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1	Microwave-assisted modification of activated carbon with
2	ammonia for efficient pyrene adsorption
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20	Abstract: With the aim to enhance the adsorption properties of polycyclic aromatic hydrocarbons
21	(PAHs) from aqueous solutions, coal-based activated carbon (CAC) was modified with three
22	different protocols: i) ammonia treatment (A-CAC), ii) microwave radiation (M-CAC) iii) and
23	combined microwave radiation in the presence of ammonia (MA-CAC). The original CAC and all
24	the modified samples were characterized by SEM, nitrogen adsorption-desorption, Boehm method,
25	point of zero charge, FTIR and XPS. The surface area increased from 764.96 to 1293.78 m^2/g for
26	CAC and MA-CAC, whereas the total groups containing oxygen decreased from 1.57 to 0.25
27	mmol/g. The pyrene adsorption capacity of all the modified samples was higher than CAC and the
28	adsorption process for pyrene to the equilibrium needed only 40 min. Adsorption isotherm fitting
29	revealed that pyrene adsorbed from the monolayer process on CAC to multilayer process on the
30	modified samples. The adsorption kinetics of pyrene onto carbons was described using the
31	pseudo-second-order kinetic model. The adsorption capacity of the CAC and modified samples had
32	a good positive correlation with surface area, carboxyl groups, and lactones groups. The modified
33	samples, especially MA-CAC, showed an enhanced adsorption of pyrene opening the way to a more
34	general application as efficient adsorbent for PAHs contaminant.

- 36 Keywords: Coal-based activated carbon; microwaves; ammonia; modification; PAHs

39 **1. Introduction**

40 The toxicity of aromatic hydrocarbons, particularly polycyclic aromatic hydrocarbons (PAHs), 41 is well known because of their mutagenicity and carcinogenicity [1-3]. Because of the high risk for 42 human health even at low concentrations, the content of PAHs has strict regulations on drinking 43 water. The PAHs removal with conventional physicochemical methods, such as flocculation, 44 sedimentation or filtration is a difficult task because of their chemical persistence and semi-volatile 45 nature [2]. For this reason a big effort has been paid to develop more efficient methods for 46 removing PAHs using pyrene as a model from water environment. 47 Several techniques, such as bioremediation [4], photo-catalyst degradation [5], and adsorption 48 [6-8] have been applied successfully for the minimization of PAHs in wastewater of domestic 49 and/or industrial plants and soils. However, adsorption is one of the most economical and effective 50 techniques for removing organic pollutants [3] and the most commonly used porous media for the 51 removal of contaminants from aqueous solution is activated carbon (AC) [9]. AC with high surface 52 area and developed pore structures are widely used in a variety of industries for applications that 53 include the separation/purification of liquids and gases, removal of toxic substances as catalysts and 54 catalyst support [10, 11]. Kong et al., [1] showed that PAHs removal by soybean stalk-based 55 carbon was superior to that of commercial AC by adsorption method. Xiao et al., showed that 56 pyrene adsorption using CAC is a comparatively fast and effective process [7]. The adsorption of 57 PAHs onto AC from various media such as oil, gaseous phase and water has been reported. Yakout

58	et al., found that low-cost AC derived from agricultural wastes is very effective in adsorption of
59	naphthalene, phenanthrene and pyrene from aqueous solution [12]. Ania et al., showed that
60	chemically modified activated carbons with a higher non-polar character (i.e., low oxygen content)
61	have proven to be more efficient for naphthalene adsorption [13]. However, some modification
62	effects of CAC was not significant [7-8, 14-15], and ammonia modified CAC adsorb PAHs solution
63	is report rarely. Shaarani showed that surface modification of the activated carbon using ammonia
64	was shown to be able to increase its adsorption capacity for 2, 4-DCP [16]. So far, CAC
65	modification by ammonia treatments under microwave irradiation and the effect on PAHs
66	adsorption from aqueous solution, still remain an unexplored area. Therefore, considering enhance
67	alkaline of CAC to modification with ammonia via microwave radiation is of great significance.
68	Based on the functional groups types of AC, the surface may have acidic, basic, and/or neutral
69	characteristics [17]. In recent years, a big research effort was focused on new process for AC
70	surface modification and characterization, in order to enhance the affinity to specific pollutants
71	[18–20]. The higher surface basicity of AC can improve the affinity to pollutants [17]. Among
72	procedures to achieve this goal, simple treatments by ammonia under microwave irradiation can be
73	quite effective [18–21]. In addition, AC is known to be an excellent microwave absorber; dielectric
74	heating can change texture and distribution of surface functional groups that affect surface
75	chemistry [22]. Volumetric microwaves dissipation on carbon particles by dipole rotation and ionic
76	conduction is extremely efficient [21]. Microwave radiation has been successfully applied for the

preparation [7], modification [8] and regeneration [14-15] processes of AC even at industrial scale
[23]. Therefore, modified CAC with ammonia combined via microwave radiation owned research
value and significance.

80 In the present study, CAC was modified by combining microwave radiation in the presence of 81 ammonia. Surface properties of CAC sample before and after modification were characterized by 82 means of scanning electron micrograph (SEM), nitrogen adsorption-desorption, Boehm method, 83 oxygen-containing groups and basicity properties, point of zero charge (pH_{PZC}), FTIR and XPS. 84 The kinetic and isotherms data of the adsorption process were then analyzed to study the adsorption 85 of pyrene from aqueous solutions on the carbon samples. The mechanism of pyrene adsorption is 86 discussed in relation to the pores structure and surface chemical properties of carbon materials. The 87 results obtained from the experiments warrant the need for seeking better, faster, and more effective 88 methods for the adsorption of PAHs from aqueous solutions.

