

URBAN MINING: CHARACTERIZATION AND RECYCLING OF SOLID WASTES

# Preparation of Pyrolytic Carbon from Waste Tires for Methylene Blue Adsorption

YUZHE ZHANG, $^1$  QIAN CHENG, $^1$  DANDAN WANG, $^1$  DA XIA, $^1$ XUDONG ZHENG, $^{\rm I}$  ZHONGYU LI, $^{1,2,3,5}$  and JIANN-YANG HWANG $^{4,6}$ 

1.—School of Environmental and Safety Engineering, Changzhou University, 417 Mingxing Building, Science and Education City, Wujin District, Changzhou 213164, Jiangsu, People's Republic of China. 2.—Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, School of Petrochemical Engineering, Changzhou University, 417 Mingxing Building, Science and Education City, Wujin District, Changzhou 213164, Jiangsu, People's Republic of China. 3.—Advanced Catalysis and Green Manufacturing Collaborative Innovation Center, Changzhou University, 417 Mingxing Building, Science and Education City, Wujin District, Changzhou 213164, Jiangsu, People's Republic of China. 4.—Department of Materials Science and Engineering, Michigan Technological University, Houghton, MI 49931, USA. 5.—e-mail: zhongyuli@mail.tsinghua.edu.cn. 6.—e-mail: Jiann-yangHwang@outlook.com

The problem of treating methylene blue dye (MB) was considered using recycled waste tires. Treating waste by the application of other wastes is a resource-saving pollution treatment strategy. Previous MB treatment methods are either expensive or have high energy demands. In this study, two pollution treatments were connected via carbon pyrolysis. Waste tire pyrolysis by high-temperature microwaves produced pyrolytic carbon, which was then used to adsorb MB. This is because of its unique pore structure and large specific surface area. The results showed that recycled pyrolytic carbon benefits the MB adsorption reaction as a spontaneous endothermic reaction. Empirically, the maximum adsorption capacity of pyrolytic carbon for MB was found to be 71.6 mg g<sup>-1</sup> at pH 7 and 298 K. These recycling processes have low cost and low energy requirements, compared to previous studies.

# INTRODUCTION

Treating of waste with waste is an environmentally economic and cost-effective waste treatment strategy. Waste is reused in a specific treatment and then used to address another pollution. This strategy can avoid high costs and resource consumption and, in addition, does not cause secondary environmental pollution. For example, steel slag from a converter in steelmaking has the advantages of high porosity and large specific surface area. Therefore, it has been used as an adsorbent or a flocculating agent for treating other contaminated wastes. $1,2$ 

In this study, two serious wastes, waste tires and methylene blue dye (MB), were considered. Waste tires cause many environmental problems, such as occupying valuable land and fostering severe disease. Meanwhile, MB is an azo dye, which is widely used in the dyeing industry.<sup>3</sup> As MB's aromatic structure is not easily decomposed, it is generally difficult to degrade<sup>[4](#page-7-0)</sup> and can cause severe health

conditions, such as Heinz-body anemia, red blood cell morphology, and necrotic swelling. Intravenous injection of MB at a dose higher than 500 mg  $kg^{-1}$ can cause nausea, dizziness, and chest pain. $5-7$  High MB concentrations can be lethal to animals. Therefore, effective MB degradation is a significant problem. If MB dye can be treated using waste tires, these two problems can be handled at a meager cost. Meanwhile, this study mainly examined the MB adsorption performance of pyrolytic carbon, with the surface of pyrolytic carbon being activated to achieve the free adsorption and desorption of MB and thus prevent secondary pollution.

The most popular traditional treatment of tires are conventional pyrolysis methods using a rotary kiln, and fixed bed, fluidized bed, moving bed, or suspension furnaces.<sup>8-10</sup> However, these methods can lead to deteriorated pyrolytic environments and large temperature gradients, which result in reduced yields of pyrolytic products[.11,12](#page-7-0) Previous studies have used photocatalytic materials, such as

graphene and titanium dioxide, to degrade MB under ultraviolet light. $13,14}$  $13,14}$  However, there are several drawbacks. For example, the degradation rates are relatively low and the temperature and illumination conditions need to be carefully controlled. Other treatment methods include electrochemical oxidation and ultrasonic chemical degradation.<sup>15–17</sup> However, these strategies also require significant energy at a high cost.

