Enhancing the adsorption capability of areca leaf biochar for methylene blue by $K_2FeO_4$-catalyzed oxidative pyrolysis at low temperature

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Catalytic oxidative pyrolysis is a promising method for the preparation of highly adsorptive biochar by introducing oxygen-containing groups. Here, a $K_2FeO_4$-catalyzed oxidative pyrolysis was described for enhancing the adsorption capability of areca leaf biochar toward methylene blue at low temperature. It was shown that the maximum adsorption capacity of the biochar pyrolyzed at 200 °C was greatly improved from 122.67 to 251.95 mg g\(^{-1}\) with the catalysis of $K_2FeO_4$ due to the introduction of surface oxygen-containing groups. In addition, a high adsorption capability was observed over a wide pH range for the $K_2FeO_4$-modified biochar and nearly neutral pH was obtained after adsorption, further demonstrating the great advantages of $K_2FeO_4$-catalyzed oxidative pyrolysis. Mechanistic studies revealed that the adsorption of the pristine biochar was mainly determined by hydrogen bonding and electrostatic interaction, whereas, the adsorption of the $K_2FeO_4$-modified biochar was attributed to cation exchange besides hydrogen bonding and electrostatic interactions.

1. Introduction

Biochar, a carbon-rich material made by thermal conversion of biomass under limited oxygen atmosphere, has attracted increasing attention as a green and low-cost adsorbent for environmental remediation. Generally, pristine biochar can be easily prepared by conventional pyrolysis, gasification, torrefaction and hydrothermal carbonization, but suffered from low adsorption capability. For expanding the application of biochar, acid, alkaline, oxidation and mineral-impregnation modifications have been developed for improving the adsorption capability of biochar in the past decay. However, excessive chemicals are usually employed, causing potential pollution during preparation. Moreover, relatively high pyrolysis temperature is required, causing high energy consumption and loss of functional groups which play an important role in adsorption. Thus, green modification with low pyrolysis temperature is highly pursued for enhancing the adsorption capability of biochar.

Catalytic pyrolysis, an efficient technology for accelerating carbonization of biomass using a catalytic amount of promoter, can be a green method for preparation of biochar. However, it is a challenge to make highly adsorptive biochar via catalytic pyrolysis as easily causing loss of surface functional groups even at low temperature. Comparing with other catalytic pyrolysis, catalytic oxidative pyrolysis can produce additional oxygen-containing groups, thereby cover the shortage of functional group decrease. Anyhow, it is of vital importance to find out a highly active catalyst for the preparation of highly adsorptive biochar. An efficient oxidation catalyst can promote oxidative carbonization of biomass to generate surface functional group-rich biochar at low temperature. To the best of our knowledge, no catalytic oxidative pyrolysis has been developed for improving the adsorption capability of biochar by now.

Methylene blue (MB), a common toxic and coloured pollutant, is widely present in wastewater discarded from printing, paper and textile industries. MB can be persisted for a long time even exposure to light and water, causing serious threat not only to human health but also to environment. Great advance has been made for removal of MB using biochar as adsorbent over the past decade. Especially, the ZnCl\(_2\), H\(_2\)\(_2\)O\(_4\)\(^{2-}\) and NaOH-engineered biochars were prepared for removal of MB from aqueous solution due to their relatively high adsorption capabilities. Yet, largely excessive modifier and high pyrolysis temperature are required for the preparation of these biochars.

Here, a $K_2FeO_4$-catalyzed oxidative pyrolysis was explored for the preparation of highly adsorptive areca leaf biochar for removal of MB from aqueous solution. Being a strong oxidant, $K_2FeO_4$ should effectively catalyze oxidative carbonization of biomass to generate oxygen-containing group-rich biochar at
low temperature. The targets of this study were to: (1) developed a green method for improving the adsorption capability of biochar, (2) evaluate the adsorption capability of the biochar toward MB in aqueous solution, (3) illuminate the adsorption mechanism.

