
118 (MCR-3) of multi-mode with continuous controllable power. The microwave radiation time
119 was set as 8 min, and different power intervals (300, 500 and 700 W) were chosen to study
120 the modification effects. The modified activated carbons were denoted as MCAC-300W,
121 MCAC-500W and MCAC-700W based on the modification power.

122 *2.3. Characterization of CAC and MCACs*

123 *2.3.1. Textural characterization*

124 Surface properties of original and modified CAC were observed through a scanning
125 electron microscope (SEM, JEOL, JSM-6490LV, Japan) at accelerating voltages of 15 KV.
126 Prior to analysis, samples were dried at 383 K and stored in a desiccator overnight. The SEM
127 enables the direct observation of the changes in the surface microstructures of the carbons
128 due to the modifications.

129 Elemental analysis of carbon, hydrogen, nitrogen and sulfur was carried out using a
130 VARIOEL III analyzer. The ash content was determined according to proximate analysis of
131 coal and the standard test method for granular activated carbon. The oxygen content was
132 determined by difference.

133 Surface area and pore size of the samples were measured using a Micromeritics ASAP
134 2020 surface area analyzer by nitrogen adsorption-desorption method. The samples were
135 degassed under N₂ flow at 350 °C for 6 h before adsorption isotherm were generated by N₂ at
136 77 K. The surface area (S_{BET}) was calculated with the BET equation, the total pore volume
137 (V_T) was obtained from the adsorption isotherm at $P/P_0 = 0.95$. The micropore area (S_{mic}) and

138 volume (V_{mic}) were obtained using the t-plot method. The average pore size (r) was estimated
139 by the following equation:

$$140 \quad r = \frac{4V_T}{S_{BET}} \quad (1)$$

141 The X-ray photoelectron spectra of CAC and MCAC samples were obtained with a
142 model PHI5700 ESCA X-ray photoelectron spectrometer. XPS was applied to determine the
143 surface complexes on CAC and MCACs. XPS analysis was conducted using Mg Ka X-ray
144 source (1,253.6 eV) under a vacuum pressure 10^{-6} Pa. The wide scans were conducted from 0
145 to 1000 eV with a pass energy of 50 eV. High-resolution scans of activated carbons were
146 performed over the 524-544 eV range for O 1s with the pass energy of 20 eV.

147 *2.3.2. Chemical characterization*

148 The amphoteric characteristics of the treated activated carbon samples were
149 characterized by measuring the amount of the surface functional groups using the acid-base
150 titration method proposed by Boehm [19]. According to this method, 200 mg of each
151 activated carbon sample was added to a series of 100 mL conical flasks containing 25 mL of
152 0.05 M: sodium hydroxide, sodium carbonate, sodium bicarbonate and hydrochloric acid,
153 respectively. The containers were then sealed and shaken for 24 h at 25 °C, after which the
154 resulting suspensions were filtered and 10 mL of accurately withdrawn aliquot of filtrates
155 were titrated up to pH 4.5 by 0.05 M hydrochloric acid in order to estimate the residual base
156 or up to pH 11.5 by 0.05 M sodium hydroxide for the residual acid. The titration value was
157 measured three times for each sample and then the amount of acidic/basic functional groups
158 was calculated using the average of the three titration data.

159 The pH at the point of zero charge (pH_{PZC}) of the activated carbon, namely the pH value

160 required to give zero net surface charge. To obtain the pH_{PZC} , the mixture contained 50.00 mL
161 of 0.01 M NaCl and 300 mg MCAC was agitated for 48 h at 30 ± 1 °C, and the pH of solution
162 was adjusted between 2 and 12 in the process. The pH which adjusted by addition of 0.10 M
163 HCl or NaOH was detected by a pH meter. The pH_{PZC} is the point where $pH_{initial} - pH_{final}$
164 versus $pH_{initial}$ was 0.