In contrast, pyrolytic carbon was first produced by pyrolyzing waste tires using microwave irradiation. Generally speaking, in conventional heating methods, heat comes from an external heat source. However, such a heating method can cause uneven heating, incomplete reaction and low pyrolytic efficiency due to the poor thermal conductivity of the tires.<sup>[18](#page-7-0)</sup> In contrast to the above techniques, microwave heating is efficient and fast. As microwaves can penetrate the material, they can heat the material uniformly.<sup>[19,20](#page-7-0)</sup> After microwave pyrolysis, pyrolytic carbon was then applied to adsorb the MB, which did not require any additional energy. Microwave pyrolysis treatment of tires has many advantages in recycling them, $21$  being a resourcesaving and environmentally friendly treatment technology. Through microwave heating, waste tires were decomposed to pyrolytic carbon, which has unique adsorption properties and can be used as an adsorbent in water treatment.<sup>[22,23](#page-7-0)</sup> This property makes waste tires the natural resource choice for MB wastewater treatment. Such pyrolytic carbon has often been used as a substitute for activated carbon, a common adsorbent especially in the adsorption of macromolecular organic matter.<sup>2</sup> When pyrolytic carbon was used to adsorb MB, it proved to be an economical and efficient way to treat this toxic dye. $<sup>2</sup>$ </sup>

In this study, collected waste tires were ground to powder and treated in a microwave high-temperature vacuum tube furnace to conduct microwave pyrolysis under a nitrogen atmosphere, producing only pyrolytic carbon and no secondary pollution. Scanning electronic microscopy, thermal gravimetric analysis, organic element analysis, and infrared spectrometry were used to analyze the physical and chemical properties of pyrolytic carbon at different pyrolysis temperatures and holding times. The adsorption mechanism of pyrolytic carbon for MB was further explored by studying the pH and the adsorption kinetics, thermodynamics, and isotherm. Through these two approaches, the high effectiveness of MB treatment using pyrolytic carbon has been demonstrated.

### EXPERIMENT

# Sample Materials, Reagents, and Instruments

Tire materials used in this experiment were made in China. Before microwave pyrolysis treatment, the collected waste tires were first screened. Then, the samples were cleaned, manually removed, and

cut into small blocks. Finally, the blocks were manually ground into pellets with diameters of  $0.5 \pm 0.05$  mm. The reagents used included analytically pure KBr, tetrachloroethylene, and MB (XinMingTai Chemical, Hubei, China).

Experimental instruments mainly included a Vario EL III organic element analyzer, (Elementar Analysensysteme, Hanau, Germany) to analyze the main sample elements, a Nicolet iS5 Fourier-transform infrared spectrometer (FTIR; Nicolet, Madison, WI, USA) to analyze sample primary functional groups, a SUPRA scanning electron microscope (SEM; Carl Zeiss, Oberkochen, Germany) to observe sample morphology, an ASAP2460 Physical Adsorber (Micromeritrics, Norcross, GA, USA) to measure sample specific surface area, and a Labsys Evo STA thermogravimetry (Setaram Instrumentation, Caluire, France) to analyze sample thermal stability.

## Microwave Equipment

The waste tire microwave pyrolysis equipment was an HY-ZG1516 multi-function microwave hightemperature vacuum tube furnace (Hunan Huaye Microwave Technology, Changsha, Hunan, China). In supplementary Fig. S-1, '4' is the main furnace body and '3' is the thermal insulation structure used to ensure that the pyrolytic products were temporally maintained. Tire material was placed in a corundum crucible and nitrogen gas (99.99%) instilled through a hole under the reactor. Gas was purged from the top at a flow rate of 0.5 L  $\mathrm{m}^{-2}$  $min^{-1}$  and held for 5 min to ensure inert atmospheric conditions. Then, the microwave oven was turned on, the nitrogen flow rate was adjusted to the set flow rate, and the tire materials were heated up to a certain temperature, maintained at this temperature, and held for a specific time. Then, the pyrolytic process was terminated. The oven was then opened and quickly cooled to room temperature. The product was collected as well as the residue and oil.

## Pyrolysis Step

The treated tire samples (3.000 g) were initially placed in a corundum crucible at room temperature. Then, the microwave equipment was adjusted to a heating power of 600 W and the tire was heated from room temperature to a target temperature in  $\sim$  15 min. Samples were pyrolyzed at 450°C,  $500^{\circ}$ C,  $550^{\circ}$ C, and  $600^{\circ}$ C and then thermalized for 20 min and 30 min at each temperature. Finally, the furnace was cooled to room temperature and the pyrolytic product was collected.

