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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

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

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ABSTRACT

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

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

1. Introduction

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

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

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

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

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

2. Materials and methods

2.1. Preparation of CAC

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

2.2. Modification of iron nitrate via microwave radiation

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

2.3. Characterization of CAC and 0.05Fe-MCAC

2.3.1. SEM

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

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

2.3.2. Fourier transform infrared (FTIR) spectrometer

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

2.3.3. BET surface area and pore structure analysis

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

2.3.4. Surface acidity and basicity

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

2.4. Adsorption test

2.4.1. Adsorption of PAHs from aqueous solution

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

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

2.4.2. Adsorption kinetic

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

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

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

2.5. Regeneration of spent carbon

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

3. Results and discussion

3.1. Adsorption capacity of Fe-MCAC for naphthalene

3.1.1. Effects of iron nitrate solution concentrations

We investigated the effects of the concentration of iron nitrate solution on the preparation of Fe-MCAC for naphthalene adsorption under the same microwave radiation conditions (Fig. 1). As the concentration of iron nitrate solution increased, the amount of naphthalene adsorbed on Fe-MCAC gradually decreased. The 0.05Fe-MCAC sample modified with 0.05 M iron nitrate solution yielded a maximum adsorption capacity of 159.00 mg/g, which was significantly higher than the adsorption capacity of the CAC sample (95.74 mg/g). The Fe^{3+} modification influenced the adsorption capacity of the adsorbent possibly because of the change in texture and chemical properties on the surface of the CAC sample. Iron modification could enrich the pore structure of the Fe-MCAC sample, which enhanced the adsorption capacity of Fe-MCAC for naphthalene [17]. However, a high iron nitrate concentration was disadvantageous for the modified CAC for naphthalene adsorption in this study because excessive amounts of iron could be blocked pore of Fe-MCAC; as a consequence, a small pore volume is obtained, and the adsorption efficiency is decreased [20]. Considering that low concentration can save resources and enhance adsorption capacity, we selected 0.05 M iron nitrate solution as the suitable modification concentration.

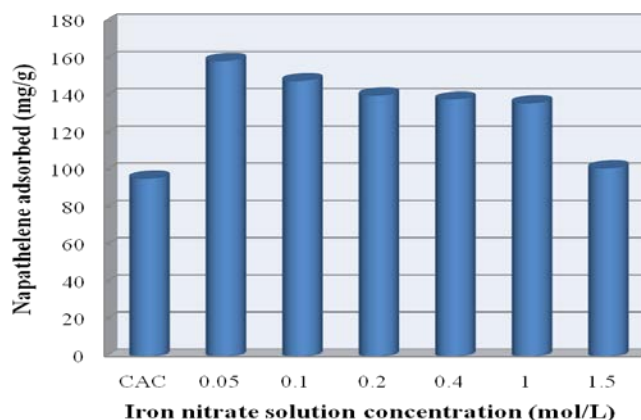


Fig. 1. Effects of iron nitrate solution concentrations on Fe-MCAC for naphthalene adsorption capacity (microwave power: 300 W, microwave radiation time: 5 min)

3.1.2. Effects of microwave power

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

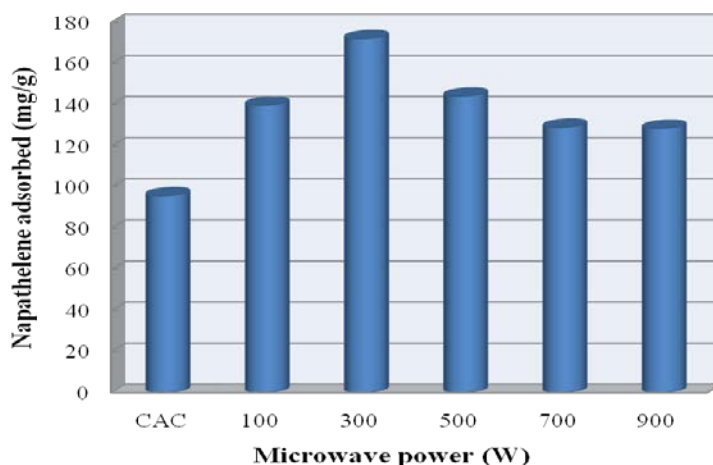


Fig. 2. Effects of microwave power on Fe-MCAC for naphthalene adsorption capacity (iron nitrate: 0.05 M, microwave radiation time: 5 min)