165 2.4. Adsorption studies

166 As far as we know, PAHs have low solubility in water. The utilization of ethanol as
167 co-solvent was efficient for the solubilization of naphthalene in aqueous medium. The
168 solutions used in the isothermal and kinetic experiments and in the construction of analytical
169 curves were prepared immediately before use, by diluting the stock solution and adjusting the
170 concentration of ethanol to 30% v/v.

171 In the adsorption isotherms experiments, naphthalene adsorption was conducted by
172 batch mode in conical flasks at 25 °C. For each sample, 15 mg activated carbon and 100 mL
173 of naphthalene solution corresponding to concentrations in the range of 10–50 mg/L were
174 mixed and shaken for 60 min in a thermostat shaker at 90 rpm. Samples were separated by
175 filtration, and naphthalene concentration was measured using a UV-75N spectrophotometer at
176 219 nm for naphthalene.

177 The amount of naphthalene adsorbed on the CAC and MCAC at equilibrium, q_e (mg/g),
178 can be calculated according to Eq. (2),

$$179 \quad q_e = \frac{(C_0 - C_e) \times V}{m} \quad (2)$$

180 where C_0 and C_e (mg/L) are the initial and equilibrium concentrations of naphthalene
181 respectively, V is the volume of the aqueous solution (mL) and m is the weight of the

182 adsorbent (g).

183 Kinetic studies were performed following a similar procedure. The initial concentration
184 was set as 30 mg/L, and the samples were separated at different contacting time intervals. The
185 mixture was filtered, and the residual concentration was determined. The amount of
186 naphthalene at time t , q_t (mg/g), was calculated by the following equation:

$$187 \quad q_t = \frac{(C_0 - C_t) \times V}{m} \quad (3)$$

188 where C_t (mg/L) is the liquid-phase concentration of naphthalene at any time, t (min).

189 2.5. Regeneration of spent carbon

190 In the experiment, 15 mg of modified CAC (MCAC-500W) was placed into 100 mL of a
191 naphthalene solution with concentration 30 mg/L and agitated at 25 °C in a thermostat shaker
192 at 90 rpm. After equilibration, the spent carbon was removed and immersed in absolute
193 ethanol for 90 min. The carbon was then dried under vacuum at 110 °C for 24 h. Desorption
194 experiment was conducted again, and the cycle was repeated four times. The amount of
195 naphthalene adsorbed at equilibrium, q_e (mg/g), was calculated each time.

196 3. Results and discussion

197 3.1. Characterization method

198 3.1.1. Scanning electron micrograph images

199 The images obtained from SEM analysis basically illustrated the surface morphologies
200 of the CAC and MCACs materials at lower magnifications (1000×). In order to observe the
201 influence of microwave power on the surface morphology, the SEM image is presented in [Fig.](#)
202 [1 \(\(b\)-\(d\)\)](#). As demonstrated in [Fig. 1\(a\)](#), the surface of the unmodified CAC surface exhibits
203 an uneven and rough surface morphology. Chen et.al also observed the phenomenon on

204 activated carbon derived from pyrolusite-modified sewage sludge [20].

205 There is little difference in the surface morphology of the samples except for some
206 pore widening on MCAC which could have occurred from the modification process.
207 Apparently the surface of MCAC has more porous structure. Moreover, Foo and Hameed
208 reported the microwave irradiated sample exhibits an even, homogeneous, highly porous and
209 well pronounced array of honey-combed structures [21]. For MCAC-700W, there was
210 happened some collapse in some pores, which could be explained that carbon was calcined
211 with the power increase leading to the temperature rise [18]. Considerable change in pores
212 and morphology are present in MCACs surface, which may benefit for adsorbing PAHs from
213 aqueous solution.

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

215 *3.1.2. Elemental analysis*

216 The elemental composition and chemical properties of CAC and MCAC samples are
217 listed in Table 1. As suggested by the result, compared with the CAC, the carbon content of
218 MCACs increased while the content oxygen of that decreased, which led to the ratio of C/O
219 increase from 2.59 to 4.85. Meanwhile, the content of nitrogen and sulfur also had a certain
220 decrease. However, different microwave power treatments did not produce any further on
221 important change of ash.