# Pyrolytic Carbon Adsorption in MB Experiments

First, 12.5 mg of MB was dissolved in pure water to form a stock 50 mg  $L^{-1}$  MB solution, which was

<span id="page-2-0"></span>then diluted to the desired concentrations. A standard curve was obtained with different MB concentrations as the abscissa and the adsorption capacity as the ordinate. Five concentrations of MB at  $0.00 \text{ mg } L^{-1}$ ,  $0.50 \text{ mg } L^{-1}$ ,  $2.00 \text{ mg } L^{-1}$ ,  $5.00 \text{ mg }$  $L^{-1}$ , and 10.00 mg  $L^{-1}$  were selected.

# pH Experiments

Masses of 10 mg of pyrolytic carbon were added to 10 mL of 50 mg  $\mathbf{L}^{-1}$  MB solution, with pH = 3, 4, 5, 6, 6.5, 7, 8, 9, 10 and 11, for 24 h at 298 K. After shaking, the mixture was centrifuged at 9000 rpm for 5 min and the adsorption capacity measured at 664 nm. The pH of MB solutions was adjusted using 0.5 M NaOH and 0.5 M HCl solution as needed. The amount of pyrolytic carbon adsorbed to the MB was calculated by

$$
Q_e = \frac{V(C_0 - C_e)}{W} \tag{1}
$$

with V being the volume of the adsorbed MB solution, W the adsorbent pyrolytic carbon mass,  $C_0$  the initial MB solution concentration, and  $C_e$  the solution concentration when the adsorption reached equilibrium.

## Adsorption Kinetics Experiment

Masses of 10 mg of pyrolytic carbon were added to 10 mL of 50 mg  $L^{-1}$  MB solution and then reacted at  $298$  K and  $pH = 7$  for 10 min, 20 min, 30 min, 60 min, 120 min, 240 min, 480 min, 960 min, and 1440 min. The product solutions were then centrifuged at 9000 rpm for 5 min, the supernatant collected, and the adsorption capacity measured at 664 nm.

## Adsorption Isotherm Experiment

Masses of 10 mg of pyrolytic carbon were added to 10 mL of different MB concentrations of 15 mg  $L^{-1}$ ,  $30 \text{ mg } L^{-1}$ ,  $50 \text{ mg } L^{-1}$ ,  $75 \text{ mg } L^{-1}$ ,  $100 \text{ mg } L^{-1}$ , 150 mg  $L^{-1}$ , 200 mg  $L^{-1}$ , and 250 mg  $L^{-1}$ . After reaction at  $pH = 7$  and 298 K for 24 h, the products were centrifuged at 9000 rpm for 5 min, the supernatant collected, and the adsorption capacity measured at 664 nm.

## Adsorption Thermodynamics Experiment

Masses of 10 mg of pyrolytic carbon were added to 10 mL of MB solutions at concentrations of 15 mg  $L^{-1}$ , 50 mg  $L^{-1}$ , 75 mg  $L^{-1}$ , and 150 mg  $L^{-1}$ . After reacting at 298 K, 318 K, or 338 K and pH = 7 for 24 h, the samples were centrifuged at 9000 rpm for 5 min, the supernatant collected, and the adsorption capacity measured at 664 nm.

# RESULTS AND DISCUSSION

# Microwave Pyrolysis Results

The composition of the tires was analyzed before microwave pyrolysis. The main chemical components of these waste tires were natural rubber, styrene butadiene rubber, butadiene rubber, and carbon black. In addition, there were some inorganic and organic additives, including sulfur, zinc oxide, a vulcanizing agent, accelerator agent, and anti-aging agent. $11,27$ 

During the pyrolytic process, the microwave equipment was heated from room temperature to  $600^{\circ}$ C at  $600$  W within 15 min. The pyrolytic carbon was collected after incubation at  $450^{\circ}$ C,  $500^{\circ}$ C, 550C, and 600C for 20 min and 30 min. The quantity of raw material was 3.00 g and the mass of residual substances after specific microwave pyrolysis is shown in Table [I](#page-3-0). The average mass of residual materials was  $\sim 1.50$  g under different temperatures and different holding times, which basically showed losses of about half. The pyrolytic temperature and holding time indicated no significant effects on the amount of microwave pyrolytic solid residue. At the same time, the pyrolytic process was observed to be relatively stable at 450 $\degree$ C, 500 $\degree$ C, 550 $\degree$ C, and 600 $\degree$ C and the pyrolytic carbon yields of the main desired pyrolytic product were relatively stable.