3.1.3. Effects of microwave radiation time

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

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

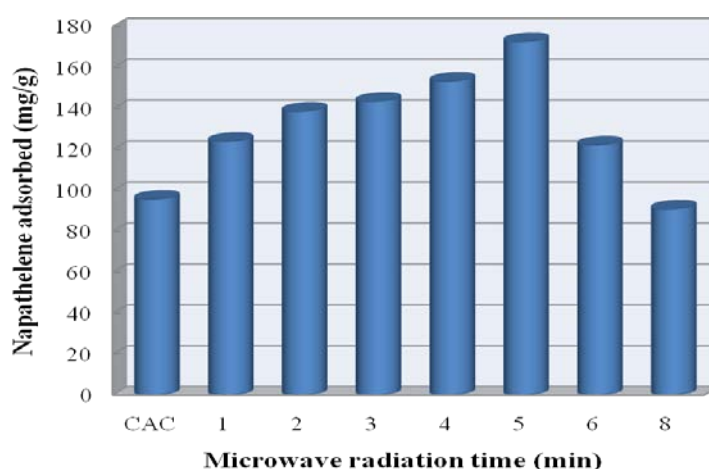


Fig. 3. Effects of microwave radiation time on Fe-MCAC for naphthalene adsorption capacity (iron nitrate: 0.05M, microwave power: 300W)

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

3.2. Characterization

3.2.1. SEM

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

irradiation, the surface of the 0.05Fe-MCAC sample was more porous than that of CAC (Fig. 4). Iron ion has high activity and easily enters the pore of 0.05Fe-MCAC. Several studies also showed that microwave radiation treatment effectively developed pores on the surface of the CAC and AC, which greatly enlarged the surface area and porous structure of the carbons [14, 25]. Therefore, the developed porous structure could benefit the adsorption of PAHs from aqueous solutions. In addition, 0.05Fe-MCAC can provide a large surface area for iron loading; and iron surface has stronger activity and can better combine with the adsorbate, which may promote 0.05Fe-MCAC adsorption [14, 26]. Chen et al. showed that iron-impregnated AC was highly effective in arsenic removal [20]. Considering these factors, the regulation of the pore structure of CAC and Fe^{3+} loading are great of significance for PAHs adsorption.

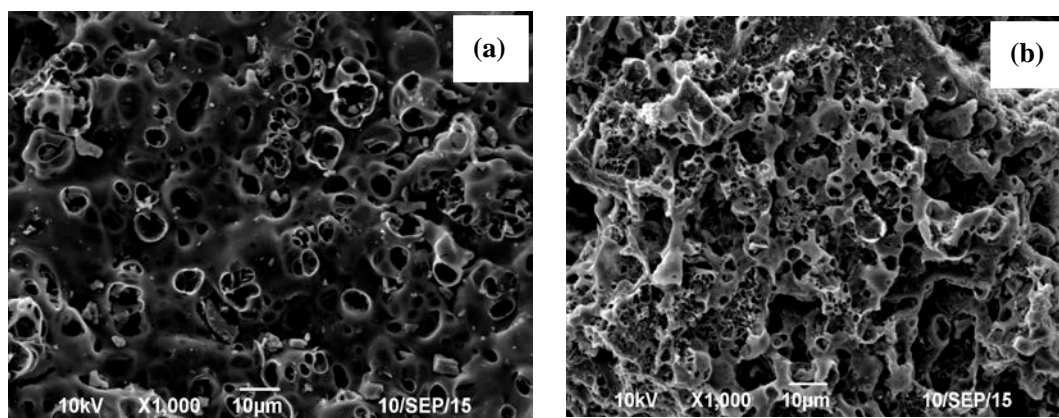


Fig. 4. Scanning electron microscope (SEM) micrograph: CAC (a); and 0.05Fe-MCAC (b)