2. Materials and methods

2.1 Materials

Area leaves were obtained from Fengyu farm in Ledong county of Hainan province, China. The chemicals including HCl, KOH, MB and K₂FeO₄ were analytically pure reagents purchased from Aladdin and Macklin in Shanghai of China. A MB solution (1000 mg L⁻¹) was prepared by dissolving 1000 mg MB into 1 L deionized water, then diluted to the desired concentrations (25-350 mg L⁻¹). The pH of MB solution was adjusted by HCl or NaOH solution with suitable concentration.

2.2 Biochar preparation

The dried area leaves were washed with water to remove impurities, dried in an oven at 60 °C for 24 h. The area leaves were cut into small pieces, then pulverized and passed through a 60 mesh sieve to obtain a powder having a particle diameter of less than 2.5 mm. The area leaf powder was pre-treated with K₂FeO₄ followed by pyrolysis to make modified biochar (MBC). Briefly, 0.5 g K₂FeO₄ was quickly dissolved in 100 mL of deionized water, then 5 g area leaf powder was added to the aqueous solution, sonicated in an ultrasonic cleaner for 120 minutes and dried in an oven at 60 °C. The pre-treated area leaf powder was pyrolyzed at different temperatures in a vacuum tube furnace under nitrogen with a heating rate of 5 °C/min for 150 minutes, and dried at 60 °C with 180 rpm speed for desired time. For investigating the effect of pyrolysis temperature, the adsorption was performed at 25 °C for 24 h using 100 mg L⁻¹ MB concentration. The effect of initial pH was investigated in 150 mg L⁻¹ MB solution over a range of pH from 3 to 9 for 24 h. The 1/8, 1/4, 1/2, 3/4, 4/4, 5/4 ratios of biochar to MB solution (mg mL⁻¹) were employed to study the effect of biochar dosage by performing the adsorption in 100 mg L⁻¹ MB solution for 36 h. The kinetic adsorption experiments were investigated at 25 °C and pH 7 with different time intervals (0.25, 0.5, 1, 2, 4, 8, 12, 16, 24, 30, 36 and 48 h). The SSA of pristine biochar was mainly comprised of C, O, N, and sharply decreased while rose to 600 °C. The SSA of pristine biochar and modi ed biochars were named PBC200, PBC300, PBC400, PBC500, PBC600 and MBC200, MBC300, MBC400, MBC500, MBC600, respectively. Additionally, the MBCs pyrolyzed at 200 °C with 1/20 and 1/5 mass ratios of K₂FeO₄ to biomass were labelled as MBC200-1 and MBC200-2, respectively.

2.3 Biochar characterization

The physical parameters including the specific surface area (SSA), pore volume (PV), and pore diameter (PD) were determined by nitrogen gas sorption isotherm on a surface area and porosity analyzer (Micromeritics ASAP 2460, America). The SSA was calculated by Brunauer–Emmett–Teller (BET) method. The PV and PD were calculated by Barret–Joyner–Halenda (BJH) method.

Fourier transform infrared spectroscopy (FTIR) was applied to determine the functional groups of biochar. A certain amount of biochar (2 mg) and KBr (1000 mg) were mixed, ground and pressed into sheet, then recorded between 400 and 4000 cm⁻¹ on a FTIR spectrometer (Bruker Tensor 27, Ettlingen, Germany). The surface functional group and element composition was characterized by an X-ray photoelectron spectrometer (XPS) (Thermo Scientific Escalab 250Xi, America).

The element content of biochar was measured on an organic element analyzer (Thermo Scientific Flash 2000 CHNS/O, America) and an inductive couple plasma (ICP) elemental analyzer (Agilent ICPOES 730, America). The possible crystalline of the biochar was examined on an X-ray diffractometer (Brucker D8 Advance, Germany).

2.4 Batch adsorption experiments

Generally, the adsorption experiments were carried out by mixing 20 mg area leaf biochar and 40 mL MB solution into a 150 mL flask, then shaken in a constant temperature oscillator with 180 rpm speed for desired time. For investigating the effect of pyrolysis temperature, the adsorption was performed at 25 °C for 24 h using 100 mg L⁻¹ MB concentration. The effect of initial pH was investigated in 150 mg L⁻¹ MB solution over a range of pH from 3 to 9 for 24 h. The 1/8, 1/4, 1/2, 3/4, 4/4, 5/4 ratios of biochar to MB solution (mg mL⁻¹) were employed to study the effect of biochar dosage by performing the adsorption in 100 mg L⁻¹ MB solution for 36 h. The kinetic adsorption experiments were investigated at 25 °C and pH 7 with different time intervals (0.25, 0.5, 1, 2, 4, 8, 12, 16, 24, 30, 36 and 48 h), respectively. All the experiments were performed in triplicates.