Some volatile pyrolytic gases contributed to the mass loss of waste tires during the pyrolytic process. The main components of these gases are methane, ethylene, ethane, and hydrogen.<sup>28</sup> These gases contain a large amount of energy and can be used as fuel. In addition, the sulfur content of these gases was very low and mostly contained hydrocarbons, making them environmentally friendly.

# Analysis of Pyrolytic Carbon Characterization Results

## SEM Analysis

The surface morphology of pyrolytic carbon was observed under different SEM magnifications. A comparison of the morphology of all pyrolytic products is presented in supplementary Fig. S-3, and the particle size distribution of pyrolytic carbon at different pyrolysis temperatures and different holding times is seen in supplementary Fig. S-5. Pores were observed on the surfaces of pyrolytic carbon produced from a pyrolytic temperature of  $550^{\circ}$ C and 20 min holding time at  $\times 300$  magnification. A plurality of pores was observed to be distributed on the surfaces, and the pore sizes varied and showed an uneven distribution (Fig. [1a](#page-3-0), b). This was because, during the microwave pyrolytic process, new volatile pores formed in the interior and on the surfaces of the pyrolytic carbon due to the continuous evolution of volatile organic gases.

<span id="page-3-0"></span>Table I. Residue quality after microwave pyrolysis





Fig. 1. The topography of pyrolytic carbon under 550°C and 20 min holding time: (a)  $\times$ 350 maganification; (b)  $\times$ 330 maganification.

## BET Analysis

BET analysis showed that there was a pore structure on the surfaces as well as inside the pyrolytic carbon. These were porous solid particles and the specific surface area significantly increased compared with carbon black. Specific surface area measurements on eight samples were performed at four different pyrolysis temperatures and two different holding times. Because the pore shapes of the pyrolytic carbon surfaces were irregular, the pore sizes were different and distributed unevenly. Therefore, specific sample surface areas were chosen for measurements, with the specific results contained in supplementary Table S-1. As the final temperature of pyrolysis increased, the specific surface area gradually increased. Overall, the specific surface areas of all samples were relatively large, at 60 m<sup>2</sup>  $g^{-1}$  or more. In comparison, pyrolytic carbon had a specific surface area of 76.18  $\mathrm{m^{2}\,g^{-1}}$  at  $500^{\circ}$ C and 20 min holding time. Therefore, pyrolytic carbon under these conditions was selected to study the MB adsorption, and its adsorption performance and optimal adsorption conditions were investigated.

## Thermogravimetry Analysis (TG)

Pyrolytic carbon was used as an MB adsorbent for its generally good adsorption properties and stability under high temperatures. Because the temperature of printing and dyeing wastewater is generally high, MB is a basic dye in the common

printing and dyeing industry. Therefore, it was judged that it was necessary to use pyrolytic carbon as an adsorbent to degrade MB and explore its thermal stability. Accordingly, 1 mg samples of pyrolytic carbon were heated in a furnace from 30 to 1000C and the resulting mass loss showed that this carbon was relatively stable under high-temperature conditions; specific results are presented in supplementary Fig. S-2. After heating at  $1000^{\circ}$ C, the pyrolytic carbon quality remained  $> 80\%$ , indicating that the weight loss was< 20%. Only under  $500^{\circ}$ C and 20 min holding time was the pyrolytic carbon mass  $loss > 30\%$ . The possible reason for this result was that the pyrolytic carbon was relatively easily burned under these conditions and the surface pore structure was relatively large. In summary, pyrolytic carbon exhibited less mass loss under high-temperature conditions, which revealed that it was an excellent high-temperature-resistant material.