3.2.2. Fourier transform infrared (FTIR) spectrometer

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

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

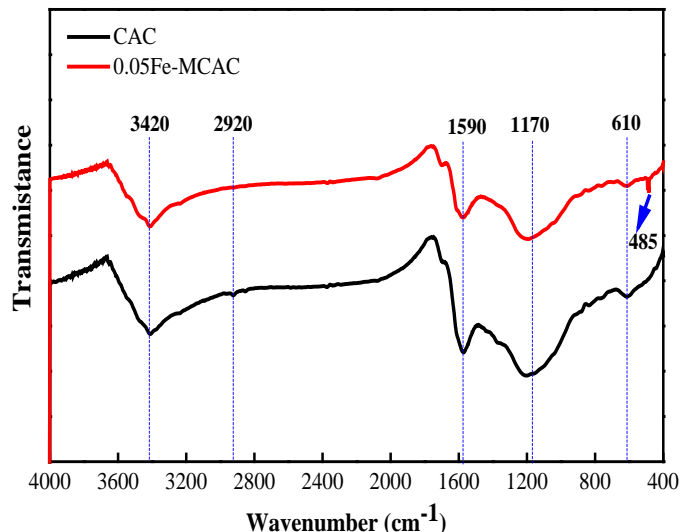


Fig. 5. FTIR analysis of the CAC and 0.05Fe-MCAC samples

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

The isotherms of the adsorption–desorption of N_2 at 77 K were determined, as shown in Fig. 6, to investigate the influence on the textural properties of the surfaces of the CAC and

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

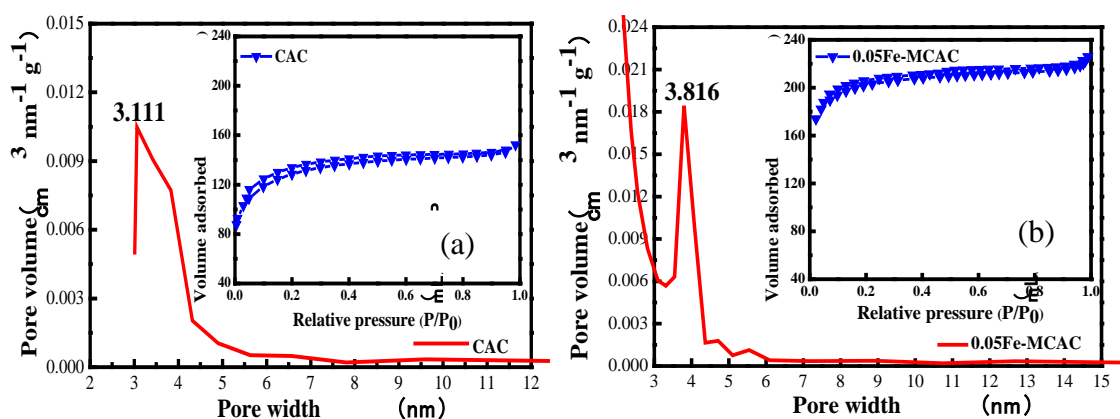


Fig. 6. Pore size distributions of CAC (a); and 0.05Fe-MCAC (b)

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

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

Table 1

BET analysis for CAC and 0.05Fe-MCAC

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

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

The total acidity and basicity of the CAC and 0.05Fe-MCAC samples are summarized in Table 2. The Fe-MCAC sample was more basic than those on its surface. One likely reason was that Fe^{3+} was loaded onto the surface of 0.05Fe-MCAC, and oxygen was removed; thus, the basicity properties were enhanced. The study by Rivera-Utrilla et al. [27] showed that the increase in the basicity of AC surface favored the adsorption of organic compounds. Strong basic properties of the 0.05Fe-MCAC sample were generally conducive to PAHs adsorption from aqueous solutions. The amount of iron loading on the 0.05Fe-MCAC sample was 0.135 mmol/g (Table 2), which could be attributed to the changes in the surface chemistry properties and increased the pore structure of the 0.05Fe-MCAC