89 2. Experimental

90 2.1. CAC sample

91 The raw material coal was purchased from Xinjiang Tebian Electric Apparatus Stock Co., Ltd, 92 China. CAC was prepared using potassium hydroxide activation via microwave irradiation under 93 N₂ atmosphere (MM823LA6-NS, Midea) with appropriate modification technology. The 94 microwave oven with 2.45 GHz frequency was punched holes to insert the quartzose tube and 95 equipped with power and time controller. The potassium hydroxide/coal (w/w) ratio was 1:1 (5 g : 5

- 96 g), microwave radiation 10 min under 700 W power. The resulting product were dried in air-drying
 97 oven at 110 °C for 4 h and marked as CAC. All chemicals and reagents used were analytical grade.
 98 2.2. *Modification of CAC*
- 99 2.2.1. The modification of CAC by ammonia impregnation
- 100 An amount of 5.0 g of dried CAC was immersed in 50 mL of 10 wt% ammonia solution
- 101 (analytical reagent grade) at 35 °C for 12 h. After this time the treated CAC was separated by
- 102 filtration and then dried at 110 °C for 4 h. The ammonia treated CAC was stored in a desiccator.
- 103 The obtained sample was labeled as A-CAC.
- 104 2.2.2. Microwave-assisted modification of CAC
- 105 A 3.0 g dried CAC was placed in a quartz tube inside the microwave reactor. The modification
- 106 treatment was carried under microwave irradiation 8 min and microwave power 500 W with N₂
- 107 flow (150 mL/min). Then the reactants were cooled to room temperature in N₂ atmosphere and then
- 108 dried at 110 °C for 4 h. The modified CAC was labeled as M-CAC.
- 109 2.2.3. Microwave-assisted modification of CAC using ammonia
- 110 A 1.5 g of dried A-CAC was placed in a quartz tube inside the microwave reactor. The
- 111 modification treatment was carried with 8 min microwave irradiation under power 500 W and N₂
- 112 flow (150 mL/min). Then cooled down and the obtained sample was labeled as MA-CAC.
- 113 2.3. Elemental analysis
- Elemental analysis of the CAC and the modified samples was performed using elemental

115 analyzer (VARIOEL III analyzer).

116 2.4. Texture structure characterization

Scanning Electron Microscopy with Energy Dispersive System (LEO 1430VP) was used to observe the surface morphology of the carbon samples. The SEM enables the direct observation of the changes in the surface microstructures of the carbons due to the modifications. The Brunauer-Emmett-Teller (BET) surface area (S_{BET}) and the porosity of the activated carbons were determined by the adsorption of N₂ at 77 K, using a Quantachrome Instruments

122 Quadrasorb SI. The system operates by measuring the quantity of nitrogen adsorbed onto or

- 122 Quadrasorb SI. The system operates by measuring the quantity of nitrogen adsorbed onto or
- 123 desorbed from a solid sample at different P/P_0 pressures. The dried and weighed samples (0.1 g)
- 124 were outgassed at 300 °C for 3 h under vacuum.
- 125 2.5. Boehm titration and pH_{PZC} value determination

The amphoteric characteristics of carbon materials were determined by the amount of the surface functional groups using the Boehm acid-base titration [24]. The specific method of titration referred to references [15, 24]. The titration value was measured three times for each sample and then the amounts of acidic/basic functional groups were calculated using the average of the three titration data.

131 By definition, pH_{PZC} is the pH at which the net surface charge of an adsorbent is zero. The

- 132 pH_{PZC} values were determined referring to reference [15].
- 133 2.6. Fourier transform infrared spectroscopy (FTIR)

134	FTIR spectra of the carbons were taken with a PHI5700 ESCA FTIR system using KBr disks
135	prepared by mixing 0.5% of finely ground carbon sample in KBr. Pellet made of pure KBr was used
136	as a reference sample for background measurements. The spectra were recorded from 4000 to 400
137	cm^{-1} at a resolution of 4 cm^{-1} .
138	2.7. Adsorption of pyrene on the CAC and the modified samples
139	PAHs have low solubility in water, thus ethanol is used as a co-solvent (30% v/v) for the
140	solubilization of pyrene from aqueous solution. A series of pyrene solution used in the isothermal
141	and kinetic experiments were prepared through diluting the stock solution with distill water.
142	2.8.1. Adsorption kinetic studies
143	For the adsorption kinetics experiments, pyrene adsorption was conducted in conical flasks at
144	20 °C. The initial concentration was set as 30 mg/L, and the carbon materials were taken out at
145	different contacting time intervals (2-180 min). The whole mixture was separated by filtration, and
146	pyrene concentration was measured using a UV-75N spectrophotometer at 237 nm. The amount of
147	pyrene at time t, q_t (mg/g), was calculated by the following equation:
148	$q_{t} = \frac{(C_0 - C_t) \times V}{m} \tag{1}$
149	where $q_t (mg/g)$ is amount of pollutant adsorbed per g of sorbent at time t (min). $C_0 (mg/L)$ and
150	$C_t(mg/L)$ are the initial and residual concentration of pyrene solution, respectively. V (mL) is the
151	volume of the aqueous solution, m (g/mol) is the molar mass of the carbons.
152	2.8.2. Adsorption isotherms studies

153 In the adsorption isotherms experiments, a 60 mg of the CAC or modified samples was added 154 to 100 mL and 20-100 mg/L of pyrene solution, and then was contacted for 60 min at 60 rpm in a 155 rotary mechanical shaker to reach equilibrium. The amount of pyrene adsorbed on the CAC and the 156 modified samples at equilibrium, q_e (mg/g), can be calculated according to Eq. (2), $q_{\rm e} = \frac{(C_0 - C_{\rm e}) \times V}{m}$ 157 (2)158 where $q_e (mg/g)$ is the amount of adsorption of pyrene at equilibrium. C_0 and $C_e (mg/L)$ are the 159 initial and equilibrium concentrations of pyrene solution, respectively. 160 2.9 Regeneration of spent carbon 161 In this study, we choose the typical sample of MA-CAC to study the regeneration capacity. 162 The MA-CAC sample adsorbed pyrene was desorbed and immersed in 100 mL ethanol for 90 min. 163 The MA-CAC sample was removed and dried in vacuum at 110 °C. The regeneration of the 164 MA-CAC sample was determined, and the pyrene adsorption capacity was calculated repeatedly. 165 Desorption experiments were conducted again using the same adsorption method. 3. Results and discussion 166 167 3.1. Characterization method

168 3.1.1. Elemental analysis

169 Modification treatments produced major changes in the contents of carbon and oxygen (Table

- 170 1). In particular, the nitrogen content is always increased. In the MA-CAC sample surface, the
- 171 content of nitrogen is 2.54%. The carbon content of the MA-CAC sample increased compared with

