One-pot fabrication of magnetic biochar by FeCl₃-activation of lotus seedpod and its catalytic activity towards degradation of Orange G

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Abstract
An advanced magnetic biochar (MBC) was facilely prepared via one-pot FeCl₃-activation of lotus seedpod. Simultaneous carbonization, activation, and magnetization formed magnetic Fe₃O₄ nanoparticles and nanowires over the biochar base. The specific surface area (Sₑₑ₄) and the total pore volume (Vₑₑ₄) of MBC were 349 m² g⁻¹ and 0.31 cm³ g⁻¹, which were 2.0-fold and 3.9-fold higher than those of biochar, respectively. In addition, the saturation magnetization of MBC reached 6.94 emu g⁻¹, facilitating its magnetic separation and recovery. In heterogeneous Fenton-like catalytic oxidation, 0.40 g l⁻¹ MBC decolorized 100% Orange G and reduced 58% COD by 350 ppm H₂O₂ within 120 min. The degradation kinetics were calculated with different MBC samples and reactions followed pseudo-first-order kinetics with the highest rate constant of 0.034 min⁻¹. Moreover, the catalytic activity dropped by only 6.4% after four reuse cycles, with negligible iron leaching of 1.31–1.44 mg l⁻¹. Based on these results, MBC could be a low-cost, highly effective, and relatively stable catalyst for treating Orange G in wastewater.

1. Introduction
Biochar (BC) is an inexpensive material produced from the carbonization of diverse renewable biomass resources [1–3]. Due to its favorable physicochemical properties, porous system and diverse functional groups [4–6], biochar is widely used for various purposes, such as wastewater treatment, soil remediation, and gas storage and separation [7, 8]. Nevertheless, the obstacle of biochar is difficult to separate from suspensions. Conventional sedimentation, filtration, coagulation, and clarification processes are generally costly or inadequate, greatly restricting the use of biochar [9]. Such reports have proposed dispersing magnetic particles like Fe₃O₄ on biochar to form magnetic biochar (MBC) [9, 10]. This combination has the potential to overcome obstacles on both sides. Magnetic particles might aid in the easy recovery and reuse of MBC by magnetic fields [11, 12]. In the opposite direction, the carbon base could prevent the magnetic particles from aggregating into larger particles [13, 14]. The MBC composite possesses attractive physicochemical properties from not only porous systems and diverse functional groups of carbon base, but also catalytic activity and magnetic recoverability of iron-based particles [5, 12].

To prepare MBC, magnetic precursors are typically impregnated onto carbon surfaces [10]. However, this traditional method not only is complicated but also locks existing pores in carbon support [15]. Recently, an innovative strategy for fabricating magnetic biochar using one-step pyrolysis of biomass and iron precursors has been introduced [12, 14]. Magnetic precursors like FeCl₃ are dispersed directly into biomass, and the mixtures are then pyrolyzed to produce MBC [16]. Simultaneous carbonization, activation, and magnetization have the potential to remarkably improve MBC properties [9, 14]. Bedia et al [17] proved that FeCl₃-activation of...
biomass offers MBC with well-developed porosity, well-dispersed iron-based nanoparticles, and high catalytic stability.

Adsorption is probably the most well-known use of BC, and as a result, the majority of MBC research in the literature is devoted to adsorption processes, notably aqueous-phase adsorption processes [7, 18–20]. This is owing to the aforementioned characteristics of MBC: well-developed porous texture, surface acidity, and superparamagnetic nature [15]. However, it may be challenging to effectively remove organic contaminants using MBC as an adsorbent alone. Adsorption is incapable of mineralizing organic contaminants; it can only transfer them from the liquid phase to the solid phase [21]. In an effort to increase the utilization of MBC, its application as an oxidation catalyst for the degradation of organic pollutants has garnered attention. According to a review by Feng et al [9], Fe-based particles in MBC have the potential to serve as active sites for the efficient degradation of organic substances via various advanced oxidation processes. Despite this, the number of studies on MBC prepared by FeCl₃-activation of biomass for application in catalysis is still limited. Furthermore, it has been discovered that the type of biomass affects the properties and performance of MBC. Different biomass resources could produce MBC with a variety of porous structures, iron-based structures, magnetic properties, functional groups, adsorption capacities, and catalytic activities [3, 9, 15, 21]. For instance, trace elements in biomass may serve as a catalyst for more rapid pyrolysis to produce MBC [22]. For a deeper insight, additional research is necessary into the preparation, characterization, and catalytic application of MBC from such biomass feedstocks. The findings can be utilized to select appropriate biomass-derived MBCs for further scientific and industrial applications.

Lotus (Nelumbo nucifera) is an aquatic herbaceous perennial plant, which is popular in such Asian countries as China, India, Thailand, Japan, Korea, and Vietnam [23, 24]. Almost all parts of lotus, like buds, flowers, anthers, stamens, leaves, stalks, rhizomes, roots, and seeds are useful [25]. Due to a high demand for food, seeds are the main product of lotus. However, seed production releases seedpods as an abundant and underutilized residue [26]. The vast majority of lotus seedpod (LSP) becomes waste in markets and factories, thereby resulting in environmental pollution [22, 27]. To valorize LSP, it was employed herein as the raw material for one-pot preparation of MBC through FeCl₃-activation. Various properties of the as-prepared MBC were intensively analyzed and discussed.

