Ultrafast removal of methylene blue from water by Fenton-like pretreated peanut hull as biosorbent

Dongcan Lv, Guangce Jiang, Chengpeng Li, Qianchen Zhu and Zhimin Wang

College of Science, Henan Agricultural University, Zhengzhou, Henan, People’s Republic of China

ABSTRACT
Modiﬁed biomass is a green and renewable sorbent to remove organic pollutants in water. In this study, an eﬃcient bio-based adsorbent was obtained by Fenton-like pretreatment of peanut hull with FeOCl, which can be used to eﬃciently remove methylene blue from water. The adsorption experiment showed that under the conditions of 25°C, pH 6.0, MB concentration of 100 mg·L−1 and adsorbent dosage of 1.0 g·L−1, the adsorption equilibrium could be achieved within 6 min, with MB removal rate of 85.1% and maximum adsorption capacity of 132 mg·g−1, which was much higher than that of untreated peanut hull (64 mg·g−1). Material characterization showed that Fenton-like pretreatment resulted in the surface morphology change and pore structure formation of peanut hull, and the speciﬁc surface area increased signiﬁcantly, which was an important reason for rapid adsorption. The adsorption mechanism showed that the adsorption of methylene blue followed pseudo-second-order models, and conformed to Redlich-Peterson and Langmuir models. According to the thermodynamic analysis results, it is concluded that the adsorption process is endothermic and spontaneous. Adsorption mechanism includes hydrogen bonding, static electricity and van der Waals force.

Abbreviations: PH: peanut hull; PHFeOCl: peanut hull pretreated with FeOCl; MB: methylene blue; FT-IR: Fourier transform infrared spectroscopy; SEM: scanning electron microscopy; XRD: X-ray power diﬀraction; SSE: sum of squared errors of prediction.

1. Introduction
Water, an irreplaceable and valuable natural resource, is constantly polluted with the rapid development of society and science (1). Textile dyeing is a well-known and complicated manufacturing process followed in industries. Over 140,000 tons of organic dyes have been discharged into water without treatment annually worldwide (2). Unfortunately, organic dyes are toxic and potentially carcinogenic, which will bring risk to human and other organisms (3, 4). In order to eliminate the hazardous effects of organic dyes on the environment, numerous attempts have been made to maintain the standards and acceptable quality levels of wastewater produced during the production and utilization of dyes worldwide.
Given the shortage of resources, adsorbent materials from biomass such as algae (11, 12), sepia shell (13), fruit peels (14) were received with concern. Especially, agricultural and forestry wastes get increasingly attention due to the unique features such as environmentally friendly, cost-effective, and renewable (15, 16). Meanwhile, agricultural residues are often abandoned or burned as firewood, resulting in major environmental problems. Hence, the utilization of agricultural wastes for adsorption would increase the economic value of the treatment process, reduce the cost of waste disposal, and decrease the extent of environmental pollution (17).

Lignocellulosic biomass consists of cellulose, hemicellulose, and lignin. Thus, it contains a large number of hydroxyl groups and can be potentially used to adsorb materials. An increasing number of studies are being conducted globally on the use of renewable agricultural wastes (18). Several natural adsorbents such as coconut leaf (19), peanut hull (20), orange peel (21), radix Angelicae dahuricae residue (22), and spent substrate of Ganoderma lucidum (23) have been used to remove pollutants. However, the adsorption capacities of most pristine substances were low because of the strong hydrophobicity of pristine biomass. Hence, it is necessary to follow the process of chemical treatment to improve the adsorption efficiency of the substances. Chemically modified biomass has been pointed out as an efficient and attractive method thanks to their functional groups that actively contribute to the fixation of dye molecules on the surface (24). There are essentially two ways to improve the adsorption ability: (i) disrupting the structures of lignin, cellulose, and hemicellulose under conditions of alkaline (25) or acid treatment (26) and (ii) introduction of active groups to promote binding between the adsorbent and pollutants such as carboxymethylation (27), citrate modification (28), and quaternization (29). The modified bio-materials exhibit good adsorption capacity. However, the pretreatment processes introduce new contaminants, including organic or inorganic solutions, which can also pollute the environment. Thus, the challenge is to find feasible and low-cost approaches that follow the principle of green chemistry and can be used to achieve a green economy.

Fortunately, effective and environmentally friendly pretreatments of biomass have been explored, and Fenton-like (nano FeOCl) pretreatment method was used in our study. The Fenton-like pretreatment process was eco-friendly because solid FeOCl could be recycled, and only hydrogen peroxide (H2O2) and water were consumed. Thus, the process of converting low-cost agricultural wastes into value-added adsorbents could help in the process of multi-treatment of environmental pollutants such as accumulated agricultural wastes. The extent of water pollution and air pollution can be potentially reduced. The aim of this work is to prepare Fenton-like modified adsorbents from renewable agricultural wastes. The influences of the initial aqueous pH, ionic strength, and temperature on MB adsorption were studied. Ultimately, the adsorption kinetics, adsorption isotherm, and recyclability were evaluated. The changes in functional groups, surface morphology, and crystallinity were also investigated. In addition, the possible MB adsorption mechanism was proposed. This work reports a method for the preparation of cost-effective, environmentally-friendly, and highly efficient natural product-based adsorbents that can be used to treat wastewater.

2. Materials and methods

2.1. Materials

Peanut hull (PH) was collected from the agricultural suburb of Shangqiu (Henan Province in China). The raw material was rinsed thoroughly using ethanol and deionized water to remove fat and dust. Following this, the samples were dried at 85 °C over a period of 12 h. Dried PH was ground and sieved. Fractions of 0.7–1.5 mm were selected. Ferric trichloride (FeCl3) and H2O2 were procured from Aladdin Chemistry Co., Ltd, China. MB (C16H10ClN3S·3H2O, molecular weight 373.8 g·mol⁻¹, purity: 98%) and H2O2 were provided by Sinopharm Chemical Reagent Co., Ltd, China. Ultrapure water was used to prepare the MB stock solutions. All reagents were of analytical grade and utilized as received (they were not purified further).

2.2. Modification of peanut hull

The preparation of FeOCl was reported in our previous study (30). Ferric chloride hexahydrate (FeCl₃·6H₂O) powder was first heated at 200 °C for 2 h. Subsequently, solid FeOCl was separated following the process of
repeated centrifugation and washing. PH (5.0 g) and FeOCl (0.16 g) nanosheets were added into a 250 mL flask containing 100 mL of 2.5% of H₂O₂ (w/w) solution. Following this, the mixed solution was agitated at 500 rpm in the temperature range of 20–50 °C over 2–12 h using a magnetic stirrer. Following this, repetitive cycles of filtering and rinsing were conducted to separate the resulting mixture until a colorless and water-clear filtrate was obtained. The product was dried, collected and labeled as PHFeOCl. The preparation route of PHFeOCl was shown in Figure 1.