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

223 *3.1.3. Brunauer–Emmett–Teller (BET) analysis*

224 Nitrogen adsorption-desorption isotherms were determined on the samples both before
225 and after modified treatments are shown in Fig. 2. The adsorption isotherms demonstrated a

226 sharp rise at low P/P_0 range, and a gradual increase was seen at relatively high P/P_0 range.
227 These isotherms clearly show the largely microporous nature of the carbons, with some
228 mesopores leading to a gradual increase in adsorption after the initial filling of the micropores,
229 followed by a more rapid increase near saturation [22]. The saturated adsorption amount of
230 N_2 increased after microwave modification, which implied an increase in the pore volume.
231 For microwave treatment samples, the saturated adsorption amount of N_2 was as follows:
232 $CAC < MCAC-300W < MCAC-700W < MCAC-500W$.

233 The textural characteristics of the CAC and MCAC samples are summarized in Table 1.
234 By comparing the pore characteristics of the samples, it is clear that the microwave
235 modification treatments used in this study caused significant effect on the textural properties
236 [23]. Table 2 shows that BET surface area, Langmuir surface area, and total pore volume of
237 modified samples were greatly improved, all of which imply pore development during the
238 modification process. The modified sample MCAC-500 W had a well-developed porosity
239 with a surface area of $1061.95 \text{ m}^2/\text{g}$. Microwave-modified samples were generally conducive
240 to well-developed pore structure of activated carbon. On the other hand, the total pore volume
241 and external specific surface area values increased with the rise of the microwave power,
242 indicating the continuous enlargement of micropores into larger ones [2]. After the
243 modification process, the average pore size increased to more than 2.26 nm for CAC, which
244 only had a certain increase. However, the contraction of carbon skeleton has the same effects
245 on micropores and mesopores and pores of different width are shrinking, so microwave
246 treatment has little effect on the average pore width [18].

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

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

249 *3.1.4 X-ray photoelectron spectra*

250 XPS has been shown to be useful for analyzing the surface chemical characteristics of
251 CAC. The survey XPS spectra of various samples are shown in Fig. 3(a). Two main peaks
252 were identified and labeled as C 1s and O 1s of CAC and MCAC. It can be seen that the C
253 content increased to some extent after microwave modification treatment, while the contents
254 of O decreased notably, implying the elimination of the oxygen groups of MCAC during the
255 modification process.

256 The high-resolution spectra of O 1s was given further analysis using a curve-fitting
257 procedure, based on the Gaussian-Lorentzian function after baseline subtraction using
258 Shirley's method. Fig. 3((b)-(e)) showed that the main peaks were identified and labeled as O
259 1s. Information concerning the components, the peak position and their concentrations were
260 summarized in Table 3. Deconvolution of the O 1s spectra for the CAC and MCAC produced
261 four peaks at 531.2, 532.4, 533.3, and 534.3 eV; these peaks represented O=C, O-C,
262 R-O-C=O, and C-OOH, respectively [24]. In an unmodified CAC, the oxygen functional
263 groups were attributed to a chemical activation process [24]. The ratios of the oxygen
264 functional groups varied with microwave power treatment conditions. For oxygen species, the
265 analysis suggested a decrease in C=O group and an increase in C-O group for the modified
266 carbons, which was consistent with C 1s spectra analysis. The number of R-O*-C=O
267 functional groups on the microwave-treated samples was lower than that on the raw CAC
268 sample, and a decrease in COOH was observed. These results were consistent with the results
269 of acid-base titration analysis. Apart from thermal decomposition of the acidic groups, the

270 content of the surface groups also depended on the formation of new groups after
271 modification [2]. Therefore, the modified samples had less acidic groups. According to
272 Menendez et al. [23], thermal treatment can create highly reactive carbon atoms at the
273 crystallite edges, and the re-exposure of such carbons to air results in oxygen adsorption and
274 the formation of new oxygen groups.