Orange G (OG) is a synthetic azo dye commonly used in the textile, food, and leather industries [28, 29]. Due to its widespread utilization, low biodegradability and high toxicity, the presence of OG in wastewater can cause serious environmental and public health issues that must be addressed [30]. Various methods for the degradation and mineralization of OG in aqueous environments have therefore gained increasing interest [31]. Among developed processes, heterogeneous Fenton-like reactions using oxidation catalysts can offer an efficient source of hydroxyl radicals for the degradation of OG [32]. As reported in the literature, Fe₃O₄ particles exhibit high catalytic activity to accelerate the decomposition of H₂O₂ into hydroxyl radicals and are inexpensive, stable, easily prepared, and magnetically separated [33, 34]. However, the particles may agglomerate, causing a reduction in their catalytic activity [14, 35]. Due to its high catalytic stability, MBC with Fe-based particles was explored as a potential catalyst for OG treatment in this study.

2. Materials and methods

2.1. Materials

The lotus seedpods were obtained from Thap Muoi District, Dong Thap Province, Vietnam. The agricultural residue was first washed with distilled water to remove adhering soil and dust, and then oven-dried at 110 °C for 24 h to a constant weight. Next, the dried biomass was crushed, sieved, and preserved in an airtight plastic container for further use. All chemicals were purchased from Xilong Scientific Co., Ltd. They were of analytical grade and were used without any purification.

2.2. Preparation of magnetic biochar from lotus seedpod

Magnetic biochar was fabricated through one-pot pyrolysis of FeCl₃—loaded lotus seedpod. First, 4.00 g dried LSP was added into an aqueous FeCl₃ solution. The mixture was stirred for 3 h at room temperature before being dried at 110 °C for 24 h. Pyrolysis was conducted in a tube furnace under a constant nitrogen flow of 250 ml min⁻¹. The tube was heated to 600 °C at a rate of 5 °C min⁻¹ and maintained at that temperature for 60 min. The resultant solid was washed with distilled water until the pH of wastewater became neutral to remove all remaining FeCl₃, and dried at 80 °C for 24 h to obtain MBC. The as-prepared samples were labeled as MBC-x, where x indicates the mass ratio of FeCl₃ to LSP. For comparison of the physical characteristics and catalytic activities, biochar (denoted as BC) was prepared by direct pyrolysis of the lotus seedpod without FeCl₃ addition under the same condition.
2.3. Characterization of magnetic biochar

The crystalline structures of MBC samples were characterized by powder x-ray diffraction (XRD) using a Bruker AXS D8 diffractometer over the 2θ range of 10°–80°. The Cu-Kα radiation was used as the target (λ = 1.5418 Å). A Perkin Elmer AAAnalyst 800 atomic absorption spectrophotometer (AAS) was used to determine the quantity of loaded iron in MBC samples that had been dissolved in concentrated hydrochloric acid. Nitrogen adsorption isotherms of BC and MBC samples were analyzed at 77 K on a Micromeritics Gemini VII. All samples were outgassed for 3 h at 200 °C. Brunauer–Emmett–Teller equation was used to calculate the specific surface area (S BET ). Total pore volume (V total ) was measured at P / P 0 = 0.99. The average pore size (d average ) was given by 4 V total / S BET equation. The magnetic properties of MBC were measured using a vibrating sample magnetometer (VSM) at room temperature. Fourier–transform infrared (FTIR) spectra of BC and MBC were analyzed by using a Tensor 27 spectrometer (Bruker Optics, Germany). The surface morphology of MBC was observed using a scanning electron microscopy with field emission source (FE-SEM, S-4800). Elemental mapping of MBC was analyzed with an energy dispersive x-ray spectroscopy (EDS) instrument, JSM-IT200. Transmission electron microscopy (TEM) images of BC and MBC were obtained from a JEOL JEM-1400 equipment.

2.4. Degradation of Orange G using magnetic biochar

The catalytic activity of MBC was investigated through OG degradation at room temperature (30 °C). 500 ml OG solution with an initial concentration of 100 ppm was contained in a 1000 ml glass cylinder. Different masses of MBC were dispersed in the solution. Initial pH values of the mixture were adjusted by adding H 2 SO 4 (0.5 M) and NaOH (0.1 M) solutions. After adsorption reached equilibrium in 20 min, H 2 O 2 was rapidly poured into the mixture to initiate catalytic oxidation. At different time intervals, a certain amount of the reaction suspension was taken out. For determination of OG concentrations, each sample was immediately added to a solution of phosphate buffer and Na 2 S 2 O 3 to adjust the pH value to ~7.0 and remove the excess H 2 O 2 . OG concentrations were then measured using a UV–vis spectrophotometer (Lovibond PC Spectro) at 480 nm.

To assess the stability and reusability of MBC, consecutive experiments were performed with the same sample. The catalyst was recovered by a magnet bar, cleaned by distilled water and ethanol, filtrated and dried at 110 °C for 24 h. The dried MBC was weighted to prepare for the next experiment. After each cycle, iron leaching was measured by the aforementioned AAS equipment. Chemical oxidation demand (COD) was measured according to the closed reflux titrimetric method (5220C) [36]. To prevent residual H 2 O 2 from interfering, all samples were added with 20 g l −1 Na 2 CO 3 , sealed to reduce evaporation losses, and heated in a water bath at 90 °C for 60 min before COD analyses, according to Wu and Englehardt [37].