2.3. Characterizations

The samples were ground to form powder before conducting the experiments. An FTIR spectrometer (ThermoFisher Scientific, is10, USA) was used to record the Fourier transform infrared spectra in the range of 4000–400 cm⁻¹. The number of scans for each spectrum was 32. The crystal structures of the samples were determined using an X-ray diffractometer (XRD, Bruker, D8 Advance, Germany). The working current was 30 mA, and the working voltage was 80° at the increasing amplitude of 0.02°/s. A scanning electron microscope (SEM, Hitachi, S-3400N, Japan) was used to study the surface morphology of the samples at an accelerating voltage of 8.0 kV. The Brunauer–Emmett–Teller (BET) measurements (Quanta-chrome, NOVA2000e, USA) were conducted to determine the specific surface area (SSA). Each adsorbent was degassed at a temperature of 120 °C under vacuum for a period of 6 h. The thermogravimetry (TG) technique was used to determine the thermal stability of the samples in the temperature range of 30–850 °C. The experiments were conducted under an atmosphere of nitrogen at a heating rate of 10 °C/min. The MB absorbance was measured using a dual-beam ultraviolet and visible (UV-vis) spectrophotometer (Shimadzu, UV-3000, Japan) (2). The point of zero charge was estimated according to the method reported in previous work (11).

2.4. Batch adsorption experiments

In MB adsorption batch assays, 0.1 g of modified PH was taken in a conical flask containing 100 mL of MB solution. The sample was agitated at 180 rpm. All adsorption experiments were operated using a constant temperature shaker. The effects of adsorbent content, ionic strength, temperature, and pH on the process were examined. The predetermined MB initial concentration was in the range of 100–500 mg·L⁻¹. The adsorption temperature was set in the range of 298–318 K, and the original pH was set in the range of 2–10. The pH value of MB solution was adjusted using 0.1 M of NaOH (or HCl). The NaCl content was maintained in the range of 0.01–0.6 mol·L⁻¹. Following adsorption, the suspensions were filtrated using a filter membrane (thickness: 0.45 µm). The UV-vis spectrophotometer was used to analyze the diluted filtrate at 665 nm. All adsorption experiments were repeated three times, and the average values were used for further analysis.

2.5. Adsorption kinetics

In brief, PHFeOCl (0.1 g) was mixed with MB solution with the initial concentration of 100 mg·L⁻¹ or 50 mg·L⁻¹ (100 mL), and the resultant mixed solution was agitated at 180 rpm at 25 °C. The adsorption amount (q) at different time and equilibrium amount (qₑ) were calculated according to Equations (1) and (2), respectively. The pseudo-first-order (Equation (3)) (31), pseudo-second-order (Equation (4)) (32), and Elovich models (Equation (5)) (33) were used to fit the kinetic data.

\[ q_t = \frac{V(c_0 - c_t)}{m} \]  
\[ q_e = \frac{V(c_0 - c_e)}{m} \]  
\[ \ln(q_e - q_t) = lnq_e - k_1t \]  
\[ \frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e} \]  
\[ q_t = \alpha + \beta \ln t \] 

where \( q_t \) (mg·g⁻¹) and \( q_e \) (mg·g⁻¹) are the amounts of MB adsorbed at time \( t \) (min) and equilibrium, respectively. \( V \) (L) represents the volume of the MB solution, \( m \) (g) represents the mass of the dry modified PH used, \( c_0 \) (mg·L⁻¹) denotes the initial concentration, \( c_e \) (mg·L⁻¹) denotes the real-time concentration, \( c_e \) (mg·L⁻¹) denotes the equilibrium concentration, \( k_1 \) (min⁻¹) and \( k_2 \) (g·mg⁻¹·min⁻¹) are the corresponding rate constants. \( \alpha \) (mg·g⁻¹·min⁻¹) and \( \beta \) (g·mg⁻¹) represent the constants related to the initial reaction rate and the activation energy, respectively.

2.6. Adsorption isotherms

PHFeOCl (0.1 g) was mixed with 100 mL of MB solution over 12 h to reach equilibrium at 303, 308, 313, and 318 K. Freundlich, Langmuir, Redlich–Peterson, and Temkin isotherm models that describe how pollutants interact with adsorbents were used to fit the experimental data. Freundlich isotherm is used to study the exponential decrease of sorption energy upon adsorption center completion. Langmuir isotherm is used to study the monolayer adsorption on the surface that contains
a certain amount of adsorption sites. Temkin equation is used to estimate the efficiency of the adsorbent (34). Redlich–Peterson isotherm is a combination of the Freundlich and Langmuir isotherms and represents an empirical isotherm incorporating three parameters (35). The nonlinear forms can be expressed as follows (Equation (6), Equation (7) (36), Equation (8) (25), and Equation (9) (37), respectively):

\[
\frac{c_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{q_m K_L}
\]

(6)

\[
\ln q_e = \ln K_F + \frac{1}{n} \ln c_e
\]

(7)

\[
q_e = \frac{R T}{b} \ln K_T + \frac{R T}{b} \ln c_e
\]

(8)

\[
q_e = \frac{K_{R-P} c_e}{1 + ac_e^n}
\]

(9)

Where \( K_L \) (L·mg\(^{-1}\)), \( K_F \) (mg·g\(^{-1}\)), \( K_T \) (L·g\(^{-1}\)), and \( K_{R-P} \) (L·g\(^{-1}\)) indicate the affinity coefficient-related bonding terms, \( a \) ((mg·L\(^{-1}\))\(^n\)) and \( b \) (J·mol\(^{-1}\)) are the constants in the isotherm models and \( n \) (dimensionless) is an exponent.