The concentration of MB solution was measured on an UV-vis spectrophotometer (MAPADA UV-3300PC, Shanghai of China) at 665 nm. The adsorption capability was determined by the difference of MB concentrations before and after adsorption. The adsorption capabilities of PBC and MBC were calculated by the equation expressed as:

\[ q_t = (C_0 - C_t)V/M \]

\( q_t \) (mg g⁻¹) is the adsorption capability of biochar; \( C_0 \) (mg L⁻¹) and \( C_t \) (mg L⁻¹) are the concentrations of MB solution at adsorption time \( t \) respectively; \( V \) (L) is the volume of MB solution; \( M \) (g) is the weight of PBC and MBC.

3. Results and discussion

3.1 Biochar characterization

As shown in Table 1, both pristine and modified biochars were of mesoporous as other ones. The SSA of pristine biochar increased as the pyrolysis temperature increased from 200 to 500 °C, and sharply decreased while rose to 600 °C. For the modified biochar, the SSA always increased with pyrolysis temperature. It was noted that both PBC200 and MBC200 were poor of SSA and PV. Thus, these properties contributed less to the adsorption capacities of PBC200 and MBC200.

The total element composition of biochar was presented in Table 2. The pristine biochar was mainly comprised of C, O, N,
Table 1 Physical characteristics of biochar

| Biochar | SSA (m² g⁻¹) | PV (cm³ g⁻¹) | PD (nm) |
|---------|--------------|--------------|---------|
| PBC200  | 0.62         | 0.0022       | 11.69   |
| PBC300  | 2.15         | 0.0103       | 16.86   |
| PBC400  | 6.45         | 0.0177       | 10.25   |
| PBC500  | 42.98        | 0.0229       | 4.03    |
| PBC600  | 1.16         | 0.0156       | 41.53   |
| MBC200  | 0.66         | 0.0033       | 17.41   |
| MBC300  | 1.28         | 0.0070       | 18.44   |
| MBC400  | 5.23         | 0.0121       | 16.01   |
| MBC500  | 5.43         | 0.0127       | 29.79   |
| MBC600  | 79.29        | 0.0234       | 9.93    |

Table 2 Element composition of biochar

| Biochar | C   | O   | N   | H   | O/Cx | N/Cx | Fe  | K  |
|---------|-----|-----|-----|-----|------|------|-----|----|
| PBC200  | 47.87 | 35.83 | 1.43 | 5.89 | 0.56 | 0.026 | 0.02 | 0.01 |
| PBC300  | 55.06 | 21.68 | 1.63 | 4.73 | 0.30 | 0.025 | 0.03 | 0.49 |
| PBC400  | 53.88 | 15.31 | 1.75 | 3.71 | 0.21 | 0.027 | 0.04 | 0.75 |
| PBC500  | 50.17 | 10.66 | 1.63 | 3.22 | 0.13 | 0.023 | 0.06 | 1.03 |
| PBC600  | 68.01 | 8.56  | 1.88 | 2.64 | 0.09 | 0.024 | 0.09 | 0.65 |
| MBC200  | 43.36 | 33.95 | 1.27 | 5.59 | 0.59 | 0.025 | 5.40 | 1.41 |
| MBC300  | 47.45 | 27.46 | 1.61 | 4.32 | 0.43 | 0.029 | 8.36 | 1.45 |
| MBC400  | 48.63 | 23.57 | 1.40 | 3.68 | 0.36 | 0.025 | 8.16 | 2.94 |
| MBC500  | 48.70 | 29.90 | 1.23 | 2.46 | 0.33 | 0.022 | 9.53 | 3.40 |
| MBC600  | 50.96 | 19.40 | 1.18 | 2.48 | 0.29 | 0.020 | 10.21 | 3.13 |