172	the CAC, while the content oxygen of the CAC decreased, which led to the ratio of C/O increase
173	from 2.89 to 6.28. The change in major element can be explained with the following reason.
174	Ammonia treatment can introduce nitrogen element into AC structure [19, 20]. In addition, Liu et
175	al., [19] reported that modification of bamboo-based AC using microwave radiation, the acidic
176	groups were decomposed and removed in the form of CO or CO ₂ , which led to the decreased of
177	oxygen element. Thus, through microwave radiation using ammonia for modify the CAC obtained
178	good basic properties. And XPS analysis had the same element analysis results referring to Table S1
179	in the Supplementary Data.
180	Table 1 should be put here.
181	3.1.2. Observation by SEM
182	As shown in Fig. 1(a), the SEM micrograph of the CAC has some pore structures and attached
183	fine particles over its surface, which formed a system of complicated pore networks. The surfaces
184	of A-CAC, M-CAC, and MA-CAC in Figs. 1(b-d) were highly porous, which could enhance
185	specific surface area for improving adsorption of PAHs from aqueous solution. The morphologies
186	usually have important functions in the adsorption procedure [25]. The SEM images of the modified
187	samples show large pores. We can see that the pore texture of the CAC changed after the
188	modification treatment, and the three carbons still keep a rich pore structure. The MA-CAC samples
189	have a well-developed pore structure, and these pores were arranged neatly and uniformly.
190	Fig. 1 should be put here.

192 According to IUPAC classification, the nitrogen adsorption isotherms of the CAC and the 193 modified samples are essentially of type IV with a type-H₄ hysteresis loop (Fig. 2). However, the 194 CAC and the modified samples showed the same type of hysteresis. This characteristic indicates 195 that absorbents present a mesoporous structure. Song et al. found that each isotherm showed a 196 distinct hysteresis loop, which is associated with the capillary condensation in mesopores, and thus 197 carbon is characteristic of mesoporous adsorbents [26]. 198 For the carbon samples, most pores have diameters of small mesopores with approximately 2-4 199 nm. Moreover, the average pore size is increased from 3.111 nm to 3.831 nm for the CAC and

200 MA-CAC, which is mainly because of the transition of micropores into mesopores after a highly 201 corrosive modification process [27]. However, the average pore sizes for the M-CAC and the

202 MA-CAC only increase from 3.830 nm to 3.831 nm, which a little increase from the M-CAC to the

203 MA-CAC. Detailed information regarding the textural properties of the CAC and modified samples

204 is presented in Fig. 3. The modification enhances pore volume and surface area of the adsorbents.

205 The BET surface area of samples is increased from 764.96 to 1293.78 m^2/g , i.e., from CAC to

206 MA-CAC. Compared to those of the untreated CAC sample, the total pore volume of A-CAC,

207 M-CAC and MA-CAC increase approximately 5.70%, 45.00% and 102.04%, respectively (Fig. 3).

208 These results suggested that modified samples are generally conducive to a well-developed pore

209 structure of activated carbons. As mentioned in our previous study, the specific surface area and

210	pore structure of the CAC are important in determining the adsorption of PAHs performance using
211	the modified samples under microwave radiation [15]. The adsorption capacity of PAHs (Pyrene) is
212	also expected to increase because the specific surface area and pore volume of the CAC increased
213	for different modified treatments. Compared with the CAC and the modified samples, the
214	considerable changes of the surface area and average pore size on the M-CAC and MA-CAC
215	samples should be attributed to the distinct mechanism of microwave radiation. As a result, the
216	interior part of M-CAC and MA-CAC are heated more favorably under microwave radiation, which
217	facilitates the modification process [19].
218	Fig. 2 should be put here.
219	Fig. 3 should be put here.
220	3.1.4. Boehm titration, surface acidity, and basicity and pH_{PZC} value
221	To confirm how the different modification treatments alter the chemistry characteristics of the
222	CAC, the content of surface functional groups on the carbon samples as well as their points of zero
223	charge (pH _{PZC}) have been ascertained. The surface acidity, basicity and functional groups of CAC
224	and the modified samples are listed in Fig. 4. The total acidic groups on the modified CAC are
225	obviously less than those on the CAC. Carboxyl, lactone, and phenol groups all decreased after
226	modification treatment. Moreover, the total acidic groups in the modified samples decrease as the
227	following order: MA-CAC < M-CAC < A-CAC < CAC. Simultaneously, the number of basic
228	groups of all modified samples increase significantly than that of the CAC sample, as expected. The

229	basic groups of the MA-CAC are the most and approximately twice the value obtained for the CAC.
230	For the decrease of acidic groups in the microwave treatment sample, which can be explained by
231	decomposed and removed in the form of CO or CO ₂ under microwave radiation [28]. Przepiorski et
232	al., study high temperature ammonia treatment of AC and indicated that nitrogen is introduced into
233	structure of AC according to treatment with ammonia [29], thus the MA-CAC and A-CAC exhibit
234	the higher basicity. These results are consistent with the XPS survey spectra of CAC and the
235	modified samples referring to the Supplementary Data in Fig. S1. The content of oxygen element
236	decreased into the modified samples surface. Therefore, we can conclude that the modification with
237	ammonia via microwave radiation can increase the basicity effectively, as well as remove
238	oxygen-containing groups.
239	The pH_{PZC} increases from 6.83 of the CAC to 12.23 of the MA-CAC (Fig. 4), which is in
239 240	The pH_{PZC} increases from 6.83 of the CAC to 12.23 of the MA-CAC (Fig. 4), which is in accordance with the results of the acid-base titration results. It is due to the decrease in acidity and
239 240 241	The pH_{PZC} increases from 6.83 of the CAC to 12.23 of the MA-CAC (Fig. 4), which is in accordance with the results of the acid-base titration results. It is due to the decrease in acidity and increase in basicity made an increase in pH_{PZC} value after modification. This also implies that the
239240241242	The pH_{PZC} increases from 6.83 of the CAC to 12.23 of the MA-CAC (Fig. 4), which is in accordance with the results of the acid-base titration results. It is due to the decrease in acidity and increase in basicity made an increase in pH_{PZC} value after modification. This also implies that the three modification samples performed better basicity properties. Compared with the three modified
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Fig. 4 should be put here.