### 2.7. Thermodynamics studies

The values of the thermodynamic parameters, such as Gibbs free energy (\( \Delta G \)), enthalpy change (\( \Delta H \)), and entropy change (\( \Delta S \)), for the MB adsorbed on the surface of the modified PH at the temperatures of 298, 303, 308, and 313 K were also determined. Equation (10) was used to determine the free energy, whereas \( \Delta H \) and \( \Delta S \) values were determined using a combination of Equation (10) and Equation (11) (Equation (12)). The equilibrium constant \( K \) was the calculated after conversion into dimensionless parameters by the previous reports (3, 38).

\[
\Delta G = -RT \ln K = -RT \ln \left( \frac{1000 M K_L C^0}{\gamma} \right)
\]

(10)

\[
\Delta G = \Delta H - T \Delta S
\]

(11)

\[
\ln K = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}
\]

(12)

Here, \( R \) is the universal gas constant (8.314 J·K\(^{-1}\)·mol\(^{-1}\)), \( T \) is the temperature (K), and \( K \) indicates the equilibrium constant, \( M \) is the molecular weight of methylene blue (g·mol\(^{-1}\)), \( C^0 \) is the standard concentration of the adsorbate (1 mol·L\(^{-1}\)), \( K_L \) is the best isotherm equilibrium constant (Langmuir equilibrium constant), the multiplication of the value of \( K_L \) by 1000 can convert L·mg\(^{-1}\) into L·g\(^{-1}\), \( \gamma \) is the coefficient of activity.

### 2.8. Regeneration and recycling

The properties of FeOCl for repeated use were investigated. The used FeOCl can be easily separated from the mixture by sucking out the upper suspension. The reusability of PHFeOCl was determined in the presence of PHFeOCl using 0.1 M of HCl. An ultrasound bath (3 × 20 min) was used to determine the reusability. The regeneration performance was evaluated by performing five adsorption–desorption cycles. The experiments were conducted three times, and the mean value was used for further studies.
3. Results and discussion

3.1. Characterization of adsorbents

Structural and functional groups in pristine PH and Fenton-like modified PH were investigated using the FTIR technique (Figure 2a). The nature of the spectra is influenced by the major constituents, such as lignin, cellulose, and hemicellulose (39). The band observed at 3500 cm\(^{-1}\) is ascribed to O-H stretching vibration (40), which was broader and stronger than that of PH. This observation clearly indicates that the number of hydroxyl groups increases following the process of Fenton-like modification. It is associated with the decreased intermolecular hydrogen bonding and increased free hydroxyl groups within cellulose and hemicellulose (41). The intensity of the adsorption bands (at 1740cm\(^{-1}\) and 1511 cm\(^{-1}\)) corresponding to the vibrations of the carbonyl group in PH\(_{FeOCl}\) increased, indicating that PH\(_{FeOCl}\) could be potentially used as a sorbent to adsorb cationic dyes (23, 41). Furthermore, the typical peaks detected at 1641 and 980 cm\(^{-1}\) suggested that C = C bonds were present in the amorphous units of lignin. The signal intensities were weaker, or the signals disappeared following Fenton-like treatment, as indicated by the degradation of the aromatic units of lignin (42). The analysis of the FTIR spectral profiles revealed that the structure of Fenton-like modified PH contained more exposed hydroxyl groups than the pristine PH.

The crystallinity of the untreated PH and PH\(_{FeOCl}\) was examined using the X-ray diffraction technique as crystallinity is an important index for biomass utilization. As shown in Figure 2b, PH exhibited a typical cellulose structure containing crystalline and amorphous areas. The peak observed at 15.8° is ascribed to the crystallographic plane (101) of the crystalline cellulose I polymorph. The peak at 18.4° and 21.9° belong to the amorphous phases and the lattice plane (110), respectively (43). It was found that the peak positions in PH\(_{FeOCl}\) did not change, indicating that the modification did not influence the initial cellulose structure (30). However, the peak corresponding to the (110) crystallographic plane of cellulose I in PH\(_{FeOCl}\) was sharper compared to that of PH. Furthermore, it was noticed that the strengths of the peaks corresponding to (101) and (102) increased significantly. This observation can be assigned to the decrease in the hemicellulose and lignin contents (25, 44). The results indicated that the process of chemical pretreatment was conducive to the degradation of hemicellulose and lignin, which influenced the adsorption capacity of peanut hull.

The thermal behavior of PH and modified PH were studied in the temperature range of 30–850 °C (Fig. S1). It can be noticed that PH and PH\(_{FeOCl}\) exhibited similar thermal degradation trends. The primary decomposition stage is observed in the temperature range of 220–380 °C, resulting in 58% (approximately) weight loss. When the weight loss exceeded 61.6%, increased temperature relative to pH was necessary for PH\(_{FeOCl}\) to achieve identical weight. This could be attributed to the decrease in the lignin and hemicellulose contents. The amount of PH\(_{FeOCl}\) residue was less than that of PH as the temperature increased to 850 °C. This can be potentially attributed to the C-C rupture within the amorphous region of cellulose (45).

The SEM analysis was carried out in order to observe the morphology and structures of PH and PH\(_{FeOCl}\). As seen in Figure 3, the surface of the pristine PH was smooth, while PH\(_{FeOCl}\) exhibited rough surface with irregular pores. The generation of irregular pores and rough surfaces can be attributed to the presence of cracks and collapses between lignin. This result indicated that FeOCl could function as an activation agent, improve the efficiency of the partial hemicellulose degradation process, and promote hole formation in the fibers (43). The textural properties of the PH samples were also analyzed by the adsorption/desorption of N\(_2\) (BET). PH\(_{FeOCl}\) had the specific surface area of 12.36 m\(^2\cdot\)g\(^{-1}\), which was higher than that of the pristine PH (5.35 m\(^2\cdot\)g\(^{-1}\)). It was inferred that FeOCl modification can enlarge the surface by the effective degradation. This is also consistent with the morphology of the samples. Besides, the pore size decreased from 40.53 Å to 33.84 Å after the modification. From these results, it can be concluded that FeOCl treatment has positive effects on the process of adsorption by creating loose structure and exerted active adsorption sites.

3.2. Adsorption performance

3.2.1. Influence of fenton-like treatment

The impact of the treatment temperature and treatment time on the MB removal efficiency was examined. As shown in Figure 4a, Fenton-like modified PH exhibited a higher MB removal efficiency than raw PH (control). This indicated that Fenton-like treatment is an effective treatment method for improving the adsorption capacity of PH. Temperature represents an important factor that affects the activation energy of numerous reactions. With a gradual increase in temperature in a range of 20–40 °C, the removal efficiency of pretreated PH increased from 66.5–76.2%. This can be attributed to the fact that more energy is required at a high
temperature to surpass the activated energy barrier to disrupt the structure of lignocellulose (46). However, the removal efficiency remained almost unchanged when the temperature was increased from 40 to 50 °C. Hence, 40 °C was selected to be the optimal temperature. The MB removal efficiency of PHFeOCl first increased

Figure 2. FTIR spectra (a) and X-ray diffraction patterns (b) of peanut hull and Fenton-like modified peanut hull.