3. Results and discussion

3.1. Characterization of magnetic biochar

3.1.1. X-ray diffraction of magnetic biochar

The effect of the mass ratios of FeCl 3 to LSP on the XRD patterns of MBC samples are demonstrated in figure 1. Typical characteristic peaks of FeO 4 crystals were detected at 2θ = 29.96, 35.33, 42.98, 56.82 and 62.44° which corresponded to (220), (311), (400), (511) and (440) planes, respectively (ICPDS Card No. 19–0629) [38]. These dominant peaks almost appeared in all MBC samples. Although no distinct peaks of FeCl 3 , FeOCl, FeOOH, γ-Fe 2 O 3 , α-Fe 2 O 3 , FeO and Fe were found in three MBC samples, several of these matters may be amorphous and are difficult to detect by XRD [39]. According to a review by Bedia et al [15], the following products could be formed during pyrolysis of FeCl 3 -biomass mixture:

\[
\text{Biomass} \rightarrow \text{H}_2, \text{CO and C} \quad (1)
\]

\[
\text{FeCl}_3 + \text{H}_2 \text{O} \rightarrow \text{FeOCl}, \text{H}_2 \text{O} \text{and Fe(OH)}_3 \rightarrow \text{FeO(OH)} \rightarrow \text{Fe}_2 \text{O}_3 \quad (2)
\]

\[
\text{Fe}_2 \text{O}_3 + \text{H}_2, \text{CO and C} \rightarrow \text{Fe}_2 \text{O}_4 \rightarrow \text{Fe} \quad (3)
\]

When the mass ratio of FeCl 3 to LSP increased from 0.1 to 0.4, the peak intensities of FeO 4 decreased gradually. At high ratios, a lack of carbon and water released from the carbonization of the LSP biomass might decrease the conversion of FeCl 3 into FeO 4 . The remaining FeCl 3 was removed from MBC through washing with distilled water. Moreover, the formation of other crystals or amorphous phases might weaken FeO 4 peaks.

3.1.2. Porous properties and iron content of magnetic biochar

As presented in table 1, increasing the mass ratio of FeCl 3 to LSP from 0.1 to 0.5 resulted in an increase of Fe content in MBC from 3.3 to 10.4 wt%. Similar trends have been reported in literature [40, 41]. Increasing the mass ratio of FeCl 3 /biomass yields materials with higher Fe and O contents but lower carbon content.
Furthermore, higher mass ratio of FeCl₃ to LSP could boost the activation process to expand existing pores and create new pores in the carbon framework \[15\]. In fact, MBC-0.4 sample possesses a specific surface area of 349 m² g⁻¹, a total pore volume of 0.31 cm³ g⁻¹, and an average pore size of 3.1 nm, which are 2.0-fold, 3.9-fold and 3.3-fold higher than those of BC sample, respectively. MBC-0.4 sample, generated from a larger mass ratio of FeCl₃ to LSP, has superior porosity characteristics than MBC-0.2 sample due to stronger activation.

3.1.3. Magnetic properties of magnetic biochar
In addition to carbonization and activation, magnetization introduces magnetic Fe₃O₄ crystals to MBC. All as-prepared MBC samples could be attracted effectively by a bar magnet. Their magnetic properties are clarified in figure 2. Generally, the magnetic hysteresis curves with very low coercivity and almost negligible magnetic hysteresis cycles describe superparamagnetic behavior. Therefore, these materials are easily magnetized and demagnetized. When the mass ratio of FeCl₃ to LSP was increased from 0.1 to 0.5, Fe content in MBC increased from 3.3 to 10.4 wt%, leading to an increase in specific saturation magnetization from 1.21 to 6.94 emg g⁻¹.

Similar tendencies have been revealed in previous studies \[40, 42\]. Assuming that all Fe element in MBC samples exists in Fe₃O₄ form only, the saturation magnetization of 100% Fe₃O₄ would be between 38–92 emu g⁻¹, which could be generally comparable with that of Fe₃O₄ nanoparticles (56 emu g⁻¹ \[43\], 50–61 emu g⁻¹ \[44\], 42–49 emu g⁻¹ \[45\]). As a result, one-pot immobilization of Fe₃O₄ on the biochar base may not considerably diminish their magnetic property. As reviewed by Bedia et al \[15\], specific saturation magnetization of MBC from one-pot pyrolysis is comparable to or higher than that from magnetic activated carbon prepared by different synthesis procedures.