249	The spectra are similar in all cases, which suggested that the CAC and the modified samples
250	have similar structures and functional groups (Fig. 5). Firstly, the broad band at approximately 3450
251	cm ⁻¹ , which may be due to the O-H stretching vibration of hydroxyl functional groups including
252	hydrogen bonding. The intense band at approximately 2920 cm ⁻¹ is attributed to the C-H stretching
253	vibration, which decreased greatly for the modified CAC, indicating that the hydrogen element is
254	removed to a large extent after modification by microwave radiation [19]. The result is consistent
255	with the above elements analysis (Table 1). A band centered near 2300 cm ⁻¹ can be seen in the
256	FTIR of all samples, the bands had been proposed to C-O bonds, which may be because of ketene.
257	The band in the MA-CAC sample decreased significantly compared with that of CAC. Some bands
258	in the range of 1600 cm ⁻¹ are left for the activated carbons, which were probably corresponded to
259	the C=O stretching vibration. Another band was found at approximately 800 cm ⁻¹ , which is
260	expected to be associated with the out-of-plane bending mode of O-H. The decrease of phenolic
261	explained the decrease peak for the modified samples. The band centered at 470 cm ⁻¹ is attributed to
262	C-N-C stretching model. The minimal acidic oxygen functional groups such as phenol and carboxyl
263	groups of the modified sample may enhance the adsorption capacity of pyrene from aqueous
264	solutions, as shown in the results of Boehm titration.

Fig. 5 should be put here.

3.2. Adsorption studies

268	The kinetics of adsorption describes the rate of adsorbate adsorption on the CAC and m	odified
269	samples and it controls the equilibrium time. The kinetic models of pseudo-first-order (E	q. (3)),
270	pseudo-second-order (Eq. (4)), were applied to study the kinetics of the adsorption process, w	vhereas
271	the intraparticle diffusion model (Eq. (5)) was further tested to determine the diffusion med	hanism
272	of the adsorption system.	
273	The pseudo-first-order kinetic rate equation is expressed as:	
274	$\frac{1}{q_t} = \frac{1}{q_e} + \frac{k_1}{q_e t}$	(3)
275	where k_1 is the rate constant of pseudo-first-order sorption (min ⁻¹).	
276	The pseudo-second-order kinetic rate equation is expressed as:	
277	$\frac{t}{q_{\rm t}} = \frac{1}{k_2 q_{\rm e}^2} + \frac{t}{q_{\rm e}}$	(4)
278	where k_2 is the rate constant of pseudo-second-order sorption [g/(mg·min)].	
279	In the intraparticle diffusion model, the relationship between the adsorption capacity at	time t,
280	$q_{\rm t}$ and $t^{0.5}$ could be written as:	
281	$q_{t} = K_{p} t^{0.5} + C$	(5)
282	where K_p is the intraparticle diffusion constant $[mg/(g \cdot min)]$ and C is the intercept of the	ne line,
283	which is proportional to the boundary layer thickness.	
284	In film diffusion model can be identified according to the following equation:	
285	$-\ln (1 - \frac{q_t}{q_e}) = K_{bf} t$	(6)
	15	

286 where K_{bf} is the liquid film diffusion constant (min⁻¹).

287 In Fig. 6, adsorption of pyrene on the carbon materials appear to have similar kinetic behaviors. 288 The removal curves are single, smooth, and continuous. After 40 min of contact between the 289 adsorbents and pyrene, the adsorption process tends to reach the equilibrium state. However, the 290 time required for pyrene solution to reach equilibrium need more time in previous studies [2, 12, 291 30]. Yakout et al., reported that 100 mg of low-cost AC adsorb 100 mg/L of naphthalene, 292 phenanthrene and pyrene in 20 mL solution required 24 h to adsorption equilibrium [12]. A 2 mg of 293 modified periodic mesoporous organosilica (PMO) adsorption of PAHs aqueous solutions (8 mg/L, 294 5 mL) adsorption equilibrium also needed 24 h [2]. These studies suggested that the modified 295 carbons in this work had the excellent adsorption performance compared with the works of previous 296 research. From the kinetic curves in Fig. 6, we could draw a conclusion: the pyrene amounts 297 adsorbed on the adsorbents had the following order: MA-CAC > M-CAC > A-CAC > CAC. The 298 modified samples could adsorb efficiently and rapidly pyrene from aqueous.

Table 2 shows three kinetic models parameters obtained. When the higher R^2 value was considered simultaneously as indicative of the best fittings (Table 2), it was found that the pseudo-two-order model could best represented the kinetic data for pyrene adsorption with high correlation coefficient ($R^2 > 0.999$). In addition, pseudo-two-order model predicted the q_{exp} values closer to the experimental q_{cal} values than pseudo-first-order, which suggested that it was appropriate for describing pyrene adsorption on the carbons at equilibrium state. According to some

305 researchers, the pseudo-second-order model may be related to the occurrence of chemical sorption, 306 which may control the reaction rate [31]. In addition, intraparticle diffusion kinetic models owned low-correlation coefficients (0.2980 < R^2 < 0.6600). In this study, the q_t versus $t^{0.5}$ graph is only 307 308 initially linear which indicates that intraparticle diffusion could be involved in the sorption process 309 of pyrene on both the CAC and modified samples. While this line not passes through the origin, 310 intraparticle diffusion was not rate determining step [32]. Likewise, by comparing the data presented in Table 3, the R^2 values (0.8420 < R^2 < 0.9540) for the film diffusion model were higher 311 312 than those of intraparticle diffusion model, thus suggesting that film diffusion could control the 313 adsorption rate of pyrene onto carbons under the studied conditions [31]. 314 If intraparticle diffusion is involved in the sorption process, a plot of the square root of time 315 versus adsorption would result in a linear relationship, and the particle diffusion would be the

- 316 determining step if this line passes through the origin.
- 317 Fig. 6 should be put here.

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

319 *3.2.2. Isotherms of pyrene on the CAC and modified samples*

320 In order to optimize the adsorption process and to forecast adsorption, Langmuir and 321 Freundlich isotherm models were applied to the equilibrium data. Langmuir model is based on the

322 assumption of a homogeneous adsorbent surface, which can be written as:

323
$$\frac{C_{\rm e}}{q_{\rm e}} = \frac{1}{q_{\rm m}}C_{\rm e} + \frac{1}{q_{\rm m}K_{\rm L}}$$
 (7)

324 where q_m (mg/g) is the maximal adsorption capacity, K_L (L/mg) is a constant related to the free 325 energy of the adsorption.

326 Freundlich model is an empirical equation assuming heterogeneous adsorbent surface, which327 can be written as:

328
$$\ln q_{\rm e} = \frac{1}{n} \ln C_{\rm e} + \ln K_{\rm F}$$
 (8)

329 where K_F is the unit capacity factor related to the adsorbent capacity and *n* is an empirical 330 parameter representing the heterogeneity of site energies, respectively.