Figure 3. SEM images of peanut hull (a, b) and Fenton-like modified peanut hull (c, d).
as the treatment time was augmented at the interval of 0–8 h (Figure 4b). Following this, the removal efficiency reached a plateau. It did not increase with a further increase in the treatment time. This can be explained by the fact that the Fenton reaction took 8 h to complete. Therefore, the removal efficiency did not improve with time. The result agreed well with previously reported results (30). Thus, considering the practical cost, PHFeOCl obtained at 40 °C and 8 h was primarily studied in subsequent experiments.

### 3.2.2. Influence of different adsorption conditions

The adsorption environment has a certain effect on the MB adsorption efficiency. The influence of the initial MB concentration, adsorption temperature, initial pH value, and interfering is presented in Figure 5. When the concentrations were in the range of 100–300 mg·L\(^{-1}\), improved adsorption efficiency was observed. The efficiency increased with an increase in concentration. This is associated with the increased contact chance between the MB molecules and adsorbent sites. An adsorption capacity of 63.5 mg·g\(^{-1}\) was achieved when the original content of the untreated PH was 100 mg·L\(^{-1}\). The results agreed well with previously reported results (47). When the initial concentration of MB was >400 mg·L\(^{-1}\), the adsorption process remained in an approximate state of equilibrium because the adsorption sites were consumed. With an increase in the original MB concentration, the MB removal capacity decreased. PHFeOCl could be used to achieve the maximum removal efficiency of 85.1% in the presence of 100 mg·L\(^{-1}\) of MB. A decrease in the removal efficiency at higher MB concentrations can be explained by the gradual occupation of the existing adsorption sites resulting in saturation. The modification method did not significantly influence the adsorption efficiency of MB. The saturation absorptive capacities of PH and modified PH adsorbents were 92.7 mg·g\(^{-1}\) (PH) and 136.4 mg·g\(^{-1}\) (PHFeOCl), respectively. The result indicated that FeOCl could efficiently improve the adsorption capacity of PH. The process of Fenton pretreatment could be used to overcome biomass recalcitrance, remove partial hemicellulose and lignin fraction, and significantly damage biomass (30, 42). Untreated PH reached saturation at lower MB concentration. This can be attributed to the fact that untreated PH contained less numbers of active functional groups.

The adsorption experiments were carried out when the original MB content was 100 mg·L\(^{-1}\) (Figure 5(b-d)). The MB removal efficiency gradually decreased as the temperature increased. The removal efficiency reduced by 13% as the temperature increased in the range of 298–318 K. It was revealed that MB adsorption was not favored at high temperatures. This can be potentially attributed to the enhanced MB mobility of the adsorbed MB achieved under an increasing temperature. Analysis of Figure 5c reveals that the solution pH had significantly influence the process of MB adsorption. Typically, when the pH value increased from 2 to 10, the removal efficiency showed a gradual increase within the range of 65.3–88.1%. The pH value also has certain effects on the surface charge and functional group states (1). The pKa of MB was close to 3.8 (3). The removal efficiency decreased when the pH value was less than 4.0. This is attributed to the fact that a large number of H\(^+\) present in the MB solution competitively adsorbed the cationic MB (2). While the point of zero charge (pH\(_{PZC}\)) of FeOCl modified peanut hull adsorbent was
Figure 5. Adsorption of MB by PHFeOCl under conditions of varying (a) initial concentrations, (b) temperatures, (c) pH values, and (d) ionic strengths. (dosage = 1.0 g/L, T = 298 K, t = 5 h, C₀ = 100 mg/L).

Figure 6. Removal efficiency at different recycling times for (a) FeOCl (b) and PHFeOCl. (dosage = 1.0 g·L⁻¹, T = 298 K, t = 5 h, C₀ = 100 mg·L⁻¹).
found close to 6.7. Thus, the surface of PHFeOCl has a negative charge when solution pH was above 6.7. With an increase in the pH value, the protonation of the sorbent decreases and the extent of electrostatic adsorption increases, resulting in higher removal efficiency. We dissolved NaCl in MB solutions of different concentrations to determine the effect of metal cations on the removal efficiency of MB. Results presented in Figure 5d reveals that Na⁺ significantly inhibited the process of MB adsorption. Within the NaCl content range of 0–0.8 M, the removal efficiency of MB in the presence of PHFeOCl decreased from 85.4% to 16.7%. This could be attributed to the presence of competitive electrostatic interactions between the positively charged Na⁺ and MB (48, 49). The results revealed that electrostatic interactions significantly influenced the process of MB removal.

3.2.3. Regeneration of Fenton-like treated PH and adsorption recyclability
To figure out the effect of reused FeOCl, the separated FeOCl was recycled five times. Those results revealed that 90% of FeOCl could be recovered after five cycles, avoiding the formation of an iron-based byproduct. More importantly, the removal efficiency of MB was reduced by only 15% when the five times-recycled FeOCl was used for the modification of PH (Figure 6a). The stability of PHFeOCl during the process of MB sorption was also studied. The MB-loaded PH was washed with a solution of hydrochloric acid (0.1 M) for regeneration. Five adsorption–desorption experiments were performed. According to Figure 6b, the adsorption performance exhibited a slight reduction after five cycles. The decrease in performance with an increase in the cycle times could be due to two reasons: (i) certain reactive sites become unavailable following the desorption of MB and (ii) MB is not completely removed, and the adsorbent is lost after the experiment (2). However, 89% of the initial adsorption efficiency could be retained after five cycles. This illustrates that Fenton-like modified PH still exhibits a high and stable adsorption capacity after five adsorption–desorption cycles. Therefore, Fenton-like based modification of biomass is an environmentally friendly and cost-effective way to remove MB.

3.2.4. Comparison with other adsorbents
Table 1 compares the MB adsorption ability achieved by us with those reported by others. The samples studied include modified orange tree sawdust, spent substrate of Ganodorma lucidum, soya waste, defatted algal, Phragmites australis, hickory, and pine corn. Even though the adsorption conditions are different across diverse adsorbents, adding to the difficulty in comparing the efficiency of different adsorbents, those results in this study demonstrate that the adsorption performance of PHFeOCl was better than the performance of numerous adsorbents. Moreover, in this study when corn stover was treated by FeOCl, the adsorption capacity of corn stoverFeOCl (116.2 mg·g⁻¹) was greatly higher than that of pristine corn stover (55.8 mg·g⁻¹) under MB initial concentration of 300 mg·L⁻¹ and dosage of 1.0 g·L⁻¹ (Fig. 52). The results indicated that Fenton-like modification method is also suitable for other biomass. What’s more, the Fenton-like modification process is cost-effective and environmentally friendly as the modified agents can be reused. This shows that Fenton-like modification is a promising treatment method for preparing biosorbents.