## Elemental Analyzer

The carbon component of pyrolytic carbon was 70%, with the high carbon content mainly derived from carbon black added to rubber in tire manufacture. In addition, pyrolytic carbon also contained trace elements, which was revealed by elemental analysis and the corresponding content (Table [II\)](#page-4-0). The carbon content in this pyrolytic carbon was observed to be relatively high,  $> 75\%$ . Under the same pyrolysis temperature, longer holding times in the microwave pyrolysis equipment obtained a

Pyrolysis temperature $(^{\circ}C)$ , holding time (min)	$N(\%)$	$C(\%)$	$S(\%)$	$H(\%)$
$450^{\circ}$ C, 20 min	0.415	77.86	3.302	0.361
$450^{\circ}$ C, 30 min	0.415	81.59	3.163	0.280
$500^{\circ}$ C, 20 min	0.416	77.46	3.435	0.265
$500^{\circ}$ C, 30 min	0.383	82.77	2.826	0.189
$550^{\circ}$ C, 20 min	0.347	80.85	3.377	0.191
$550^{\circ}$ C, 30 min	0.376	83.20	3.352	0.261
$600^{\circ}$ C, 20 min	0.371	80.39	3.579	0.226
$600^{\circ}$ C, 30 min	0.373	85.55	2.686	0.238

<span id="page-4-0"></span>Table II. Elemental analysis of pyrolytic carbon at different pyrolysis temperatures and different holding times



Fig. 2. Infrared spectra of pyrolytic carbon at different pyrolysis temperatures and different holding times.

higher proportion of carbon in the pyrolytic carbon. This was because, when the holding time was relatively long, the microwave pyrolysis of the waste tires was more complete. In addition, the sulfur content of the pyrolytic carbon was relatively high, 2.6% or more, and mainly derived from some sulfur-containing additives, accelerators, and vulcanizing agents added to the tire rubber. The nitrogen and hydrogen content in this pyrolytic carbon was relatively low, with the hydrogen content at 0.18–0.37% and the nitrogen content at 0.34–0.42%. The nitrogen was mainly derived from anti-oxidants added to the tire rubber.

## Fourier Transform Infrared Spectroscopy (FTIR)

In addition to the analysis of the physicochemical properties of the pyrolytic carbon, compositional analysis of its internal functional groups was also crucial in understanding the microwave pyrolysis mechanism of pyrolytic carbon. Here, FTIR was used to analyze pyrolytic carbon under eight different conditions, with different absorption peaks representing different functional groups (Fig. 2). Among these, strong absorption peaks at  $\sim$  3484 cm-<sup>1</sup> were due to stretching vibrations of hydroxyl



Fig. 3. Adsorption of MB by pyrolytic carbon at different pH values.

groups on the carbon surfaces and the absorption peak caused by water absorption of the solid dispersion medium, KBr. The appearance of an absorption peak at  $2975 \text{ cm}^{-1}$  indicated the presence of a  $-CH_3$  group on the surfaces. An absorption peak around  $1690 \text{ cm}^{-1}$  was a characteristic absorption peak formed by stretching vibrations of C=O on  $-$ COOH. The weak absorption peak near 1047 cm<sup>-1</sup> indicated that there were single C–O bonds on the carbon black surfaces. Therefore, from infrared spectral analysis, it was concluded that there were hydroxyl and carboxyl groups on these pyrolytic carbon surfaces.

## Pyrolytic Carbon Adsorption MB Experiments

Based on all the characterization results above,  $500^{\circ}$ C and 20 min holding time were chosen as the pyrolytic conditions for preparing pyrolytic carbon. Therefore, pyrolytic carbon produced under these conditions was used as the test material for MB adsorption tests.

## pH Effects

Solution pH is an important factor affecting adsorption. As the pH of dye wastewater varies greatly, a total of 10 pH values from 3 to 11 were

selected for measurement (Fig. [3](#page-4-0)). Under acidic conditions, the adsorption rate of pyrolytic carbon was low, which was due to the combination of adsorbent pyrolytic carbon surface properties and MB's chemical nature, appearing as cations in solution. According to infrared spectral analysis, pyrolytic carbon surfaces possessed hydroxyl and carboxyl groups, which easily combined with aqueous H<sup>+</sup> ions to yield positively charged pyrolytic carbon surfaces. Electrostatic repulsion thus occurred between the positively charged species, thereby impeding adsorption effects. As the pH increased, the amount of pyrolytic carbon adsorbed to the MB gradually increased because the surfaces became negatively charged under alkaline conditions and, as MB is a positive dye, electrostatic attraction occurred between them.