and H with small amount of Fe and K. The modified biochar had similar elements with PBC200, but owned much more iron and potassium which could be derived from K₂FeO₄. The O content of both biochars decreased with increasing pyrolysis temperature as expected. Importantly, the O/C ratio of the modified biochar was usually higher than that of the pristine biochar, so new oxygen containing groups were introduced through K₂FeO₄ oxidation. N/C ratio of MBC200 was comparable to PBC200, suggesting nitrogen-containing groups could survive with K₂FeO₄ catalysis.

The FTIR spectra of biochars pyrolyzed at different temperatures were shown in Fig. 1. The broad peaks at approximately 3446 cm⁻¹ were assigned to –OH stretching vibrations. The peaks around 1634 cm⁻¹ attributed to C=O and aromatic C=C stretching vibrations. The adjacent peaks at about 1425 cm⁻¹ were also assigned to aromatic C=C stretching vibrations. The peaks around 1383 cm⁻¹ represented COOH asymmetric bending vibrations. The peaks around 1101 and 1059 cm⁻¹ corresponded to aromatic and aliphatic C–O stretching vibrations, respectively. The peaks at 897 cm⁻¹ represented aromatic C–H bending vibrations.

The pristine biochar was mainly consisted of OH, COOH, C=O, C=O, C–O and aliphatic C–H groups as prepared at low temperature (≤ 400 °C). As previous reports, the C=O peaks decreased and aromatic structure formed while higher temperature was applied. Interestingly, the pristine biochar prepared at 500 and 600 °C was still rich of C=O groups as C=O peaks (1101 cm⁻¹) became stronger. This was opposed to other reports. Comparing to the corresponding pristine biochar, the modified biochar was much richer in aliphatic C–O and COOH groups as pyrolyzed at 200 °C. The aliphatic C–O groups of modified biochar decreased but no aromatic rings formed while increasing pyrolysis temperature. Moreover, strong peaks of C=O around 1634 cm⁻¹ were always observed for the modified biochar. This demonstrated that K₂FeO₄ catalyzed pyrolysis could generate oxygen containing groups. As a result, K₂FeO₄ catalysis was beneficial to preparing oxygen containing group-rich biochar at low temperature.

The morphology of PBC200 and MBC200 was shown in Fig. 2. PBC200 was consisted of inhomogenous microparticles of which the surface was embedded with nbeans in row. With catalysis of K₂FeO₄, smaller microparticles with flocculences and micropores were obtained for MBC200. Therefore, K₂FeO₄ could efficiently accelerate the decomposition of areca leaf, which was helpful for making thermostable biochar at low pyrolysis temperature.

XPS spectra showed that the surface oxygen of MBC200 was much more than that of PBC200 due to K₂FeO₄ oxidation (Fig. 3). Whereas, only trace amount of iron was detected on the surface of MBC200, thereby iron was mostly embedded
inside MBC200. The C 1s and O 1s spectra and their deconvolution results were shown in Fig. 4. The peaks centered at 284.8, 286.3 and 288.6 eV represented C–C, C–O and –CO2 groups, respectively. Both biochars were consisted of C–C/C=C, C–O and –CO2 groups. Obviously, both C–O and –CO2 groups of MBC200 were higher than that of PBC200, indicating new oxygen-containing groups were generated onto the surface of MBC200 with K2FeO4 oxidation. Moreover, a new peak at 530.5 eV, which could be assigned to Fe–O groups, was observed on MBC200, indicating iron oxides were introduced.

The XRD patterns showed that a sharp diffraction peak at 21.38° and a broad diffraction peak between 8.30° and 27.02° (Fig. 5) were obtained for both PBC200 and MBC200. The peak around 21.38° could be attributed to well crystalline aliphatic carbon. The broad peaks represented (110) and (200) planes of cellulose I. The diffraction peak intensity of MBC200 was much weaker than that of PBC200 due to the oxidation of K2FeO4. No diffraction peaks of magnetic iron oxides such as Fe3O4 and γ-Fe2O3 were observed for MBC200, so no magnetism was obtained.