331 The similar shapes of the isotherms for pyrene adsorption on CAC and the modified samples 332 suggest that the adsorption process occurred via the similar pathways (Fig. 7). The modified 333 samples for pyrene adsorption belong to the L type according to the Giles classification [15]. As 334 shown in Fig. 7, the initial isotherms rise rapidly during the initial stage of adsorption when $C_{\rm e}$ and 335 $q_{\rm e}$ values are both lower, there are many readily accessible sites available on the surface of carbons. 336 However, the adsorption isotherms rate of decrease gradually at high concentrations, it is due to 337 more time is required to reach to equilibrium. This is because that it is difficult for the molecules to 338 penetrate the adsorbed layer of absorbent, which are filled as more sites [12]. For the CAC, the 339 monolayer adsorption capacity of pyrene was 142.86 mg/g. And as presented in Fig. 7, all the 340 modified samples have better adsorption properties for pyrene solution. The parameters of the two 341 isotherm models are calculated and summarized in Table 3. In this work, the Langmuir isotherm 342 best fits the experimental data of CAC samples for the adsorption of pyrene, indicating that the

343	adsorption process is a monolayer phenomenon [2, 8]. However, the Freundlich model have higher
344	R^2 value ($R^2 \ge 0.9991$) for the modified samples. Therefore, the adsorption belongs to a multilayer
345	process, which means that the modification treatments probably make the adsorption of pyrene
346	became multilayer adsorption and adsorption more effectively. Moreover, all 1/n values between
347	0.1 and 1.0 indicate a strong interaction between adsorbent and pyrene with a favorable adsorption
348	[2]. The results show that the equilibrium adsorption data fitted well with the Freundlich model,
349	which could adequately describe the adsorption behavior of pyrene onto the modified samples.
350	The pyrene adsorption from wastewaters on different adsorbents such as PMO, chitin, green
351	coconut shell, and immature coal [2, 30, 33] had been investigated. The intensity of adsorption and
352	the Freundlich adsorption constant K_F calculated for each adsorption system are given in Table 4. A
353	comparison between the CAC and the modified samples indicate that the modified samples in our
354	study have a good and effective adsorption for pyrene from aqueous solution.
355	Fig. 7 should be put here.
356	Table 3 should be put here.
357	Table 4 should be put here.

358 3.2.3. Thermodynamic parameters

359 Thermodynamic parameters were evaluated to confirm the adsorption nature of CAC and 360 MCAC. The thermodynamic constants, free energy change (ΔG^{o} , kJ/mol), enthalpy change (ΔH^{o} , 361 kJ/mol) and entropy change (ΔS^{o} , J/(K·mol)) were calculated. The thermodynamics equations were 362 as following:

$$363 \quad \Delta G^{\Theta} = -RT \ln K_{\rm F} \tag{10}$$

$$364 \qquad \Delta G^{\Theta} = \Delta H^{\Theta} - T \Delta S^{\Theta} \tag{11}$$

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

366 where $K_{\rm F}$ is the adsorption equilibrium constant in Eq. (8) for pyrene.

367 The ΔG^{θ} values of the different carbons for pyrene adsorption were decreased with an increase 368 in temperature (Table 5). This indicates that the adsorption process was spontaneous and the 369 spontaneity decreased with the temperature increasing. This shows that the removal process is 370 favored at lower temperature; it was consistent with the results obtained in our previous study [7]. 371 The negative value of ΔH^{θ} indicated an exothermal adsorption process, which indicated the removal 372 process for pyrene was generally favored at a low temperature. It was in agreement with what 373 described above. The positive values ΔS^{Θ} obtained shows the affinity of carbon materials for pyrene 374 and the increasing randomness at the solid-solution interface during the adsorption process [15, 34]. 375 Table 5 should be put here. 376 3.3. The effect of surface physicochemical characteristics on adsorption capacity 377 The adsorption capacity of AC rely on their surface characteristics, e.g. texture and surface

378 physicochemical properties [35]. Comparing the relationship of the adsorption capacity of PAHs 379 and their surface characteristics is necessary. This comparison will provide a good basis for better 380 orientation of the modified CAC. Correlation analysis is used for studying the effects of some

381	factors on pyrene adsorption, which is shown in Figs. 8(a-c). The BET surface area presents a
382	certain correlation with the adsorption capacity of pyrene for the CAC and the modified samples
383	(Fig. 8). This BET surface area suggests that a high surface area would generally result in a high
384	adsorption capacity for pyrene solution. For the all samples, MA-CAC has the highest BET surface
385	area (Fig. 8), thus it implies the highest adsorption capacity of pyrene solution. In addition,
386	MA-CAC has the largest pore volume than other carbons in this work. However, the other modified
387	samples (A-CAC and M-CAC) had a similar result, i.e., they have a higher pyrene adsorption than
388	the CAC. Fig. 8 shows that the adsorption capacities of the CAC and modified carbons increased
389	with the decrease in total surface oxygen-containing groups. The MA-CAC containing the least
390	surface oxygen groups present the highest adsorption capacities for pyrene. From Fig. 8b we can
391	see that the amount of surface oxygen containing groups, especially carboxylic functional and
392	lactones groups, have good linear correlations with $R^2=0.945$ and $R^2=0.987$. This result could be
393	explained using the low surface oxygen that is beneficial to the adsorption of pyrene solution. The
394	result is similar to that of previous reports [36].

395 Moreover, the basicity properties and adsorption of pyrene have a linear correlation (R^2 =0.857). 396 Higher basicity can increase the affinity of the modified samples to pyrene, and consequently the 397 modified samples sites are more available for the PAHs molecules. The enhanced basicity may 398 attribute to -NH₂ and nitrogen-containing groups introducing into the MA-CAC surface (Fig. 9). In 399 addition, combined microwave radiation in the presence of ammonia modification increases the

400	amount of nitrogen atoms (2.54%) on MA-CAC surface (Table 1). Thus it increases the affinity of
401	the alkaline MA-CAC samples to pyrene solution [17]. This could be explained by the fact that
402	PAHs and benzene molecules from π - π complex and enhanced the interaction between the
403	π -electrons of benzene rings and active sites on the MA-CAC sample surface [37, 38].
404	In all, basicity, carboxylic functional and lactones higher affect the adsorption of pyrene. In
405	our previous study, the adsorption pyrene on CAC or A-CACs modified by different ammonia
406	concentrations had the similar results that the higher basicity and lower acidity is beneficial to
407	pyrene adsorption. The high surface area, the amount of low oxygen-containing groups and basicity
408	of the modified samples made them good adsorption properties for pyrene from aqueous solution.
409	Fig. 8 should be put here.
410	Fig. 9 should be put here.
411	3.4 Regeneration of the MA-CAC sample
412	The MA-CAC sample still had a high adsorption capacity for pyrene, which reached a level of
413	90.30% of the initial value after three cycles (Fig. 10). This indicated that the MA-CAC samples
414	had good stability, reusability, and effective adsorption for pyrene from aqueous solutions.
415	Fig. 10 should be put here.
416	4. Conclusions