#### Kinetic Analysis of Adsorption

According to Eq. [1](#page-2-0), the MB adsorption at time  $t$ was calculated according to Eq. 2:

$$
Q_t = \frac{V(C_0 - C_t)}{W} \tag{2}
$$

in which  $Q_t$  (mg  $\mathrm{g}^{-1}$ ) represents MB adsorption at time t, and  $C_0$  and  $C_t$  (mg L<sup>-1</sup>) the initial solution concentrations before adsorption and solution concentration at equilibrium at time  $t$ , respectively, with  $V$  (mL) the solution volume, and  $W$  (mg) the adsorbent mass.

Kinetic model fitting was performed based on data from the adsorption kinetics. The commonly used fitting model was mainly a pseudo-first-order kinetic model (PFOKM) and pseudo-second-order kinetic model (PSOKM). $^{29,30}$  $^{29,30}$  $^{29,30}$  The fitting equations for these two models were

$$
Q_t = Q_e - Q_e e^{-k_1 t} \tag{3}
$$

$$
Q_t = \frac{k_2 Q_{\rm e}^2 t}{1 + k_2 Q_{\rm e} t} \tag{4}
$$

with  $Q_t$  the MB adsorption amount at time t,  $Q_e$  the adsorption amount when adsorption reached equilibrium,  $t$  the time, and  $k_1$  and  $k_2$  the rates of PFOKM and PSOKM, respectively. The value " $h$ " is the initial adsorption rate, calculated using Eq. 5, and the half equilibrium time,  $t_{1/2}$ , required in PSOKM calculated using Eq. 6:

$$
h = k_2 Q_e^2 \tag{5}
$$

$$
t_{1/2} = \frac{1}{k_2 Q_{\rm e}} \eqno(6)
$$

The adsorption kinetics of pyrolytic carbon adsorption of MB showed that the MB adsorption rate on pyrolytic carbon initially rose rapidly (Fig. [4a](#page-6-0)). When adsorption equilibrium was approached, MB adsorption gradually decreased. After about 16 h, adsorption reached equilibrium,

and the adsorbed amount of MB became constant. According to the results, it can be clearly seen that the pyrolytic carbon adsorption of MB was most in line with PSOKM with a correlation coefficient,  $R^2$ , of 0.992. This meant that the adsorption rate was linear with the reactant concentrations, which implied that the adsorption process was chemical adsorption.<sup>[31](#page-7-0)</sup> As a cationic dye, MB might have been bound to groups, such as hydroxyl and carboxyl, on the carbon surfaces during adsorption. Specific kinetic data are shown in supplementary Table S-2.

#### Adsorption Isotherm

The MB adsorption mechanism on pyrolytic carbon was investigated by performing isothermal adsorption experiments under different MB concentrations. Isothermal adsorption data were nonlinearly fitted using the Langmuir and Freundlich models. Of these, the Langmuir model assumed that the adsorption process was monolayer and homogeneous adsorption, while the Freundlich model assumed that the entire adsorption process was heterogeneous surface adsorption and that the surface adsorption heat distribution was not uniform[.32–](#page-7-0)[34](#page-8-0) The equations for the Langmuir and Freundlich models were expressed as

$$
Q_{\rm e} = \frac{K_{\rm L} Q_{\rm m} C_{\rm e}}{1 + K_{\rm L} C_{\rm e}}\tag{7}
$$

$$
Q_{\rm e} = K_{\rm F} C_{\rm e}^{1/n} \tag{8}
$$

in which  $Q_{\rm m}$  (mg  ${\rm g}^{-1}$ ) is the maximum adsorption amount,  $Q_{\rm e}^{\rm im}$  (mg g<sup>-1</sup>) and  $C_{\rm e}$  (mg L<sup>-1</sup>) the adsorption amount and solution concentration at adsorption equilibrium, respectively,  $K_{\text{L}}$  and  $K_{\text{F}}$  the affinity constants of the Langmuir isotherm and the direction constant of the Freundlich isotherm, respectively, and  $1/n$  a heterogeneous factor and related to adsorption strength.

The results of the adsorption isotherm analysis showed that the adsorption isotherm of pyrolytic carbon adsorption MB was more consistent with the Langmuir model, with a correlation coefficient,  $R^2$ , of 0.994, which indicated that the adsorption process was monolayer adsorption (Fig. [4](#page-6-0)b). Also, the maximum adsorption capacity of this pyrolytic carbon on MB was 71.6 mg  $g^{-1}$  at pH 7 and 298 K. The specific adsorption isotherm data are shown in supplementary Table S-3.