3.2 Adsorption behaviours toward MB

3.2.1 Effect of preparation parameters on adsorption capability. Pyrolysis temperature, a vital preparation parameter determining the physicochemical properties of biochar, significantly affected adsorption capability. As seen in Fig. 6a, the adsorption capabilities of pristine and modified biochars toward methylene blue sharply decreased as the pyrolysis temperature increased from 200 to 300 °C. While further increasing pyrolysis temperature, the adsorption capabilities tardily decreased. Hence, the optimal pyrolysis temperature was 200 °C. The adsorption capability of modified biochar was always better than that of pristine one pyrolyzed at the same temperature. It was worthy to note that the adsorption capability of the biochar prepared at 200 °C was greatly raised from 76.62 to 189.32 mg g−1 with K2FeO4 modification. This could be ascribed to the introduction of additional oxygen-containing groups.

The dosage of K2FeO4 was also investigated (Fig. 6b). It was found that the adsorption capability remarkably increased as enhancing the weight ratio of K2FeO4 to biomass from 1/20 to 1/10, and rarely increased as further rising the dosage to 1/5. Anyway, these modifications all leded to the increase of adsorption capability, demonstrating that the improvement of adsorption capability could be realized by using catalytic amount of K2FeO4. Considering both adsorption efficiency and K2FeO4 dosage, PBC200 and MBC200 were applied for studying their adsorption behaviours in the following experiments.

3.2.2 Effect of adsorption parameters on adsorption capability. As a crucial factor influencing the ion state of MB and surface functional groups of biochar, solution pH played an important role in adsorption of MB. The adsorption capability of PBC200 gradually increased with initial pH (Fig. 7a). For
MBC200, the adsorption capability greatly increased from 112.86 to 190.10 mg g\(^{-1}\) as the initial pH was raised from 3 to 4, and almost maintained at this level while further increasing pH.

This indicated that high adsorption capability was obtained for MBC200 over a wide pH range. Moreover, MBC200 always exhibited higher adsorption capability than PBC200 at the same initial pH.

The change of pH was recorded after adsorption (Fig. 7b). For PBC200, the pH slightly increased as the adsorption was performed between pH 3 and pH 6, and almost kept constant at about 7 while carried out beyond pH 6. For MBC200, the pH increased a little as pH 3 was applied and almost maintained around 7 when the adsorption was performed above pH 3.

The effect of biochar dosage was also investigated (Fig. 8). The removal rate of MB by PBC200 gradually increased as enhancing the dosage from 0.125 to 1.25 g L\(^{-1}\). Removing 90% of MB required 1.25 g L\(^{-1}\) PBC200. For MBC200, the removal rate of MB rapidly increased up to 92.16% with the increase of dosage from 0.125 to 0.5 g L\(^{-1}\), and slightly rose as further increasing the dosage. This also demonstrated that MBC200 surpassed PBC200 for removing MB from aqueous solution.

3.2.3 Adsorption kinetics. The adsorption kinetics was depicted in Fig. 9. The adsorption of MB by PBC200 increased with adsorption time and reached equilibrium after 30 h. The removal of MB by MBC200 quickly increased during initial 5 h, then gradually slowed down and finally reached equilibrium after 30 h. The equilibrium adsorption capability of MBC200 was more than two times higher than that of PBC200. Thus, K\(_2\)FeO\(_4\)-catalyzed modification resulted in the improvement of adsorption rate for MB.

The adsorption kinetic data was matched by pseudo-first-order and pseudo-second-order model (Table 3). The adsorption kinetics of PBC200 and MBC200 were better fitted by pseudo-second-order model than pseudo-first-order model with extremely high determination coefficients. Moreover, the calculated equilibrium adsorption capabilities of pseudo-second-order model were much closer to the experimental results than that of pseudo-first-order model for both biochars. This suggested that the adsorptions should be chemisorption-controlled processes.