417 With the aim to enhance PAHs adsorption from aqueous solution, different procedures of CAC

418 modification have been compared: i) with ammonia, ii) with microwave radiation and iii) with

419	ammonia under microwave. This study showed that all modified samples had higher adsorption
420	capacity for pyrene than the CAC, especially the MA-CAC sample. It is attributed to the significant
421	decrease of the oxygen-containing functional groups of MA-CAC. Meanwhile, BET surface area,
422	total pore volume and average pore size were increased most distinct, compared with the CAC.
423	The kinetics of pyrene with the CAC and the modified samples showed a similar behavior.
424	After 40 min of contact between the adsorbent and pyrene, a tendency of the system to reach the
425	equilibrium was observed, and MA-CAC showed the highest adsorption capacity with 61.96 mg/g.
426	The adsorption isotherm experimental data were best described using the Freundlich isotherm
427	model for the modified samples, and the kinetic model of pseudo-second order best represented the
428	adsorption kinetic data of pyrene for the CAC and the modified samples. Thus, pyrene adsorbs on
429	the modified samples from the monolayer process to multilayer process. Moreover, we can
430	conclude that the adsorption of pyrene is a chemical sorption, which may control the reaction rate.
431	The sorption of pyrene onto carbons was spontaneous, exothermal, and entropically driven. The
432	modified CAC has a great potential as absorbents for the adsorption of PAHs from aqueous solution
433	and the adsorption process is fast and effective. We concluded that obtaining a high surface area,
434	low oxygen-containing groups, and a high basicity are necessary to improve the activated carbons
435	for pyrene adsorption capacity. The MA-CAC sample from the microwave-assisted treatment with
436	ammonia is a low cost, high adsorption capacity, and regeneration efficiency adsorbent with great
437	potential industrial applications.

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444	References
445	[1] H.L. Kong, J. He, Y.Z. Gao, J. Han, X.Z. Zhu, J. Environ. Qual. 40 (2011) 1-8.
446	[2] C.B. Vidal, A.L. Barros, C.P. Moura, A.C.A. de Lima, F.S. Dias, L.C.G. Vasconcellos, P.B.A.
447	Fechine, R.F. Nascimento, J. Colloid Interf. Sci. 357 (2011) 466-473.
448	[3] M.J. Yuan, S.T. Tong, S.Q. Zhao, C.Q. Jia, J. Hazard. Mater. 181 (2010) 1115-1120.
449	[4] B.V. Chang, S.W. Chang, S.Y. Yan, Adv. Environ. Res. 7 (2003) 623-628.
450	[5] Seul-Yi Lee, Soo-Jin Park, J. Ind. Eng. Chem. 19(2013) 1761-1769.
451	[6] A.M. Ghaedi, M. Ghaedi, A. Vafaei, N. Iravani, M. Keshavarz, M. Rad, I. Tyagi, S.
452	Agarwalc, V. K. Gupta, J. Mol. Liq. 206 (2015): 195-206.
453	[7] X.M. Xiao, F. Tian, Y.J. Yan, Z.S. Wu, J. Shihezi Univ. 32 (2014) 485-490.
454	[8] X.Y. Ge, Z.S. Wu, Y.J. Yan, Y.X. Zeng, J. Shihezi Univ. 34 (2016): 92-99.
455	[9] B.L. Chen, M.X. Yuan, H. Liu, J. Hazard. Mater. 188 (2011) 436-442.
456	[10]K.B Yang, J.H. Peng, C. Srinivasakannan, L.B. Zhang, H.Y. Xia, X.H. Duan, Bioresource
457	Technol. 101 (2010) 6163-6169.
458	[11]S.H. Moon, J.W. Shim, J. Colloid Interf. Sci. 298 (2006) 523-528.
459	[12]S. M. Yakout, A. A. M. Daifullah, S. A. El-Reefy, Adsorpt. Sci. Technol. 31 (2013) 293-302.
460	[13]C.O. Ania, B. Cabal, C. Pevida, A. Arenillas, J.B. Parra, F. Rubiera, J.J. Pis, Water Res. 41

461 (2007) 333-340.

- 462 [14] V.K. Gupta, I. Tyagi, S. Agarwal, O. Moradi, H. Sadegh, R. Shahryari-ghoshekandi, A.S.H.
 463 Makhlouf, M. Goodarzi, A. Garshasbi, Crit. Rev. Env. Sci. Tec. 42(2016): 93-118.
- 464 [15]X.Y. Ge, F. Tian, Z.L. Wu, Y.J. Yan, G. Cravotto, Z.S. Wu, Chem. Eng. Process. 91 (2015)
 465 67-77.
- 466 [16] F.W. Shaarani, B.H. Hameed, Chem. Eng. J. 169 (2011) 180-185.
- 467 [17] V.K. Gupta, A. Nayak, S. Agarwal, I. Tyagi, J. Colloid Interf. Sci., 417 (2014) 420-430.
- 468 [18] Z.J. Zhang, M.Y. Xu, H.H. Wang, Z. Li, Chem. Eng. J. 160 (2010) 571-577.
- 469 [19]Q.S. Liu, T. Zheng, N. Li, P. Wang, G. Abulikemu, Appl. Surf. Sci. 256 (2010) 3309-3315.
- 470 [20] S. Bashkova, T.J. Bandosz, J. Colloid Interf. Sci. 333 (2009) 97-103.
- 471 [21]L.Q. Zhang, M. Mi, B. Li, Y. Dong, Res. J. Appl. Sci. Eng. Technol. 5 (2013) 1791-1795.
- 472 [22]R. Cherbanski, M. Komorowska-Durka, G.D. Stefanidis, A.I. Stankiewicz, Ind. Eng. Chem.
 473 Res. 50 (2011) 8632-8644.
- 474 [23]B. Heibati, S. Rodriguez-Couto, M.A. Al-Ghouti, M. Asif, I. Tyagi, S. Agarwal, V.K. Gupta, J.
- 475 Mol. Liq. 208 (2015) 99–105.
- 476 [24]X.L. Song, H.Y. Liu, L. Cheng, Y.X. Qu, Desalination 255 (2010) 78-83.
- 477 [25]G.X. Yu, M. Jin, J. Sun, X.L. Zhou, L.F. Chen, J.A. Wang, Catal. Today 212 (2013) 31-37.
- 478 [26]L. Song, M. Junichi, K. Hirofumi, Carbon 44 (2006) 1884-1890.
- 479 [27] Jr.V. Strelko, D.J. Malik, J. Colloid Interf. Sci. 250 (2002) 213-220.
- 480 [28]C. Moreno-Castilla, F. Carrasco-Marin, A. Mueden, Carbon 35 (1997) 1619-1626.
- 481 [29] J. Przepiorski, M. Skrodzewicz, A.W. Morawski, Appl. Surf. Sci. 225 (2004) 235-242.
- 482 [30]Z.C. Zeledon-Toruno, C. Lao-Luque, F.X.C. de las Heras, M. Sole-Sardans, Chemosphere 67
 483 (2007) 505-512.
- 484 [31] A. Benhouria, M.A. Islam, H. Zaghouane-Boudiaf, M. Boutahala, B.H. Hameed, Chem. Eng. J.
- 485 270 (2015) 621-630.