## Adsorption Thermodynamics

Considering the adsorption thermodynamics, the details of the adsorption process and its affecting factors were revealed by analyzing the adsorption thermodynamics of the adsorbent pyrolytic carbon to MB at different temperatures, which were calculated using  $(Fig. 5)$  $(Fig. 5)$  $(Fig. 5)$  in Eqs. 9 and [10](#page-6-0):

$$
\Delta G = -RT \ln K_0 \tag{9}
$$

<span id="page-6-0"></span>

Fig. 4. (a) Kinetic simulation curve of adsorption of pyrolytic carbon on MB; (b) absorption isotherm curve of pyrolytic carbon on MB.



Fig. 5. Thermodynamic properties of MB on pyrolytic carbon at 298, 318, and 338 K: (a) is a plot of ln Cs/Ce against Cs; (b) van't Huff plots of ln  $K_0$  against 1/T.

$$
\ln K_0 = \frac{\Delta S}{R} - \frac{\Delta H}{RT}
$$
 (10)

in which  $\Delta G$  (kJ mol<sup>-1</sup>) is Gibbs free energy and used to predict the adsorption mode,  $K_0$  the adsorption equilibrium constant at different temperatures, R the gas molar constant, 8.314 J  $K^{-1}$  mol<sup>-1</sup>, T (K) the temperature,  $\Delta S$  (J  $K^{-1}$  mol<sup>-1</sup>) the entropy, and  $\Delta H$  (kJ mol<sup>-1</sup>) the enthalpy or metamorphosis. Also,  $\ln(K_0)$  was linear with  $T^{-1}$  and the values of  $\Delta H$  and  $\Delta S$  were obtained from the slope of the  $\Delta H/R$  line and the intercept  $\Delta S/R$ , respectively. Specific adsorption thermodynamic related data have been collected in supplementary Table S-4. The obtained calculations, in the temperature range of 298– 318 K, Gibbs free energy of  $\Delta G < 0$  and enthalpy change of  $\Delta H > 0$ , indicated that the MB adsorption on pyrolytic carbon was a spontaneous endothermic process and that temperature elevation facilitated the adsorption reaction.<sup>[35](#page-8-0)</sup>

There have been many studies to date regarding MB adsorption. We compared here the maximum adsorption capacity of MB adsorbents under optimal conditions, and the pyrolytic carbon used here was found to have a large adsorption capacity. The results are shown in Table [III](#page-7-0). In addition, compared with these adsorbents, the cost of pyrolytic carbon was very low because it was a product from waste tires. Meanwhile, the carbon material's high adsorption efficiency for MB without any modification presents an outstanding advantage with the pyrolytic carbon displaying excellent reusability as an efficient adsorbent for the recovery of MB. The results are presented in supplementary Fig. S-4. Thus, pyrolytic carbon has been found to be an effective adsorbent for adsorbing MB.

## **CONCLUSION**

The structure and physicochemical properties of carbon pyrolytic products from waste tires were studied under high-temperature microwave



<span id="page-7-0"></span>

pyrolysis. The main conclusion was that pyrolytic carbon has a porous structure and large specific surface area, which facilitated its application in MB adsorption. Experimental results showed that MB adsorption by this carbon conformed to the Langmuir model, which addressed monolayer adsorption. MB adsorption behavior conformed to the pseudosecond-order kinetic equation and the whole adsorption process was a spontaneous endothermic reaction. At  $pH = 7$  and 298 K, the maximum adsorption capacity of pyrolytic carbon for MB was 71.6 mg  $g^{-1}$ , which meant that this carbon exhibits great promise for adsorbing dyes. Waste tires were microwave-pyrolyzed to form pyrolytic carbon, and then the carbon was applied for MB adsorption from MB wastewater, indicating a good use for recycled waste tires. Based on the present contributions, these results support the use of pyrolytic carbon as an adsorbent with an adsorption performance equivalent to commercial activated carbon.

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# ELECTRONIC SUPPLEMENTARY MATERIAL

The online version of this article [\(https://doi.org/](https://doi.org/10.1007/s11837-019-03658-7) [10.1007/s11837-019-03658-7](https://doi.org/10.1007/s11837-019-03658-7)) contains supplementary material, which is available to authorized users.

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