3.1.4. FTIR spectra of biochar and magnetic biochar
Figure 3 shows that different functional groups were present in both BC and MBC. With only carbonization, BC remained the main characteristic peaks: 3380 cm⁻¹ (O–H in carbonyl and phenol groups); 3040 cm⁻¹ (C–H

| Samples   | Fe content (wt%) | S_{BET} (m² g⁻¹) | V_{total} (cm³ g⁻¹) | d_{average} (nm) | Saturation magnetization (emg g⁻¹) |
|-----------|------------------|------------------|---------------------|-----------------|------------------------------------|
| BC        | —                | 150              | 0.08                | 1.1             | —                                 |
| MBC-0.1   | 3.3              | —                | —                   | —               | 1.21                               |
| MBC-0.2   | 5.7              | 277              | 0.13                | 1.9             | 1.56                               |
| MBC-0.4   | 7.9              | 349              | 0.31                | 3.6             | 3.90                               |
| MBC-0.5   | 10.4             | —                | —                   | —               | 6.94                               |

| Figure 1. X-ray diffraction of MBC prepared with different mass ratios of FeCl₃ to LSP. |
| --- | |
stretches vibration); 1593 cm$^{-1}$ (C=C stretching vibration in the aromatic rings); 1428 cm$^{-1}$ (C–H derived from lignin and holocellulose); 1165 and 1046 cm$^{-1}$ (C–O–C and C–C from cellulose and hemicellulose); 875, 818 and 753 cm$^{-1}$ (C–H from aromatic rings) [22, 46–48]. Moreover, it was found that the peak of C=O stretching vibration at 1755 cm$^{-1}$ was close to disappearance, indicating that carbonyl and ester groups of hemicellulose were decomposed during pyrolysis [49].

With FeCl$_3$-activation, MBC introduced a broad spectral feature of 3150 cm$^{-1}$ derived from O–H stretching vibration. While the peaks at 1570 (C–C), 1138 (C–O–C) and 1046 (C–C) cm$^{-1}$ were present in both BC and MBC, the peak at 2410 cm$^{-1}$ related to the stretching vibration of O–H was found in MBC only [15]. The disappearance of the peak at 1428 cm$^{-1}$ and the very short peak at 875 cm$^{-1}$ proved that the activation process carbonized almost all lignin and holocellulose. Generally, FeCl$_3$-activation considerably varied functional groups on the carbon surface. The enhancement of oxygen functional groups could increase the polarity of the material surface, making it more favorable for interactions with water-soluble organic matters. Moreover, it is
worth noting that the vibration peak of the Fe–O bond was discovered at 570 cm\(^{-1}\) [42, 43], which was attributed to the existence of Fe\(_3\)O\(_4\), implicitly confirming the successful synthesis of MBC.

### 3.1.5. SEM images of magnetic biochar

The surface morphology of MBC samples is depicted in figure 4. In general, the materials have a smooth surface and fragments with sharp edges. Crushing, carbonization, and activation may reduce MBC to the microscale. When the mass ratio of FeCl\(_3\) to LSP was increased, no significant change in the surface morphology of MBC was observed. Interestingly, the lack of spheres from obviously aggregated Fe\(_3\)O\(_4\) particles was shown on the surface of MBC samples. This reveals that Fe\(_3\)O\(_4\) components seem to be diffused onto the biochar surface without gathering. Bedia et al [17] reported that nanoscale Fe\(_3\)O\(_4\) particles generated by FeCl\(_3\)-activation of biomass can be entrapped inside the carbon base rather than on its surface. As a result, the particles can maintain their stable performance during long-term operation.

### 3.1.6. EDS elemental mapping of magnetic biochar

EDS analysis was used to determine the type and amounts of constituent elements in the chemical structure of MBC (figure 5). The results showed that the contents of C, Fe, and O in MBC-0.4 were 80.15, 7.74, and 10.90 wt\%, respectively. Interestingly, the surface Fe content determined by EDS was comparable to the bulk Fe content determined by AAS (7.9 wt\%). This finding suggests that Fe may be highly dispersed both inside and outside the carbon framework. In addition, the high oxygen content revealed that this element existed in not only Fe\(_3\)O\(_4\) but also oxygen functional groups, as discussed in the FTIR results. According to Chen et al [22], LSP derived-biochar may contain such trace amounts of K, Ca, Mg, N, S, P, and Cl. However, no metal elements were discovered in MBC, indicating that these minerals were removed by cleaning or did not exist in the raw material. In reverse, P and Cl elements were detected at 0.20 and 1.00 wt\%, respectively. P could only originate from LSP. However, Cl could partially or entirely come from the addition of FeCl\(_3\). After multiple cleanings of MBC, the wastewater was analyzed using various techniques (pH, electrical conductivity, NaOH, AgNO\(_3\)) to ensure that no further leaching of Fe\(^{3+}\) and Cl\(^-\) and PO\(_4^{3-}\) ions from MBC occurred. Hence, these minor elements could be trapped tightly within the carbon framework by strong mechanical or chemical bonds. Finally, microscale element mapping images revealed that all existing elements were uniformly distributed on the MBC surface. To clarify the internal structure of MBC, nanoscale TEM analysis was presented in the following section.

![Figure 4. SEM images of MBC prepared with different mass ratios of FeCl\(_3\) to LSP.](image-url)
**Figure 5.** EDS elemental mapping of MBC-0.4.