3.3. Adsorption kinetics, isotherm and mechanism
3.3.1. Adsorption kinetics
Figure 7 (a and b) presents the influence of time on the adsorption efficiency of MB in the presence of modified PH with the MB initial concentration of 100 and 50 mg·L⁻¹. During the adsorption assay, we continued to measure the remaining MB content in the solution in the time range of 0–120 min to determine the adsorption capacity. The adsorption process reached equilibrium within 6 min, revealing fast diffusion of MB into PHFeOCl. The results indicate that Fenton-like treatment can accelerate the adsorption of MB in aqueous solutions. This can be attributed to the presence of an adequate number of active sites and large spacing on the PHFeOCl surface and the active sites get gradually saturated with time. To describe the adsorption process, the kinetic data were fitted using the pseudo-first-order, pseudo-second-order, and Elovich models. Table 2 summarizes the fitting kinetic parameters for the adsorption of MB in the presence of Fenton-like modified peanut hull. The appropriateness of the models was analyzed applying determination coefficient (R²) and error analysis (sum of squared errors of prediction (SSE)) (17). The experimental data were well fitted using the pseudo-second-order model (R² = 0.9976; 0.9972). The maximum accuracy in predicting the equilibrium adsorption capacity for MB in the presence of PHFeOCl also could be achieved using the pseudo-second-order model. The lowest SSE values (0.1699, 0.1486) were also obtained from the pseudo-second-order model. Analysis of the results revealed that the rate-limiting process was possibly the chemical adsorption process, where the removal of MB was controlled by the process of electron transfer (57). However, the
data could also be effectively fitted using the pseudo-first-order and Elovich models. The pseudo-first-order model has a correlation coefficient of 0.9954 and 0.9894, indicating that the pseudo-first-order model was suitable to describe the adsorption behavior. Consequently, it could be well predicted that the interactions between PH and MB involve both physisorption and chemisorption (33).

Table 1. Comparison of adsorption capacities of pritine and modified bioadsorbents.

| Adsorbents            | Pretreatment agent | Dosage (g/L) | pH   | Q max of MB (mg·g⁻¹) | Reference |
|-----------------------|--------------------|--------------|------|----------------------|-----------|
| Ganodorma lucidum     | –                  | 10.0         | 7.0  | 9.6                  | (23)      |
| Coconut leaf          | –                  | 1.3          | 8.6  | 112.3                | (19)      |
| Dragon fruit peels    | –                  | 0.6          | 5.6  | 192.3                | (14)      |
| Rice straw            | –                  | 1.0          | 7.0  | 158.0                | (16)      |
| Yellow passion fruit waste | –              | 10.0         | 8.0  | 44.7                 | (50)      |
| Algae                 | –                  | 1.0          | 7.0  | 833.3                | (51)      |
| Peanut hull           | –                  | 1.0          | 7.0  | 64.0                 | This work |
| Peanut hull FeOCl     | FeOCl              | 1.0          | 7.0  | 132.4                | This work |
| Soya waste            | Silica             | 2.0          | 7.0  | 47.0                 | (52)      |
| Sugarcane bagasse     | Citrate            | 1.2          | 10.0 | 224.0                | (28)      |
| Defatted algal        | Sulfuric acid      | 1.0          | 7.0  | 7.8                  | (33)      |
| Phragmites australis  | Epichlorohydrin, sodium sulfite | 5.0  | 6.5  | 46.8                 | (54)      |
| Cotton                | NaOH               | 1.0          | 7.0  | 49.6                 | (55)      |
| Pine corn             | NaOH               | 0.3          | 7.0  | 33.7                 | (56)      |
| – a                  |                   |              |      | 9.6                  | This work |

*–* untreated.

Figure 7. (a and b) MB adsorption kinetics of PHFeOCl. (c and d) MB adsorption isotherms (Freundlich, Langmuir, Redlich–Peterson, Temkin) of PHFeOCl.
onto PHFeOCl.

Table 2. Nonlinear kinetic fitting parameters for MB adsorption onto PHFeOCl.

| Model                  | Parameters | Values               |
|------------------------|------------|----------------------|
|                        |            | $q_e$ = 50 mg·L$^{-1}$ | $q_e$ = 100 mg·L$^{-1}$ |
| Pseudo-first-order     | $q_e$ (mg·g$^{-1}$) | 48.2378 | 83.2483 |
|                        | $k_1$ (min$^{-1}$)  | 1.1696  | 1.2561  |
|                        | $R^2$        | 0.9894  | 0.9954  |
|                        | SSE (mg·g$^{-1}$)  | 1.3456  | 2.8385  |
| Pseudo-second-order    | $q_e$ (mg·g$^{-1}$) | 49.7248 | 85.5637 |
|                        | $k_2$ (g·mg$^{-1}$·min$^{-1}$) | 0.0392  | 0.0429  |
|                        | $R^2$        | 0.9972  | 0.9976  |
|                        | SSE (mg·g$^{-1}$)  | 0.1699  | 0.1486  |
| Elovich equation       | $\alpha$ (mg·g$^{-1}$·min$^{-1}$) | 4.492×10$^4$ | 2.585×10$^4$ |
|                        | $\beta$ (g·mg$^{-1}$) | 0.2631  | 0.2856  |
|                        | $R^2$        | 0.9189  | 0.9676  |
|                        | SSE (mg·g$^{-1}$)  | 3.0255  | 4.5635  |

3.3.2. Adsorption isotherm

The adsorption data obtained at the temperature of 298 K fitted by the Langmuir, Freundlich, Temkin, and Redlich–Peterson isotherm models by nonlinear regression analysis are presented in Figure 7(c and d). Table 3 lists the parameters of the adsorption isotherms. Initially, the adsorption ability rapidly increased. Following this, it reached a plateau. The maximum adsorption capacity of MB onto PHFeOCl was 134.5 mg·g$^{-1}$ at 298 K. Based on the Langmuir model fitting results, PHFeOCl could be used to achieve the maximum adsorption capacity of 134.5 mg·g$^{-1}$. The result agreed well with the result obtained previously. It was observed that the adsorption process conformed to the Redlich–Peterson isotherm models by nonlinear regression analysis are presented in Figure 7(c and d). That is, the MB adsorption onto modified PH could be explained by a monolayer surface adsorption process. The dimensionless separation factor ($R_L$) represents the key factor that is used to analyze the process of adsorption (58). PHFeOCl exhibited an $R_L$ value in the range of 0–1, which indicated that it promoted MB adsorption. The experimental data for Freundlich and Temkin model do not agree with each other. However, the empirical parameter in the Freundlich isotherm associated with the adsorption intensity (n) suggests that the process of adsorption was a physical and favorable process (n < 1). Furthermore, the value of $R^2$ obtained using the Redlich–Peterson isotherm model was above 0.99, and the values of $\nu$ (0.9964) obtained from the Redlich–Peterson equation were in the range of 0–1. Therefore, those adsorption data can be interpreted using the Redlich–Peterson model as well. It was concluded that the MB monolayer adsorption is the dominant mechanism (59).