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

Table 2

Total acidity 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

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

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

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

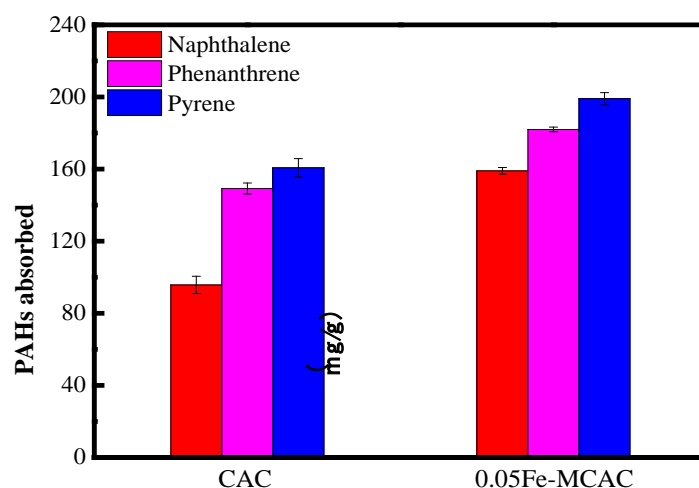


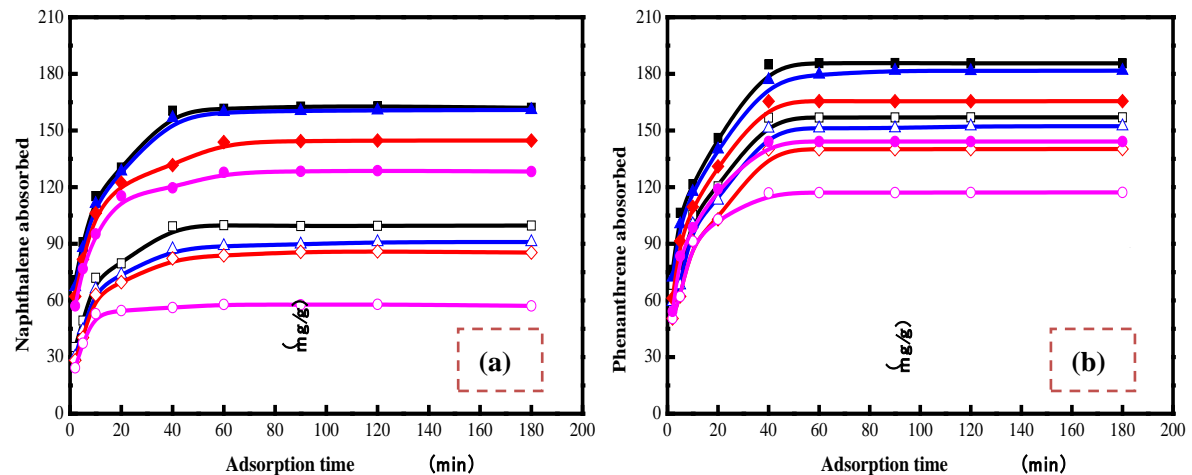
Fig. 7. Adsorption of PAHs on CAC and 0.05Fe-MCAC at 20 °C

3.4. Adsorption kinetics

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

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

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



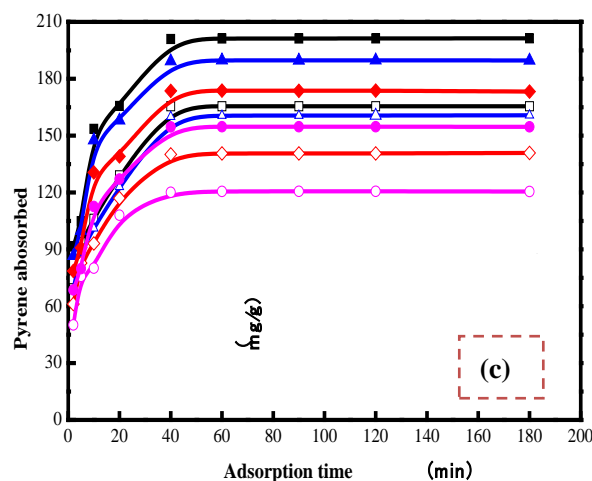


Fig. 8. Naphthalene (a), phenanthrene (b), and pyrene (c) on the CAC and 0.05Fe-MCAC kinetic curves at different temperature