**Figure 6.** TEM images of BC and MBC-0.2.
3.1.7. TEM images of biochar and magnetic biochar

The internal structure and spatial distribution of BC and MBC were explored by TEM images (Figure 6). Biochar at the nanoscale had relatively regular brightness in a large area. After the pyrolysis process, the carbon framework together with functional groups was formed by covalent bonds, resulting in a relatively homogeneous BC structure. In contrast, irregular brightness in MBC showed the morphology of Fe₃O₄. It seems that not only nanoparticles but also nanowires were formed. Typically, the formation of Fe₃O₄ nanoparticles in MBC has been described in such reports [39, 49, 50]. Even though the nanoparticles had a non-uniform shape and were grouped into clusters, their size was small, with some below 20 nm. Notably, the presence of nanowires in MBC was uncommon. The lengths and diameters of these nanowires were generally lower than 10 nm and 100 nm, respectively. The FeCl₃-activation process could generate and expand mesopores in the carbon framework. Therefore, it seems possible that Fe₃O₄ nanowires could develop in tube-like mesopores. In regard to the dispersion of ionic Fe₃O₄ in MBC, these nanostructures were embedded well within the carbon framework by mechanical bonds. Thus, MBC is expected to maintain its stability during long-term operation.

3.2. Degradation of orange G using magnetic biochar

3.2.1. Adsorption capacities of magnetic biochar with orange G

The catalytic activity of MBC in OG degradation with H₂O₂ was explored. The experiment consists of two steps: adsorption for the first 20 min, followed by 90 min of oxidation (Figures 7–10). Parameters including different MBC samples, MBC dosage, pH and H₂O₂ concentration were detailed in Table 2. All of the results indicated that the adsorption process had nearly reached equilibrium before the subsequent oxidation step. At low concentrations (0.10 to 0.60 g l⁻¹), 1.0 g MBC could adsorb 2.0–17.0 mg OG and eliminate up to 4.5% OG within the first 20 min (Table 2). Regarding adsorption mechanisms, OG might interact with functional groups on biochar base through π–π bonds, hydrogen bonds, and electrostatic interactions [15, 51]. On the other hand, ionic crystals of Fe₃O₄ might not attract organic molecules effectively. This revealed that, under appropriate conditions, MBC could be a potential adsorbent for OG removal.

3.2.2. Effect of magnetic biochar prepared with different mass ratios of FeCl₃ to LSP on orange G degradation

The degradation of OG catalyzed by BC and MBC samples was shown in Figure 7a. BC removed a small amount of OG, mainly due to adsorption. On the contrary, all MBC samples were capable of decolorizing OG during the oxidation step. Thus, the catalytic activity almost exclusively originated from Fe₃O₄ rather than LSP-derived biochar base. However, the porous carbon base may have a certain contribution, more pronounced as the role of surface area and functional groups. The catalytic mechanism of heterogeneous Fe(II) and Fe(III) sites for the degradation of organic compounds by H₂O₂ is as follows [9, 52]:

$$\equiv \text{Fe(II)} \text{H}_2\text{O} + \text{H}_2\text{O}_2 \rightarrow \equiv \text{Fe(II)}\text{H}_2\text{O}_2 + \text{H}_2\text{O}$$

(4)
When Fe content in MBC samples increased from 3.3 to 10.4 wt%, the degradation efficiency improved significantly from 20.3 to 96.0% (table 2). Increasing the number of Fe active sites on MBC might improve degradation efficiency. However, the degradation rate of MBC-0.5 was slower than that of MBC-0.4. The catalytic activity of MBC might be influenced by the crystal structure, size and content of Fe₃O₄. Excessive Fe(II) sites could also diminish ·OH, as shown in equation 9 [32, 38]:

\[
\text{Fe(II)} + \cdot\text{OH} \rightarrow \text{Fe(III)} + \text{OH}^-
\]  

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\[
\text{Fe(III)} \text{H}_2\text{O} + \text{H}_2\text{O}_2 \rightarrow \text{Fe(III)}\text{H}_2\text{O}_2 + \text{H}_2\text{O} \\
\text{Fe(II)}\text{H}_2\text{O}_2 \rightarrow \text{Fe(III)} + \text{OH} + \text{OH}^- \\
\text{Fe(III)}\text{H}_2\text{O}_2 \rightarrow \text{Fe(II)} + \text{H}^+ + \text{OOH} \\
\text{Organic compounds} + \text{OH} \rightarrow \text{Intermediates} \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\]  

(5)  
(6)  
(7)  
(8)

In addition to catalytic iron sites, minor elements present in MBC might affect its catalytic activity. Chloride ions may be detrimental to OG degradation [53, 54]. The inhibitive effect of Cl⁻ ions on the decolorization of OG could come from the interaction of Cl⁻ ions with ·OH. Similarly, phosphate ions have been shown to inhibit catalytic oxidation processes [55, 56]. However, minor amounts of Cl and P in the carbon framework may not exist in ion form. In addition, they may be difficult to leach into treatment media, as discussed in EDS results.
With the efficient catalytic activity of MBC on OG degradation, the role of these minor elements might be negligible.

### 3.2.3. Effect of magnetic biochar dosage on orange G degradation

Figure 8 depicts the effect of MBC-0.4 dosage on OG degradation. Without MBC, H2O2 was not able to process OG, indicating that the presence of catalysts significantly contributed to the OG degradation. As expected, when the MBC dosage was increased from 0.10 g l\(^{-1}\) to 0.40 g l\(^{-1}\), the degradation rate increased. As mentioned before, high catalyst dosage could enhance the number of active sites for H2O2 decomposition into \(\cdot\)OH and the adsorption of OG. However, the originally generated radicals can be deactivated because of the excess catalyst [57, 58]. In the first 30 min, the degradation rate with 0.60 g l\(^{-1}\) MBC-0.4 was faster than that with 0.40 g l\(^{-1}\), but slowed in subsequent periods. The excess of Fe(II) sites might reduce the number of \(\cdot\)OH radicals (equation 9).
3.2.4. Effect of pH on orange G degradation
The pH of the reaction mixture significantly affected OG degradation (figure 9). The OG concentration almost remained constant at a high pH of 5.0. Wang et al. [32] found that under high pH conditions, Fe(OH)₃ could be formed from Fe(III), lowering the amount of Fe(II) and the number of free radicals ·OH. When the pH dropped from 4.0 to 2.0, the degradation rate accelerated dramatically. Low pH could facilitate the reduction of Fe(II) to Fe(III), hence favoring ·OH generation [14].