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

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

277 *3.1.5 Surface acidity and basicity, surface functional groups and pH_{pzc} value*

278 The amounts of acidic functional groups and basicity are determined by Boehm method
279 and the result is shown in Fig. 4. Taking into account that NaOH titrates carboxyl, lactone and
280 phenolic groups, Na_2CO_3 titrates carboxyl and lactone, and $NaHCO_3$ titrates only carboxyl
281 groups, which can therefore obtain the amount of the different acid groups present on the
282 activated carbons [25]. The modification process influenced the functional groups of
283 activated carbons. The modified carbons exhibited an increase in basicity and a decrease in
284 the amount of surface acidic functional groups. As a consequence, the acidic groups were
285 decomposed and removed in the form of CO or CO_2 under microwave radiation [26]. The
286 greatest surface basicity and lowest acidity were obtained from MCAC-500W samples. Total
287 acid groups in the samples decreased in the following order:
288 $CAC > MCAC-300W > MCAC-700W > MCAC-500W$. It has been proposed that the basic
289 nature of activated carbon derives primarily from the delocalized π -electrons on the
290 condensed polyaromatic sheets, which would be reinforced if oxygen is removed from the
291 activated carbon surface [4].

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

293 The pH_{PZC} is an important property of activated carbons. By definition, pH_{PZC} is the pH
294 at which the net surface charge of an adsorbent is zero. The results of pH_{PZC} titrations for
295 modified samples can be seen in Fig. 5. The pH_{PZC} values were 6.83, 8.59, 9.81, and 9.15 for
296 CAC, MCAC-300W, MCAC-500W, and MCAC-700W, respectively; this result was in
297 accordance with the results of the above acid–base titration results. The modification process
298 changed pH_{PZC} of activated carbon, and MCACs possessed higher pH_{PZC} than CAC, which
299 was an evidence of the presence of basic functional groups. Therefore, acidic functional
300 groups also decreased after modification treatments. Most of the acidic oxygen groups were
301 removed from the carbon surface, which resulted in a significant increase in the carbon pH.
302 Menendez et al. [23] modified an activated carbon by a microwave device in a nitrogen flow
303 observed that only a few minutes was sufficient to reduce the oxygen content and to increase
304 its pH_{PZC} .

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

306 3.2. Adsorption studies

307 3.2.1 Adsorption kinetic models

308 The kinetics of adsorption describes the rate of adsorbate adsorption on activated carbon
309 and it controls the equilibrium time. The kinetic models of pseudo-first-order (Eq. (4)),
310 pseudo-second-order (Eq. (5)), were applied to study the kinetics of the adsorption process,
311 whereas the intraparticle diffusion model (Eq. (6)) was further tested to determine the
312 diffusion mechanism of the adsorption system.

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

314
$$\frac{1}{q_t} = \frac{1}{q_e} + \frac{k_1}{q_e t} \quad (4)$$

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

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

319
$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

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

323 In the intraparticle diffusion model, the relationship between the adsorption capacity at
324 time t , q_t and $t^{0.5}$ could be written as:

325
$$q_t = K_p t^{0.5} + C \quad (6)$$

326 where K_p is the intraparticle diffusion constant (mg/(g·min)) and C is the intercept of the line,
327 which is proportional to the boundary layer thickness.

328 The adsorption kinetics study was carried out to determine the time required for the
329 adsorption equilibrium to be reached. The kinetic curves obtained in our study are shown in
330 [Fig. 6](#). The original and modified samples showed much similar kinetic behavior for
331 naphthalene adsorption. Removal curves were single, smooth, and continuously leading to
332 saturation. The amount of adsorption increased with an increase in contact time. Adsorption
333 equilibrium was observed at 40 min of contact between adsorbent (CAC and MCACs) and
334 naphthalene, beyond which almost no further increase in the amount of adsorption occurred;