3.3.3. Thermodynamics studies

In order to calculate the value of adsorption equilibrium constant, the equilibrium constant values ($K_e$) of the Langmuir isotherm model in the temperature range of 298–313 K were calculated. The experimental data were analyzed using van’t Hoff equation (38). The values of $\Delta H$ and $\Delta S$ were obtained from the slope and intercept of the plot of ln ($K_e$) versus 1/T (Fig. S3), as extensively explained in the literature (38, 60). The thermodynamic parameters for the adsorption of methylene blue onto modified peanut hull are summarized in Table 4. The adsorption thermodynamics model yielded a straight line ($R^2 = 0.9958$), indicating the suitability of model in explaining MB adsorption on Fenton-like modified PH. The $\Delta G$ values were less than 0, indicating spontaneity. Further, it was evident that both $\Delta H$ and $\Delta S$ values were also negative, revealing the exothermic character of the process. It was revealed that MB adsorption was primarily a chemical process (23). The results agreed with the results obtained by analyzing the Langmuir isotherm.

3.3.4. Adsorption mechanism

Based on the structure of FeOCl modified peanut hull and the kinetic, equilibrium and thermodynamic data of adsorption, the potential mechanism underlying the process of MB adsorption was proposed (Figure 8).
Combined with the specific surface area and SEM analyses before and after Fenton-like treated peanut hull, the larger specific surface area (12.36 m²·g⁻¹) of PHFeOCl and pore structure promoted the adsorption interaction. As a result, the MB molecules diffused through the pores on the PHFeOCl surface. Besides, van der Walls, hydrogen bond, and electrostatic interactions also existed between PHFeOCl and MB. The highly reactive ·OH produced in the Fenton-like system can break the internal covalent bonds present in cellulose–hemicellulose and cellulose–lignin, which could lead to partially discard of hemicellulose and lignin (42). Oxidation of ·OH free radicals might induce the production of carboxyl ions. The electron pair in tertiary amine nitrogen allows the direct binding with the hydrogen unit in the hydroxyl group exploiting van der Waals interactions and hydrogen bonding (28). The presence of the Na⁺ ions negatively affected the efficiency of removal of MB, revealing that MB can bond with the electron-rich groups and oxygen atoms by electrostatic interactions. Therefore, the PHFeOCl surface properties, van der Waals interactions, hydrogen bonding, and dye structure influence the process of MB adsorption.

4. Conclusion
A simple and green Fenton-like modified peanut hull adsorbent was successfully fabricated under a mild condition (40 °C). This bioadsorbent is efficient for rapid adsorption of MB from aquatic environment. Fenton-like treatment endowed the resultant adsorbent with a maximum adsorption ability of 136 mg·g⁻¹ and an adsorption equilibrium time of less than 6 min. Adsorption results at different conditions indicated that adsorption capacity of Fenton-like modified peanut hull was greatly affected by MB initial concentration, pH value and ionic strengths. In addition, FeOCl retained 85% activity even after 5 cycles, and the MB removal efficiency was maintained at 89% after five adsorption–desorption experiments. Adsorption kinetic and isotherm experiments showed that the adsorption kinetic process followed the pseudo-second-order model and the adsorption process conformed to the Redlich–Peterson and Langmuir models. The adsorption mechanism was controlled by van der Waals interactions, hydrogen bonding, and electrostatic interactions. As a result, The Fenton-like treatment method can be potentially used as a facile and green method for the generation of bioadsorbents with desirable adsorption capacity due to comprehensive economic and environmental considerations.

Declarations
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Disclosure statement
No potential conflict of interest was reported by the author(s).
Funding
This work was supported by Key R & D and promotion projects in Henan Province (CN) [Grant Numbers 192102310220, 202102310267]; the Scientific Research Foundation of Henan Agricultural University [Grant Numbers 36060132, KJXX2019A20]; Program for Science & Technology Innovation Talents in Universities of Henan Province [Grant Number 18HASTIT038].

Availability of data and materials
All data generated or analysed during this study are included in this published article and its supplementary information files.

Authors’ contributions
Dongcan Lv: Funding acquisition, Conceptualization, Investigation, Data curation, Writing – original draft. Guanxue Jiang: Data curation, Writing-review & writing. Chengpeng Li: Formal analysis, Methodology & Writing. Qianchen Zhu: Methodology, Formal analysis, Writing – review & editing. Zhimin Wang: Formal analysis, Data curation, Editing, and supervision.