3.2.5. Effect of H₂O₂ dosage on orange G degradation

The OG complete mineralization equation is proposed according to the literature. Based on equation 10 [30], 100 ppm OG requires a minimum H₂O₂ dosage of 316 ppm for complete mineralization. Thus, different H₂O₂ dosages from 250 to 400 ppm were investigated (figure 10). As H₂O₂ dosage increased from 250 to 350 ppm, the OG degradation rate was observed to improve slightly. In contrast to the degradation rate at 350 ppm H₂O₂, the rate at 400 ppm H₂O₂ is faster than in the initial 50 min of oxidation but slower than in the latter period. On the surface of MBC, H₂O₂ reacts with Fe₃O₄ to create ·OH and ·OOH radicals. Hence, the higher H₂O₂ dosage is used, the more ·OH free radicals are generated, thereby accelerating the reaction rate. However, these radicals could react with H₂O₂ and also themselves, leading to their decrease, according to the following reactions [59]:

\[
\cdot\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{OOH} + \text{H}_2\text{O} \\
\cdot\text{OH} + \text{OOH} \rightarrow \text{O}_2 + \text{H}_2\text{O} \\
\cdot\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2
\]

3.2.6. Kinetics of orange G degradation catalyzed by magnetic biochar
The kinetics of OG degradation are presented in figure 7b. C₀ is the initial OG concentration (100 ppm), Cₜ represents the dye concentration at time t, and k is the reaction rate constant. As a result, the pseudo-first-order rate constants for MBC-0.1, MBC-0.2, MBC-0.4 and MBC-0.5 catalysts were 0.002 min⁻¹ (R² = 0.976), 0.006 min⁻¹ (R² = 0.990), 0.034 min⁻¹ (R² = 0.993) and 0.016 min⁻¹ (R² = 0.967), respectively. These R² values from regression lines indicated that the reactions approximately obeyed pseudo-first-order kinetics. This kinetics is similar with many previous studies for advanced oxidation processes of Orange G using Fe-based catalysts [54, 57, 60, 61].

3.2.7. Stability and reusability of MBC catalyst
Stability and reusability play an important role in the application of catalysts in industrial pollutant treatment. Hence, four consecutive experiments were conducted to investigate these characteristics of MBC. As presented in figure 11, the removal efficiencies after each cycle were 96.0, 93.0, 92.1 and 89.6%, respectively. It means that
MBC lost only 6.4% catalytic activity after four cycles and an average of 1.6% after each cycle, establishing its reusability. The slight decrease in the removal efficiency could be partly caused by Fe leaching. AAS results revealed that only 1.31–1.44 mg l\(^{-1}\) of Fe leaching was detected after each cycle. This leaching corresponded to 4.1%–4.6% Fe in MBC-0.4 sample. Furthermore, these Fe concentrations were lower than the legal limit of the European Union at 2 mg l\(^{-1}\). As described in the literature, one-pot FeCl\(_3\) activation of biomass could provide MBC catalysts with improved stability and reduced metal leaching\[9, 15\]. The dispersion of nanoscale Fe\(_3\)O\(_4\) within the carbon framework may slow the rate of Fe leaching into the aqueous medium. Moreover, with very low concentrations of Fe leaching in the treatment medium, homogeneous catalysis could be neglected. Thus, MBC proved to be a potential catalyst for the treatment of organic pollutants thanks to its relative stability and reusability.

3.2.8. COD reduction during Orange G degradation catalyzed by magnetic biochar
COD is the total quantity of oxygen required to convert organic matter to carbon dioxide and water. To assess the mineralization during the catalytic degradation of OG, COD was monitored. As a result, figure 12 illustrates the decrease in OG and COD as the Fenton-like degradation proceeds. Initially, the adsorption process decreased both OG and COD concentrations. Subsequently, according to the pseudo-first-order kinetics, the concentration of OG decreased continuously. Within the first 30 min of catalytic oxidation, COD also decreased significantly from 86 to 50 mg l\(^{-1}\). In the subsequent period, however, there was a very slow decline in COD to 40 mg l\(^{-1}\). The MBC catalyst enabled the removal of 58% COD in 120 min. Even though almost all OG had vanished, mineralization was not yet complete. The degradation of OG molecules may lead to the formation of certain smaller organic intermediates\[60, 61\]. According to Gan et al\[62\], the mechanism for Fenton-like degradation of OG is complicated. \(\cdot\)OH radicals can attack species nonselectively, producing a variety of intermediates such as aniline, phenol, 7-hydroxy-8-(hydroxyamino) naphthalene-1, 3-disulfonic acid, 7, 8-dihydroxy-naphthalene-1, 3-disulfonic acid, alpha naphthol, and carboxylic acid. Additional treatment time may be required for complete mineralization of OG.