3.2.4 Adsorption isotherms. The adsorption isotherms were investigated at different temperatures (Fig. 10). The adsorption capacity of PBC200 generally increased with initial concentration until reached maximum. MBC200 exhibited

![Fig. 7 Effect of solution pH (a) and pH variation after adsorption (b) [20 mg biochar, 40 mL MB solution (150 mg L\(^{-1}\)), pH = 7, 25 °C, 180 rpm, 24 h]. The error bars represented the standard deviation of triplicates.

![Fig. 8 Effect of biochar dosage (100 mg L\(^{-1}\) MB solution, pH = 7, 25 °C, 180 rpm, 36 h). The error bars represented the standard deviation of triplicates.

![Fig. 9 Adsorption kinetics (20 mg biochar, 40 mL MB solution, pH = 7, 25 °C, 180 rpm). The error bars represented the standard deviation of triplicates.

| BC            | \(C_0\) (mg L\(^{-1}\)) | \(q_{e,exp}\) | \(q_{e,cal}\) | \(k_1\) | \(R^2\) | \(q_{e,exp}\) | \(q_{e,cal}\) | \(k_2\) | \(R^2\) |
|---------------|------------------------|---------------|---------------|--------|-------|---------------|---------------|--------|-------|
| PBC200        | 75                     | 81.06         | 27.97         | 0.079  | 0.96380 | 81.06         | 81.16         | 0.0134 | 0.99855 |
|               | 100                    | 92.14         | 41.22         | 0.136  | 0.92976 | 92.14         | 93.37         | 0.0118 | 0.99866 |
|               | 150                    | 105.27        | 46.53         | 0.121  | 0.96643 | 105.27        | 106.61        | 0.0098 | 0.99884 |
| MBC200        | 75                     | 118.46        | 63.08         | 0.128  | 0.98586 | 118.46        | 120.92        | 0.0068 | 0.99835 |
|               | 100                    | 146.38        | 54.28         | 0.215  | 0.94167 | 146.38        | 146.62        | 0.0169 | 0.99984 |
|               | 150                    | 214.70        | 95.92         | 0.309  | 0.94537 | 214.70        | 218.34        | 0.0052 | 0.99954 |
|               | 200                    | 231.17        | 103.21        | 0.283  | 0.90626 | 231.17        | 234.74        | 0.0044 | 0.99932 |

Table 3 The fitted results of kinetic data
higher adsorption capacity than PBC200. The maximum adsorption capacities of both biochars slightly rose with adsorption temperature, implying these adsorptions were exothermic.

The adsorption isotherm data was simulated by Langmuir and Freundlich models (Table 4). The adsorption processes of PBC200 and MBC200 were better described by Langmuir model than Freundlich model with extremely high correlation coefficients. In addition, the experimental maximum adsorption capacities approximated to the calculated results of Langmuir model. This indicated the removal of MB was a monolayer adsorption process.

It was noted that the adsorption capacity of MBC200 was superior or comparable to that of most adsorbents reported in the literature (Table 5).

### 3.2.5 Adsorption mechanism

As performing the adsorption of MBC200 at pH 4, the pH significantly rose after adsorption (Fig. 7b), indicating MBC200 had high cation exchange capability due to the generation of carboxylates (Fig. 4). Therefore, it could be concluded that cation exchange played an important role in the adsorption of MBC200. Instead, the pH change was not obvious after adsorption for PBC200, implying cation exchange less occurred. Thus, the introduction of new carboxylates contributed to the increase of adsorption capability with K2FeO4 modification.

As shown in Fig. 11, the C–N feature peaks of MB at 1398 and 1339 cm\(^{-1}\) shifted to 1385 and 1325 cm\(^{-1}\) as MB was adsorbed onto PBC200 and MBC200. Meanwhile, the COOH peaks of PBC200 and MBC200 around 1733 cm\(^{-1}\) almost disappeared after adsorption, probably attributing to the red shift of COOH peaks to lower wave-numbers which was overlapped by the peaks around 1628 cm\(^{-1}\). Moreover, the COOH peaks appeared after desorption of MB in mixture of acetic acid/ethanol (1/9 volume ratio). These clearly demonstrated that hydrogen bonds were formed between MB and both biochars during adsorption.