335 thus, the adsorption process was fast. Yakout et al. [10] and Yuan et al. [27] both found that
336 found that the equilibrium time needed for naphthalene adsorption on activated carbon was
337 almost 24 h. Cabal et al. [28] found that the equilibrium time needed for naphthalene
338 adsorption on activated carbons obtained from bean pods was 72 h. Hence, the adsorption
339 performance of MCACs in this study was excellent in comparison with the works done by
340 previous researchers. The adsorption kinetic curves of MCACs showed a great improvement
341 in capacity for the removal of naphthalene over an untreated CAC. The naphthalene amounts
342 adsorbed on MCAC had the following order: MCAC-500W > MCAC-700W > MCAC-300W
343 (Table 4). The experimental points of the pseudo-second-order kinetic model of naphthalene
344 indicated an extremely high-correlation coefficient ($R^2 > 0.999$). The theoretical q_e values
345 computed from this model were consistent with the experimental q_{exp} values. The results
346 showed that pseudo-second-order kinetic model fitted for the adsorption of naphthalene well.
347 According to some authors, the pseudo-second-order model may be related to the occurrence
348 of chemical sorption, which may control the reaction rate [29]. The pseudo-second-order
349 model is reported to be usable in the whole adsorption range, and has been applied
350 successfully in many studies [30]. According to the Weber and Morris model, if a linear curve
351 is obtained and it passes through the origin, then the predominant mechanism for adsorption
352 is diffusion [10]. In this work, the behavior of q_t versus $t^{0.5}$ graph had relatively
353 low-correlation coefficients ($0.613 < R^2 < 0.961$) and was initially linear, which indicated that
354 diffusion occurred during the adsorption of naphthalene on CAC and MCACs. However, this
355 process was not the only rate-controlling step.

356 **Fig. 6 should be positioned here.**

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

358 3.2.2. Adsorption isotherm models

359 In order to optimize the adsorption process and to forecast adsorption, Langmuir and
360 Freundlich isotherm models were applied to the equilibrium data. Langmuir model is based
361 on the assumption of a homogeneous adsorbent surface, which can be written as:

$$362 \frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m K_L} \quad (7)$$

363 where q_e (mg/g) is the amount adsorbed per gram of adsorbent, C_e (mg/L) is the adsorbate
364 concentration in the liquid phase, q_m (mg/g) is the maximal adsorption capacity, K_L (L/mg) is a
365 constant related to the free energy of the adsorption.

366 Freundlich model is an empirical equation assuming heterogeneous adsorbent surface,
367 which can be written as:

$$368 \ln q_e = \frac{1}{n} \ln C_e + \ln K_F \quad (8)$$

369 where K_F is the unit capacity factor related to the adsorbent capacity and n is an empirical
370 parameter representing the heterogeneity of site energies, respectively.

371 The adsorption isotherms of naphthalene from solution on the CAC and MCAC are
372 depicted in Fig. 7. The similar initial shapes of the isotherms for naphthalene adsorption on
373 both the CAC and MCAC suggest that the adsorption occurred via the similar pathways.
374 Naphthalene adsorption on the carbon samples belong to the L type according to the Giles
375 classification [31]. Therefore, no strong competition of the solvent takes place for the active
376 sites of adsorption. The parameters of the two isotherm models are calculated and
377 summarized in Table 5. In this work, the Langmuir isotherm best fits the experimental data

378 for lower values of C_e , indicating that initially adsorption occurs as a monolayer phenomenon.
379 However, this mechanism does not persist under higher concentration ranges, and in these
380 cases the adsorption seems to be a multi-layer process. Yakout et al. [10] also observe this
381 result by using low-cost activated carbon derived from agricultural wastes. In addition, the
382 adsorption equilibrium q_e on CAC and MCAC samples increased from 12.85 to 180.87 mg/g
383 with an increase in the initial concentration from 5 to 60 mg/L. This observation could be
384 explained by the fact that the mass transfer driving force would become large and result in
385 high naphthalene adsorption when the initial concentration increased, whereas the active
386 vacant sites available on the activated carbon were sufficient to adsorb most of the
387 naphthalene molecules at low initial concentration. MCAC had higher adsorption capacities
388 of naphthalene than the original CAC, and the naphthalene amounts adsorbed on these
389 carbons had the following order: MCAC-500W > MCAC-700W > MCAC-300W > CAC.
390 Thus, a relationship existed between the sample surface area, pore volume, and basic
391 properties and the adsorption capacity for naphthalene. As shown in Table 1, the modification
392 samples had some increase in surface area and pore volume. In sum, minimal total acidic
393 groups and a high surface area on the surface of carbons lead to high adsorption capacity of
394 CAC for naphthalene.