4. Conclusion
This study proposed an advanced route to facilitate the preparation of magnetic biochar via one-step pyrolysis of lotus seedpod and FeCl\(_3\) mixture. The formation of Fe\(_3\)O\(_4\) nanoparticles and nanowires on the carbon framework was demonstrated by XRD, FTIR, SEM, EDS and TEM results. The presence of the magnetic components contributed to a specific saturation magnetization of 6.94 emu g\(^{-1}\) for MBC. In addition, FeCl\(_3\) activation improved carbon-based pores, resulting in the as-prepared MBC with a high specific surface area of 349 m\(^2\) g\(^{-1}\) and a large total pore volume of 0.31 g cm\(^{-3}\). The experimental findings showed that MBC was not only a useful adsorbent but also an efficient catalyst for the treatment of Orange G. At pH 3.0, 350 ppm H\(_2\)O\(_2\), 0.40 g l\(^{-1}\) MBC-0.4, 100% Orange G (100 ppm) and 58% COD were eliminated after 120 min of treatment. The degradation with MBC catalysts approximately followed pseudo-first-order kinetics with the highest rate.
constant of 0.034 min⁻¹. In addition, the catalytic activity declined by only 6.4% following four reuse cycles, with minimal iron leaching of 1.31–1.44 mg l⁻¹. Overall, environmentally friendly, sustainable and low-cost MBC could be a potential catalyst for the treatment of Orange G in wastewater.

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Data availability statement

No new data were created or analysed in this study.

Conflicts of interest

The authors declare no conflicts of interest.