- 486 [32]C. Valderrama, X. Gamisans, X. de las Heras, A. Farran, J.L. Cortina, J. Hazard. Mater. 157
 487 (2008) 386-396.
- 488 [33]R. Crisafulli, M.A.L. Milhome, R.M. Cavalcante, E.R. Silveira, D. Keukeleire, R.F.
 489 Nascimento, Bioresource Technol. 99 (2008) 4515-4519.
- 490 [34]S. Agarwal, I. Tyagi, V.K. Gupta , N. Ghasemi, M. Shahivand, M. Ghasemi, J. Mol. Liq. 218
 491 (2016) 208-218.
- 492 [35]L. Li, S.Q. Liu, J.X. Liu, J. Hazard. Mater. 192 (2011) 683-690.
- 493 [36]T. Garcia, R. Murillo, D. Cazorla-Amoros, A.M. Mastral, A. Linares-Solano, Carbon 42 (2004)
 494 1683-1689.
- 495 [37] A.M. Dowaidar, M.S. EI-Shahawi, I. Ashour, Sep. Sci. Technol. 42 (2007) 3609-3622.
- 496 [38]X.M. Xiao, D.D. Liu, Y.Y. Yana, Z.L. Wu, Z.S. Wu, G. Cravotto, J. Taiwan Inst. Chem. Eng.
 497 53 (2015) 160-167.
- 498 [39] S. Dağdelen, B. Acemioğlu, E. Baran, O. Koçer, Water Air Soil Pollut. 225 (2014) 1899-1914.
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- 508 Fig. 1. Scanning electron micrographs of CAC and the modified samples (a) CAC; (b) A-CAC; (c)
- 509 M-CAC; (d) MA-CAC
- 510 Fig. 2. Nitrogen adsorption-desorption isotherms and pores size distribution of different activated
- 511 carbons: (a) CAC; (b) A-CAC; (c) M-CAC; (d) MA-CAC
- 512 Fig. 3. Comparison of BET surface area and the porous texture of the CAC and the modified
- 513 samples (a) BET surface area; (b) Total pore volume
- 514 Fig. 4. The surface acidity, basicity, surface functional groups, and pH_{PZC} value of the CAC and the
- 515 modified samples
- 516 **Fig. 5.** FTIR spectra of the CAC and the modified samples
- 517 Fig. 6. Adsorbed amount of various carbon materials for pyrene as a function of adsorption time at
- 518 20 °C (pyrene concentration: 30 mg/L, pyrene solution volume: 100 mL, adsorbents amount: 60
- 519 mg)
- 520 Fig. 7. The adsorbed amount per gram of carbon materials for pyrene as a function of pyrene
- 521 concentration in solutions at 20 °C (pyrene solution volume: 100 mL, adsorbents amount: 60 mg)
- 522 Fig. 8. Adsorption capacity of CAC and the modified samples for pyrene as a function of BET
- 523 surface area (a); Oxygen-containing groups (b); Basic groups (c)
- 524 Fig. 9. The change in functional groups of CAC modified to MA-CAC
- 525 Fig. 10. Adsorption capacities of pyrene onto MA-CAC for three cycles
- 526



- 528 Fig. 1. Scanning electron micrographs of CAC and the modified samples (a) CAC; (b) A-CAC; (c)
- 529 M-CAC; (d) MA-CAC



533 Fig. 2. Nitrogen adsorption-desorption isotherms and pores size distribution of different activated

534 carbons: (a) CAC; (b) A-CAC; (c) M-CAC; (d) MA-CAC



539 Fig. 3. Comparison of BET surface area and the porous texture of the CAC and the modified

540 samples (a) BET surface area; (b) Total pore volume





545 modified samples



Fig. 5. FTIR spectra of the CAC and the modified samples





555 Fig. 6. Adsorbed amount of various carbon materials for pyrene as a function of adsorption time at

556 20 °C (pyrene concentration: 30 mg/L, pyrene solution volume: 100 mL, adsorbents amount: 60

557 mg)

558



Fig. 7. The adsorbed amount per gram of carbon materials for pyrene as a function of pyrene
concentration in solutions at 20 °C (pyrene solution volume: 100 mL, adsorbents amount: 60 mg)





565 surface area (a); Oxygen-containing groups (b); Basic groups (c)

- 566 (Conditions: (a) and (c): \diamond CAC, \diamond A-CAC, \diamond A-CAC, \diamond MA-CAC; (b) in order: CAC, A-CAC,
- 567 M-CAC, MA-CAC)
- 568





Fig. 9. The change in functional groups of CAC modified to MA-CAC



Fig. 10. Adsorption capacities of pyrene onto MA-CAC for three cycles

Table 1

Samples	Relative c	C/O				
	С	Н	Ν	S	0	
Coal	69.75	3.36	0.48	0.45	25.97	2.69
CAC	72.58	1.53	0.51	0.27	25.10	2.89
A-CAC	73.68	1.40	0.73	0.36	23.87	3.09
M-CAC	78.31	1.63	1.59	0.39	18.08	4.33
MA-CAC	82.84	1.11	2.54	0.30	13.20	6.28