395 Moreover, the role of the hydrophobic nature of the carbons, along with an enhanced
396 basicity, which contribute to enhanced removal of naphthalene [32]. From Table 4, we can
397 see that the models which best represented the data obtained were the Freundlich model (with
398 higher $R^2 > 0.999$) for naphthalene. And all $1/n$ values between 0.1 and 1 indicated a strong
399 interaction between adsorbent and naphthalene with a favorable adsorption.

400 Naphthalene adsorption from wastewaters has been investigated by using different
401 substances [10, 29, 34]. The intensity of adsorption and the Freundlich adsorption constant K_F
402 calculated for each adsorption system are given in Table 6. Compared with the different
403 substances for naphthalene adsorption, the modified samples in our study had a certain
404 advantage with high adsorption capacity.

405 **Fig.7 should be positioned here.**

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

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

408 3.2.3. Thermodynamic parameters

409 In engineering practice, the activation energy, E_a , is obtained from an Arrhenius
410 equation (8):

$$411 \ln k_2 = \ln A - \frac{E_a}{R} \left(\frac{1}{T} \right) \quad (9)$$

412 where k_2 is the rate constant of second-order adsorption, E_a (kJ/mol) is called the activation
413 energy, representing the minimum energy that reactants must have for the reaction to
414 proceed.

415 Thermodynamic parameters were evaluated to confirm the adsorption nature of CAC and
416 MCAC. The thermodynamic constants, free energy change (ΔG° , kJ/mol), enthalpy change
417 (ΔH° , kJ/mol) and entropy change (ΔS° , J/(K·mol)) were calculated to evaluate the
418 thermodynamic feasibility and the spontaneous nature of the process. The thermodynamics
419 equations were as following:

$$420 \Delta G^\circ = -RT \ln K_F \quad (10)$$

$$421 \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (11)$$

422
$$\ln K_F = \frac{\Delta S^\theta}{R} - \frac{\Delta H^\theta}{RT} \quad (12)$$

423 where K_F is the adsorption equilibrium constant in Eq. (8) for naphthalene.

424 The calculated values of ΔG° , ΔH° , ΔS° and E_a for adsorption of naphthalene on the CAC
425 and MCAC samples are listed in Table 6. The activation energy values during the adsorption
426 processes were calculated. Low activation energies were a characteristic for physisorption,
427 which indicated that the main adsorption process to remove naphthalene was physical
428 adsorption.

429 The thermodynamics parameters of naphthalene adsorption at 10, 25, and 40 °C are
430 listed in Table 7. The negative ΔG° values of CAC and MCACs indicated that the adsorption
431 process was spontaneous. This spontaneity could be explained by the fact that the affinity
432 between naphthalene and MCAC surface weakened with increasing temperature. The removal
433 process for naphthalene was generally favored at a low temperature. The negative value of
434 ΔH° indicated an exothermal adsorption process, which was consistent with the results
435 obtained earlier in this study, in which naphthalene adsorption decreased with increasing
436 temperature. Naphthalene adsorption onto CAC was clearly entropically driven [9]. The
437 positive values of ΔS° showed the high affinity of the activated carbon for naphthalene and the
438 increasing randomness at the solid-solution interface in the adsorbates and adsorbents during
439 the adsorption process [34]. Thus, the adsorption of naphthalene onto CAC and MCAC
440 samples was a complex process.