As PBC200 and MBC200 were rich of surface oxygen containing groups, negatively charged surface might be generated under neutral conditions. Hence, the MB cation could be adsorbed onto the biochar surface by electrostatic interaction at pH 7.

### Table 4 The fitted parameters of isotherm data

| BC    | \(T\) (°C) | \(q_{\text{exp, max}}\) (mg g\(^{-1}\)) | \(q_{\text{cal, max}}\) (mg g\(^{-1}\)) | \(K_l\) | \(R^2\) | \(K_F\) | \(1/n\) | \(R^2\) |
|-------|------------|----------------------------------------|----------------------------------------|--------|-------|--------|-------|-------|
| PBC200| 15         | 89.66                                  | 90.09                                  | 0.444  | 0.9993| 52.03  | 0.107 | 0.64727|
|       | 25         | 110.40                                 | 113.64                                 | 0.073  | 0.9907| 45.41  | 0.158 | 0.85621|
|       | 35         | 122.57                                 | 125.15                                 | 0.102  | 0.9955| 48.61  | 0.172 | 0.85968|
|       | 45         | 122.67                                 | 125.47                                 | 0.123  | 0.9987| 49.43  | 0.173 | 0.90803|
| MBC200| 15         | 211.05                                 | 213.22                                 | 0.279  | 0.9994| 85.99  | 0.179 | 0.51464|
|       | 25         | 213.47                                 | 216.45                                 | 0.352  | 0.9997| 87.13  | 0.183 | 0.50834|
|       | 35         | 223.71                                 | 226.75                                 | 0.259  | 0.9996| 86.25  | 0.191 | 0.56792|
|       | 45         | 251.95                                 | 257.73                                 | 0.169  | 0.9990| 81.84  | 0.226 | 0.66859|

### Table 5 List of different adsorbents and their maximum adsorption capabilities (\(q_{\text{max}}\)) towards MB

| Adsorbent                                                                 | \(q_{\text{max}}\) (mg g\(^{-1}\)) | Ref. |
|---------------------------------------------------------------------------|-----------------------------------|------|
| NaOH-activated carbon                                                     | 890                               | 47   |
| Ca(NO\(_3\)_2)-activated carbon fiber                                     | 295                               | 48   |
| Carbon polyhedral                                                         | 354                               | 49   |
| Magnetic chitosan/graphene oxide composite                                | 180.83                            | 50   |
| Graphene oxide                                                            | 598.8                             | 51   |
| Citric acid modified kenaf core fibre                                    | 131.6                             | 52   |
| Lotus leaf                                                                | 221.7                             | 53   |
| Biochar/AIOOH nanocomposite                                               | 85.03                             | 54   |
| H\(_2\)O\(_2\)-assisted microwave activated biochar                       | 91.0                              | 21   |
| K\(_2\)FeO\(_4\)-modified biochar                                        | 251.95                            | This work |

Fig. 10 Adsorption isotherms of PBC200 and MBC200 (20 mg biochar, 40 mL MB solution, pH = 7, 48 h, 180 rpm). The error bars represented the standard deviation of triplicates.

Fig. 11 FTIR spectra of biochars after adsorption and desorption. (PBC200-A or MBC200-A: biochar after adsorption; PBC200-D or MBC200-D: regenerated biochar).
In brief, the adsorption of PBC200 could be mainly attributed to hydrogen bonding and electrostatic interaction. Differently, the adsorption of MBC200 involved cation exchange besides hydrogen bonding and electrostatic interaction.

4. Conclusions

A catalytic amount of K$_2$FeO$_4$ could effectively promote oxidative pyrolysis of areca leaf for preparation of highly adsorptive biochar for MB at 200 °C. The oxygen-containing groups were introduced onto the biochar through K$_2$FeO$_4$-catalyzed oxidative pyrolysis, where the functional groups of areca leaf were also mostly reserved. Therefore, the biochar displayed much higher adsorption capability than the pristine one. Moreover, high adsorption capability was observed over a wide pH range and nearly neutral pH was gained after adsorption. This will make the biochar serve as a promising adsorbent for remediation of MB-polluted wastewater in practice.

Conflicts of interest

There are no conflicts of interest to declare.

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