578 Elemental composition of the carbon samples used in the experiment

Table 2

582 Parameters of adsorption pseudo-first-order, pseudo-second-order, and intraparticle diffusion

583 kinetic models

		Pseudo-first-order		Pseudo-second-order		Webber and Morris		Film diffusion			
Samples	$q_{ m exp}$	q _{e,cal} (mg/g)	<i>k</i> ₁ (min ⁻¹)	R^2	q _{e,cal} (mg/g)	k₂ (g/(mg· min))	R^2	$K_{\rm p}$ mg/(g·min ^{0.5})	<i>R</i> ²	K _{bf} (min ⁻¹)	<i>R</i> ²
CAC	41.73	36.62	4.58	0.9740	42.63	0.0010	0.9992	0.094	0.2980	0.062	0.8420
A-CAC	54.85	45.00	3.28	0.9900	55.56	0.0013	0.9994	0.430	0.5110	0.052	0.8930
M-CAC	57.93	50.63	3.41	0.8670	58.62	0.0015	0.9996	1.610	0.4810	0.040	0.9380
MA-CAC	61.96	59.97	2.02	0.9340	62.34	0.0019	0.9997	1.440	0.6600	0.025	0.9540

Table 3

Isotherms	Donomotono	Carbon sam	Carbon samples						
models	Parameters	CAC	A-CAC	M-CAC	MA-CAC				
Langmuir	$q_{\rm m}({\rm mg/g})$	142.86	166.67	200.00	250.00				
	$K_{\rm L}({\rm L/mg})$	0.47	1.20	0.42	0.44				
	R^2	0.9982	0.9620	0.6390	0.9200				
Freundlich	$K_{ m F}$	50.60	56.49	66.15	74.66				
	1/n	0.3009	0.2370	0.3684	0.3200				
	R^2	0.9560	0.9993	0.9991	0.9995				

587 Parameters of the isotherms models on the carbon samples

Table 4

591 Freundlich parameters for adsorption of pyrene obtained by various kinds of adsorbents

Adapathant	Freundlich	Deferences	
Adsorbent	$\overline{K_{\mathrm{F}}(\mathrm{mg/g})}$		- References
РМО	0.12	1.68	[2]
Chitosan	50.00	0.21	[12]
Rice husk activated carbon	29.71	0.80	[12]
Immature coal	10.00	0.62	[30]
Chitin	120.00	0.14	[33]
MA-CAC	74.66	0.32	This work

599 Table 5 Thermodynamic parameters for adsorption of pyrene onto the CAC and the modified

600

samples

Samples	<i>T</i> (K)	k_2	$K_{ m F}$	$\Delta G^{\scriptscriptstyle \Theta}$	$\Delta H^{ m e}$	ΔS^{Θ}
		(g/(mg·min)		(kJ/mol)	(kJ/mol)	$(J/(K \cdot mol))$
CAC	283.15	0.0015	51.23	-9.267		
	298.15	0.0010	42.60	-9.144	-11.68	8.56
	313.15	0.0006	36.94	-9.097		
A-CAC	283.15	0.0019	58.08	-9.562		
	298.15	0.0013	45.49	-9.304	-13.47	13.98
	313.15	0.0009	39.85	-9.288		
M-CAC	283.15	0.0023	65.76	-9.854		
	298.15	0.0015	49.87	-9.528	-18.44	30.34
	313.15	0.0012	39.23	-9.248		
MA-CAC	283.15	0.0029	74.25	-10.14		
	298.15	0.0019	53.38	-9.694	-20.64	37.18
	313.15	0.0017	41.66	-9.399		

Supplementary material

603 S.1 X-ray photoelectron spectroscopy (XPS)

604 The X-ray photoelectron spectra of the CAC and the modified samples were obtained with a 605 model PHI5700 ESCA X-ray photoelectron spectrometer. XPS was applied to determine the surface 606 complexes on the CAC and the modified samples. XPS analysis was conducted using Mg Ka X-ray source (1,253.6 eV) under a vacuum pressure 10^{-6} Pa. The wide scans were conducted from 0 to 607 608 1000 eV with a pass energy of 50 eV. 609 **XPS** analysis 610 XPS has been shown to be useful for analyzing the surface chemical characteristics of carbons 611 [19]. Fig. S1 shows the XPS survey spectra of the CAC and the modified samples. The survey

612 spectra of the carbon samples contain distinct peaks for carbon and oxygen. The relationship 613 between the relative peak area and relative content of elements in the carbons is shown in Table 2. 614 The carbon content in modified samples increase, and the oxygen content show the opposite change 615 trend. Meanwhile, the ratio of C/O is rise from 2.41 in CAC surface to 6.22 in the surface of the 616 MA-CAC. Above all, this result still agrees with the results of the element analysis. We can 617 conclude that some oxygen-containing groups are eliminated from the carbons surface. In addition, 618 the result is consistent with the results of surface acidity and basicity.

- 619
- 620
- 621

Relative contents (%) Carbons C/O S С Ο Ν CAC 69.97 29.06 0.49 1.48 2.41 A-CAC 75.58 21.68 1.65 1.09 3.49 M-CAC 81.02 0.30 4.93 16.43 2.25 MA-CAC 82.91 13.32 3.55 0.22 6.22

622 **Table S1** Relative content of various elements on carbon surface in at. %





625 **Fig. S1.** XPS survey spectra of the CAC and the modified samples

626

627 S.2 Effects of ionic strength

Effects of ionic strength to the removal of 100 mL, 30 mg/L pyrene solution by 0.06 g of CAC
and the modified samples were studied in the presence of NaCl ions. The concentrations of NaCl
were selected as 0.05, 0.10, 0.20, and 0.30 M (mol/L). The mixture was contacted for 60 min. The

631 whole mixture was separated by filtration, and pyrene concentration was measured, then the pyrene

632 adsorption capacity was calculated.

633 Effect of ionic strength on pyrene adsorption

The results obtained are shown in Fig. S2. It was seen that the adsorption capacity of the pyrene increased in the presence of NaCl. These dissociated Na⁺ ions caused a decrease in the adsorption of the pyrene due to electrostatic effects between the carbons and the pyrene molecules [39] (see Fig. S2). The enhanced adsorption capacity of pyrene on CAC and the modified samples also can be explained by the fact that the affinity increased between carbons and pyrene through form a π - π complex between the π -electrons of benzene rings and active sites on the carbons surface [37, 38].



642 **Fig. S2.** Effect of ionic strength on pyrene adsorption