ORCID
Dongcan Lv http://orcid.org/0000-0002-7316-663X

References
[1] Wang, Z.; Li, T.T.; Peng, H.K.; Ren, H.T.; Lin, J.H. Low-cost Hydrogel Adsorbent Enhanced by Trihydroxy Melamine and β-Cyclodextrin for the Removal of Pb(II) and Ni(II) in Water. J. Hazard. Mater. 2021, 417, 125029.
[2] Ren, L.; Tang, Z.; Du, J.; Chen, L.; Qiang, T. Recyclable Polyurethane Foam Loaded with Carboxymethyl Chitosan for Adsorption of Methylene Blue. J. Hazard. Mater. 2021, 417, 126130.
[3] Elwakeel, K.Z.; Elgarahy, A.M.; El-Shobaky, G.A.; Hamza, M.F.; Guibal, E. 2-Mercapto-2-Benzimidazole-functionalized Chitosan for Enhanced Removal of Methylene Blue: Batch and Column Studies. J. Environ. Chem. Eng. 2021, 9 (4), 105609.
[4] Yakout, A.A.; Shaker, M.A.; Elwakeel, K.Z.; Alshihabi, W.; Lauryl Sulfate@Magnetic Graphene Oxide Nanosorbent for Fast Methylene Blue Recovery from Aqueous Solutions. J. Dispersion Sci. Technol. 2019, 40 (5), 707–715.
[5] Li, W.; Mu, B.; Yang, Y. Feasibility of Industrial-Scale Treatment of dye Wastewater via bio-Adsorption Technology. Bioresour. Technol. 2019, 277, 157–170.
[6] Elwakeel, K.Z.; Elgarahy, A.M.; Elshohbaky, G.A.; Mohammad, S.H. Microwave Assist Sorption of Crystal Violet and Congo red Dyes Onto Amphoteric Sorbent Based on Upcycled Sepia Shells. J. Environ. Health Sci. Eng. 2020, 18 (1), 35–50.
[7] Sz, A.; Hc, A.; Xin, T.B.; Zw, D.; Jcc, B.; Mha, D. Integration of a Photo-Fenton reaction and a Membrane Filtration Using CS/PAN@FeOOH/g-C3N4 Electrospun Nanofibers: Synthesis, Characterization, Self-Cleaning Performance and Mechanism. Appl. Catal., B 2020, 281, 119519.
[8] Chan, P.Y.; El-Din, M.G.; Bolton, J.R. A Solar-Driven UV/ Chlorine Advanced Oxidation Process. Water Res. 2012, 46 (17), 5672–5682.
[9] Yang, Y.; Ali, N.; Khan, A.; Khan, S.; Khan, H.; Xiaoqi, S.; Ahmad, W.; Uddin, S.; Ali, N. Chitosan-capped Ternary Metal Selenide Nanocatalysts for Efficient Degradation of Congo red dye in Sunlight Irradiation. Int. J. Biol. Macromol. 2021, 167, 169–181.
[10] Elgarahy, A.M.; Elwakeel, K.Z.; Akhdhar, A.; Hamza, M.F. Recent Advances in Greenly Synthesized Nanengineered Materials for Water/Wastewater Remediation: An Overview. Nanotechnol. Environ. Eng. 2021, 6, 9.
[11] Elgarahy, A.M.; Elwakeel, K.Z.; Elshohbaky, G.A.; Mohammad, S.H. Microwave-accelerated Sorption of Cationic Dyes Onto Green Marine Algal Biomass. Environ. Sci. Pollut. Res. 2019, 26 (22), 22704–22722.
[12] Elgarahy, A.M.; Elwakeel, K.Z.; Mohammad, S.H.; Elshohbaky, G.A. Multifunctional eco-Friendly Sorbent Based on Marine Brown Algae and Bivalve Shells for Subsequent Uptake of Congo red dye and Copper(II) Ions. J. Environ. Chem. Eng. 2020, 8 (4), 103915.
[13] Elgarahy, A.M.; Elwakeel, K.Z.; Elshohbaky, G.A.; Mohammad, S.H. Untapped Sepia Shell-Based Composite for the Sorption of Cationic and Anionic Dyes. Water, Air, & Soil Pollut. 2019, 230 (9), 217.
[14] Jawad, A.H.; Kadhum, A.M.; Ngoh, Y.S. Applicability of Dragon Fruit (Hylocereus Polyrhizus) Peels as low-Cost Biosorbent for Adsorption of Methylene Blue from Aqueous Solution: Kinetics, Equilibrium and Thermodynamics Studies. Desalin. Water Treat. 2018, 109, 231–240.
[15] Lv, B.-W.; Xu, H.; Guo, J.-Z.; Bai, L.-Q.; Li, B. Efficient Adsorption of Methylene Blue on Carboxylate-Rich Hydrochar Prepared by one-Step Hydrothermal Carbonization of Bamboo and Acrylic Acid with Ammonium Persulphate. J. Hazard. Mater. 2022, 421, 126741.
[16] Jawad, A.H.; Hum, N.N.M.F.; Farhan, A.M.; Mastuli, M.S. Biosorption of Methylene Blue dye by Rice (Oryza Sativa L) Straw: Adsorption and Mechanism Study. Desalin. Water Treat. 2020, 190, 322–330.
[17] Elgarahy, A.M.; Elwakeel, K.Z.; Mohammad, S.H.; Elshohbaky, G.A. A Critical Review of Biosorption of Dyes, Heavy Metals and Metalloids from Wastewater as an Efficient and Green Process. Cleaner Eng. Technol. 2021, 4, 100209.
[18] Hassan, M.M.; Carr, C.M. Biomass-derived Porous Carbonaceous Materials and Their Composites as Adsorbents for Cationic and Anionic Dyes: A Review. Chemosphere 2021, 265, 129087.
[19] Jawad, A.H.; Rashid, R.A.; Mahmood, R.M.A.; Ishak, M.A.M.; Kasim, N.N.; Ismail, K. Adsorption of Methylene Blue Onto Coconut (Cocos Nucifera) Leaf: Optimization, Isotherm and Kinetic Studies. Desalin. Water Treat. 2016, 57 (19), 8839–8853.
[20] Tanyildizi, M. Modeling of Adsorption Isotherms and Kinetics of Reactive dye from Aqueous Solution by Peanut Hull. Chem. Eng. J. 2011, 168 (3), 1234–1240.
[21] Nascimento, G.; Duarte, M.; Campos, N.F.; Rocha, O.R.S.D.; Silva, V. Adsorption of azo Dyes Using Peanut Hull and Orange Peel: A Comparative Study. *Environ. Technol.* 2014, 35 (9-12), 1436–1453.

[22] Sun, Q.; Saratate, R.G.; Saratate, G.D.; Kim, D.-S. Pristine and Modified Radix Angelicae Dahuricae (Baizhi) Residue for the Adsorption of Methylene Blue from Aqueous Solution: A Comparative Study. *J. Mol. Liq.* 2018, 265, 36–45.

[23] Wu, J.; Zhang, T.; Chen, C.; Feng, L.; Su, X.; Zhou, L.; Chen, Y.; Xia, A.; Wang, X. Spent Substrate of Ganoderma Lucidum as a new bio-Adsorbent for Adsorption of Three Typical Dyes. *Bioreasour. Technol.* 2018, 266, 134–138.

[24] Azzaz, A.A.; Jellali, S.; Akrout, H.; Assadi, A.A.; Boussemli, L. Dynamic Investigations on Cationic dye Desorption from Chemically Modified Lignocellulosic Material Using a Low-Cost Eluent: Dye Recovery and Anodic Oxidation Efficiencies of the Desorbed Solutions. *J. Cleaner Prod.* 2018, 201, 28–38.