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

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

3.4.1. Pseudo-first-order kinetics

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

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

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

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

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

3.4.2. Pseudo-second-order kinetics

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

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

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

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

3.4.3 The activation energy of PAHs adsorption

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

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

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

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

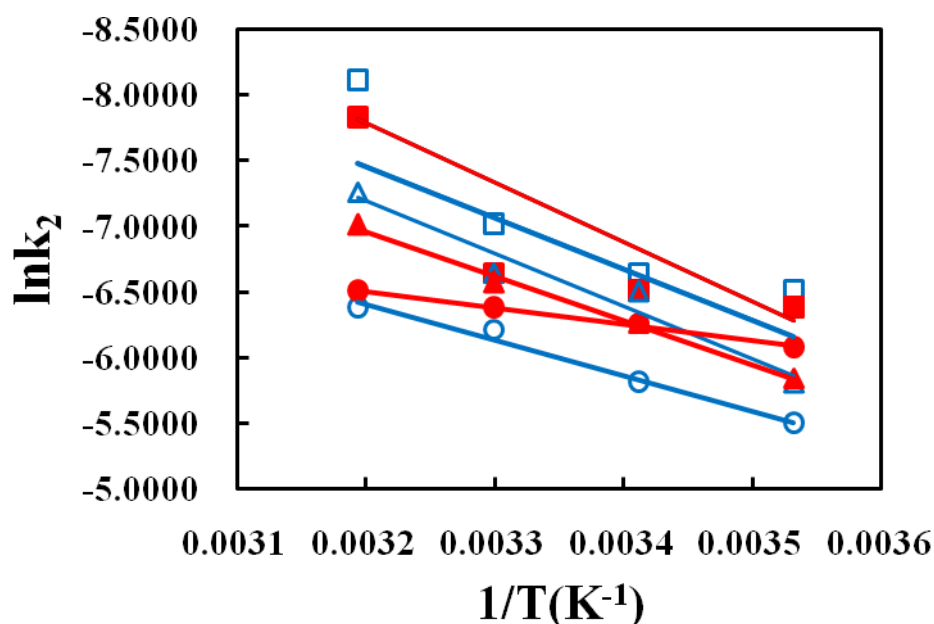


Fig. 9. Plots of $\ln k_2/T^{-1}$ for adsorption of naphthalene, phenanthrene and pyrene on CAC and

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

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

Table 3 Kinetic models parameters for the adsorption of naphthalene, phenanthrene and pyrene on CAC and 0.05Fe-MCAC

Adsorbates	Samples	T (°C)	q_{exp} (mg/g)	Pseudo-first-order			Pseudo-second-order			E_a (kJ/mol)
				q_e (mg/g)	k_1 (min ⁻¹)	R^2	q_e (mg/g)	k_2 (g/(mg·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	

3.5 Regeneration of 0.05Fe-MCAC

The results of regeneration studies are presented in Fig. 10. The 0.05Fe-MCAC sample still had a high adsorption capacity for pyrene, which reached a level of 92.14% (183.43 mg/g) of the initial value after three cycles. This indicated that the modified sample had good

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

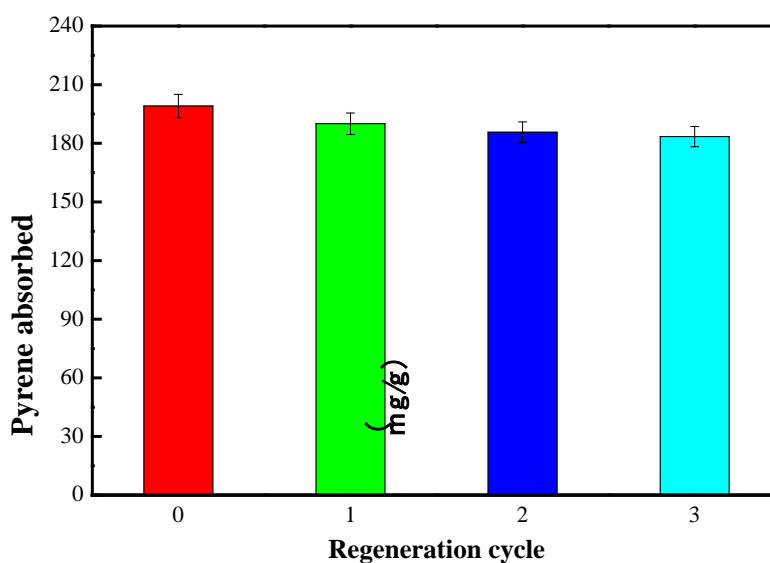


Fig.10. Adsorption capacities of pyrene onto 0.05Fe-MCAC for three cycles

4. Conclusions

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

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

Acknowledgments

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

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