441 **Table 7 should be positioned here.**

442 3.3 Effect of surface physicochemical characteristics on adsorption capacity

443 The adsorption capacity of the CAC and MCAC samples rely on its surface
444 characteristics, e.g. texture and surface physicochemical properties. Correlation analysis was
445 conducted to study the effect of each factor on naphthalene adsorption. BET surface area

446 presented a good linear relationship with the naphthalene-adsorption capacity for the tested
447 carbons (Fig. 8(a)). A high surface area will generally result in high naphthalene-adsorption
448 capacity. Among all samples, MCAC-500 W had the highest BET surface area (Table 2),
449 which implied that it had the highest capacity of naphthalene. In addition, MCAC-500 W had
450 a larger pore volume than the original CAC. The other microwave-modified samples had
451 similar result, i.e., they had higher naphthalene adsorption than CAC. From Fig. 8(b), we can
452 see that a decrease in surface oxygen containing groups ($R^2=0.913$) and carbonyl groups
453 ($R^2=0.997$) have significant effects on the adsorption capacity of naphthalene. By correlation
454 of the adsorption capacity of naphthalene and total surface oxygen containing groups in Fig.
455 8(b) showed that adsorption capacities of carbons decreased with the increase in total surface
456 oxygen-containing groups. MCACs with minimal surface oxygen groups presented high
457 naphthalene adsorption capacities. Thus, a combination of high surface area and low surface
458 oxygen group is desired for MCACs with high naphthalene adsorption capacity. This result is
459 in agreement with previous research on hydrophobic volatile organic compounds adsorption
460 [35] and adsorption of phenanthrene in gaseous phase [36].

461 The well-developed total pore volume, high surface area, and low oxygen content of
462 MCAC samples made them good adsorbents for naphthalene. To improve activated carbon
463 performance for hydrophobic naphthalene adsorption, pore volume and surface area should
464 be as high as possible, and surface oxygen-containing groups need to be reduced.

465 **Fig. 8 should be positioned here.**

466 3.4. Regeneration

467 The results of regeneration studies are shown in Fig. 9. MCAC-500 W still had a high

468 adsorption capacity, which reached a level of 92.8% of the initial value after four cycles. This
469 result indicated the effectiveness of alcohol treatment for the regeneration of spent carbon.
470 Therefore, alcohol treatment is a good choice for the regeneration of naphthalene-exhausted
471 MCAC-500 W. Shi et al. observed that naphthalene adsorption onto a high-surface-area
472 carbon has high capacity after three cycles by the alcohol treatment for the regeneration of the
473 spent carbon [37].

474 **Fig. 9 should be positioned here.**

475 **4. Conclusion**

476 The surface chemistry and physical properties of CAC samples play important roles on
477 naphthalene adsorption. Changes in the surface chemistry and physical properties of MCACs
478 were studied to obtain thorough understanding of the microwave modification process using
479 various microwave powers.

480 The pore volume and average pore size of MCAC samples, which were mainly BET
481 surface area, increased under microwave treatment. The surface acidic groups were
482 eliminated from MCACs, but the basic nature was enhanced, as shown by Boehm titration
483 and X-ray photoelectron spectra. MCACs by microwave radiation could effectively adsorb
484 naphthalene and had high adsorption capacity for naphthalene from aqueous solution.
485 Therefore, the well-developed total pore volume, high surface area, and low oxygen content
486 of MCAC samples made them good adsorbents for naphthalene adsorption.

487 The adsorption kinetics of naphthalene on CAC and MCAC samples showed similar
488 behavior for all analytes. After 40 min of contact between adsorbent and naphthalene, a
489 tendency of the system to reach equilibrium was observed. The kinetic model of

490 pseudo-second order best represented the adsorption kinetic data of naphthalene. The
491 adsorption isotherm experimental data were best described by Freundlich isotherm models.
492 Activation energies for the adsorption processes were relatively low and a characteristic for
493 physisorption. The thermodynamic parameters obtained in this study indicated the
494 spontaneous and endothermic nature of the naphthalene adsorption on CAC and MCAC
495 samples.

496 Microwave radiation was proved to be an efficient and rapid method to modify activated
497 carbons. MCAC was a promising low cost and fast adsorbent to be used to remove
498 naphthalene from aqueous solutions.

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