[25] Emam, A.A.; Faraha, S.; Kamal, F.; Gamal, A.M.; Basseem, M. Modication and Characterization of Nano Cellulose Crystalline from Eichhornia Crassipes Using Citric Acid: An Adsorption Study. *Carbohydr. Polym.* 2020, 240, 116202.

[26] El-Shafey, E.I. Removal of Se(VI) from Aqueous Solution Using Sulphuric Acid-Treated Peanut Shell. *J. Environ. Manag.* 2007, 84 (4), 620–627.

[27] Zhang, W.; Yan, H.; Li, H.; Jiang, Z.; Dong, L.; Kan, X.; Yang, H.; Li, A.; Cheng, R. Removal of Dyes from Aqueous Solutions by Straw Based Adsorbents: Batch and Column Studies. *Chem. Eng. J.* 2011, 168 (3), 1120–1127.

[28] Mpatani, F.M.; Aryee, A.A.; Kani, A.N.; Wen, K.; Han, R. Removal of Methylene Blue from Aqueous Medium by Citrate Modified Bagasse: Kinetic, Equilibrium and Thermodynamic Study. *Bioresour. Technol. Rep.* 2020, 11, 100463.

[29] Zhang, R.; Leiviska, T. Surface Modification of Pine Bark with Quaternary Ammonium Groups and its Use for Vanadium Removal. *Chem. Eng. J.* 2020, 385, 123967.

[30] Wang, Z.; Zhang, F.; Lv, D.; Jiang, G.; Song, A. Iron Oxycarbonate-Based Heterogeneous Fenton Pretreatment of Corn Stover for Enhanced Sugars Production. *Chem. Eng. J.* 2020, 9, 127073.

[31] Svenska, K.; Lagergren, S. About the Theory of so-Called Adsorption of Soluble Substances. *Handlingar 1898*, 24 (4), 1–39.

[32] Blanchard, G.; Maunaye, M.; Martin, G. Removal of Heavy Metals from Waters by Means of Natural Zeolites. *Water Res.* 1984, 18 (12), 1501–1507.

[33] Xiong, S.; Gong, D.; Deng, Y.; Tang, R.; Li, L.; Zhou, Z.; Zheng, J.; Yang, L.; Su, L. Facile one-pot Magnetic Modification of Enteromorpha Prolifera Derived Biochar: Increased Pore Accessibility and Fe-Loading Enhances the Removal of Butachlor. *Bioreasour. Technol.* 2021, 337, 125407.

[34] Rizzi, V.; Gubitosa, J.; Signorile, R.; Fini, P.; Ceccone, C.; Matencio, A.; Trota, F.; Cosma, P. Cyclodextrin Nanosponges as Adsorbent Material to Remove Hazardous Pollutants from Water: The Case of Ciprofloxacsin. *Chem. Eng. J.* 2021, 411, 128514.
from KOH Activated Biomass Waste: Surface Mechanistic Study of Methylene Blue dye Adsorption. *Water Sci. Technol*. 2021, 84 (8), 1858–1872.

[50] Pavan, F.A.; Lima, E.C.; Dias, S.L.P.; Mazzocato, A.C. Methylene Blue Biosorption from Aqueous Solutions by Yellow Passion Fruit Waste. *J. Hazard. Mater.* 2008, 150 (3), 703–712.

[51] Mokhtar, N.; Aziz, E.A.; Aris, A.; Ishak, W.F.W.; Mohd Ali, N.S. Biosorption of azo-dye Using Marine Macro-Alga of Euchema Spinosum. *J. Environ. Chem. Eng.* 2017, 5 (6), 5721–5731.

[52] Batool, A.; Valiyaveettil, S. Chemical Transformation of Soya Waste Into Stable Adsorbent for Enhanced Removal of Methylene Blue and Neutral red from Water. *J. Environ. Chem. Eng.* 2021, 9 (1), 104902.

[53] Chandra, T.S.; Mudliar, S.N.; Vidyashankar, S.; Mukherji, S.; Sarada, R.; Krishnamurthi, K.; Chauhan, V.S. Defatted Algal Biomass as a non-Conventional low-Cost Adsorbent: Surface Characterization and Methylene Blue Adsorption Characteristics. *Bioresour. Technol.* 2015, 184, 395–404.

[54] Kankilic, G.B.; Metin, A.U.; Tuzun, I. Phragmites Australis: An Alternative Biosorbent for Basic dye Removal. *Ecol. Eng.* 2016, 86, 85–94.

[55] Ding, Z.; Hu, X.; Zimmerman, A.R.; Gaq, B. Sorption and Cosorption of Lead (II) and Methylene Blue on Chemically Modified Biomass. *Bioresour. Technol.* 2014, 167, 569–573.

[56] Yagub, M.T.; Sen, T.K.; Ang, M. Removal of Cationic dye Methylene Blue (MB) from Aqueous Solution by Ground raw and Base Modified Pine Cone Powder. *Environ. Earth Sci.* 2014, 71 (4), 1507–1519.

[57] Hosseini, H.; Zirakjou, A.; McClements, D.J.; Goodarzi, V.; Chen, W.-H. Removal of Methylene Blue from Wastewater Using Ternary Nanocomposite Aerogel Systems: Carboxymethyl Cellulose Grafted by Polyacrylic Acid and Decorated with Graphene Oxide. *J. Hazard. Mater.* 2021, 421, 126752.

[58] Yang, T.; Xu, Y.; Huang, Q.; Sun, Y.; Liang, X.; Wang, L.; Qin, X.; Zhao, L. Adsorption Characteristics and the Removal Mechanism of two Novel Fe-Zn Composite Modified Biochar for Cd(II) in Water. *Bioresour. Technol.* 2021, 333, 125078.

[59] An, T.; Cheng, H.; Qin, Y.; Su, W.; Deng, H.; Wu, J.; Liu, Z.; Guo, X. The Dual Mechanisms of Composite Biochar and Biofilm Towards Sustainable Nutrient Release Control of Phosphate Fertilizer: Effect on Phosphorus Utilization and Crop Growth. *J. Cleaner Prod.* 2021, 311, 127329.

[60] Thue, P.S.; Adebayo, M.A.; Lima, E.C.; Sieliechi, J.M.; Machado, F.M.; Dotto, G.L.; Vaghetti, J.C.P.; Dias, S.L.P. Preparation; Characterization and Application of Microwave-Assisted Activated Carbons from Wood Chips for Removal of Phenol from Aqueous Solution. *J. Mol. Liq.* 2016, 223, 1067–1080.