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References

[1] Suwunwong T, Hussain N, Chantrapromma S and Phoungthong K 2020 Facile synthesis of corncob biochar via in-house modified pyrolysis for removal of methyl blue in wastewater Mater. Res. Express 7 015518
[2] Mullai P, Vishali S, Kobika P, Dhiya K S, Mukund A and Sirraaman M 2022 Biochar production and its basket full of benefits - a review ECS Trans. 107 18747–52
[3] Wang J and Wang S 2019 Preparation, modification and environmental application of biochar: a review J. Clean. Prod. 227 1002–22
[4] Tan X, Liu Y, Zeng G, Wang X, Hu X, Gu Y and Yang Z 2015 Application of biochar for the removal of pollutants from aqueous solutions Chemosphere 125 70–85
[5] Kumi A G, Ibrahim M G, Nasr M and Fuji M 2020 Biochar synthesis for industrial wastewater treatment: a critical review Mater. Sci. Forum 1008 202–12
[6] He Q, Zhang K, Luo Y and Wang F 2021 Magnetic biochar particles prepared by ion cross-linking to remove phosphate from water Mater. Res. Express 8 076102
[7] Xiang W, Zhang X, Chen J, Zou W, He F, Hu X, Tsang D C W, Ok Y S and Gao B 2020 Biochar technology in wastewater treatment: a critical review Chemosphere 252 126339
[8] Xiang G, Long S, Liu H and Wu X 2021 Cd(II) removal from aqueous solutions by pomelo peel derived biochar in a permeable reactive barrier: modelling, optimization and mechanism Mater. Res. Express 8 115508
[9] Feng Z, Yuan R, Wang F, Chen Z, Zhou B and Chen H 2021 Preparation of magnetic biochar and its application in catalytic degradation of organic pollutants: a review Sci. Total Environ. 765 142673
[10] Thines K R, Abdullah E C, Mubarak N M and Ruthiraan M 2017 Synthesis of magnetic biochar from agricultural waste biomass to enhancing route for waste water and polymer application: a review Renew. Sust. Energ. Rev. 67 257–76
[11] Siddiqui M T H, Nizamuddin S, Baloch H A, Mubarak N M, Al-Ali M, Mazari S A, Bhutto A W, Abro R, Srinivasan M and Griffin G 2019 Fabrication of advanced magnetic carbon nano-materials and their potential applications: a review J. Environ. Chem. Eng. 7 102812
[12] Astuti W, Sulistyaningsih T, Prastiyanto D, Purba B S A and Kusumawardani R 2020 Synthesis of magnetically separable activated carbon from pineapple crown leaf for zinc ion removal Mater. Sci. Forum 1007 71–5
[13] Wu Z, Li W, Webley P A and Zhao D 2012 General and controllable synthesis of novel mesoporous magnetic iron oxide@carbon encapsulates for efficient arsenic removal Adv. Mater. 24 485–91
[14] Nguyen D V, Do H N, Do H N and Nguyen L Q 2020 One-step preparation of rice husk-based magnetic biochar and its catalytic activity for p-nitrophenol degradation Chem. Eng. Trans. 78 379–84
[15] Bedia J, Peñas-Garzón M, Gómez-Avilés A, Rodríguez J and Belver C 2020 Review on activated carbons by chemical activation with FeCl₃ C 6 21
[16] Liu P, Li H, Liu X, Wan Y, Han X and Zou W 2020 Preparation of magnetic biochar obtained from one-step pyrolysis of salix mongolica and investigation into adsorption behavior of sulfadimidine sodium and norflloxacin in aqueous solution J. Dispers. Sci. Technol. 41 214–26
[17] Bedia J, Monsalvo V M, Rodríguez J and Mohedano A F 2017 Iron catalysts by chemical activation of sewage sludge with FeCl₃ for CWPO Chem. Eng. J. 318 224–30
[18] Qu J et al 2022 Applications of functionalized magnetic biochar in environmental remediation: a review J. Hazard. Mater. 434 128841
[19] Hussain N, Chantrapromma S, Suwunwong T and Phoungthong K 2020 Cadmium (II) removal from aqueous solution using magnetic spent coffee ground biochar: kinetics, isotherm and thermodynamic adsorption Mater. Res. Express 7 085503
[20] Tao T, Li G, He Y and Sheng L 2019 Magnetic bamboo chars with fluffy graphene surface for efficient dye removal Mater. Res. Express 6 115089
[21] Lyu H, Zhang Q and Shen B 2020 Application of biochar and its composites in catalysis Chemosphere 240 124842
[22] Chen Z et al 2018 Characteristics and mechanisms of cadmium adsorption from aqueous solution using lotus seedpod-derived biochar at two pyrolytic temperatures Environ. Sci. Pollut. Res. 25 11854–66
[23] Lin Z, Zhang C, Cao D, Damaris R N and Yang P 2019 The latest studies on lotus (Nelumbo nucifera) - an emerging horticultural model plant Int. J. Mol. Sci. 20 3680
[24] Li A, Huang W, Qiu N, Mou F and Wang F 2020 Porous carbon prepared from lotus leaves as potential adsorbent for efficient removal of rhodamine B Mater. Res. Express 7 055505
[25] Sheikh S A 2014 Ethno - medicinal uses and pharmacological activities of lotus (Nelumbo nucifera) J. Med. Plants Stud. 2 42 – 6
[26] Nguyen M H, Nguyen T L, Nguyen T K L, Lam H H, Tran - Thuy T M, Nguyen Q L and Nguyen D V 2021 Facile preparation of lotus seedpod - derived magnetic porous carbon for catalytic oxidation of Poncere 4R IOP Conf. Ser.: Earth Environ. Sci. 947 012019
[27] Liu B, Zhou X, Chen H, Liu Y and Li H 2016 Promising porous carbons derived from lotus seedpods with outstanding supercapacitance performance Electrocim. Acta 208 55 – 63
[28] Tarkw A B, Oturan N, Ayancaya L, Laminis S and Oturan M A 2019 Photo - Fenton oxidation of Orange G azo dye: process optimization and mineralization mechanism Environ. Chem. Lett. 17 473 – 9
[29] Samsami S, Mohamadzianian M, Sarrazfzadeh M - H, Rene E R and Firoozbahr M 2020 Recent advances in the treatment of dye - containing wastewater from textile industries: overview and perspectives Process Saf. Environ. Prot. 143 138 – 63
[30] Wang Y, Prantiombo R, Zhang H and Huang Y - H 2015 Degradation of the azo dye Orange G in a fluidized bed reactor using iron oxide as a heterogeneous photo - Fenton catalyst RSC Adv.: 5 45276 – 83
[31] Dinya N, Bansal A and Jana A 2009 Degradation of acidic Orange G dye using UV - H2O2 in batch photoreactor Int. J. Biol. Chem. Sci. 3 54 – 62
[32] Wang N, Zheng T, Zhang G and Wang P 2016 A review on Fenton-like processes for organic wastewater treatment J. Environ. Chem. Eng. 4 762 – 87
[33] Rodrigues C D S, Soares O S G P, Pinho M T, Pereira M F R and Madeira L M 2017 p - Nitrophenol degradation by heterogeneous Fenton’s oxidation over activated carbon - based catalysts Appl. Catal. B: Environ. 219 109 – 22
[34] Nguyen M D, Tran H - V, Xu S and Lee T R 2017 Fe3O4 nanoparticles: structures, synthesis, magnetic properties, surface functionalization, and emerging applications Appl. Sci. 11 11301
[35] Chen Z, Ma Y, Geng B, Wang M and Sun X 2017 Photocatalytic performance and magnetic separation of TiO2-functionalized γ-Fe2O3, Fe3O4, and FeO magnetic particles J. Alloys Compd. 700 113 – 21
[36] Rice E W, Eaton A D and Baird R B 2017 Standard Methods for the Examination of Water and Wastewater 23 (Washington, DC: American Public Health Association, American Water Works Association, Water Environment Federation)
[37] Wu T and Engelhardt J D 2012 A new method for removal of hydrogen peroxide interference in the analysis of chemical oxygen demand Environ. Sci. Technol. 46 2291 – 8
[38] El Ghandour H, Zidan H, Khalil M M and Ismail M 2012 Synthesis and some physical properties of magnetite (Fe3O4) nanoparticles Int. J. Electrochem. Sci. 7 5734 – 45
[39] Yi Y, Tu G, Eric Tsang P and Fang Z 2020 Insight into the influence of pyrolysis temperature on Fenton-like catalytic performance of magnetic biochar Chem. Eng. J. 380 1215218
[40] Cazetta A L, Pezoti O, Bedin K C, Silva T L, Paesano Junior A, Asfa T and Almeida V C 2016 Magnetic activated carbon derived from biomass waste by concurrent synthetic: efficient adsorbent for toxic dyes ACS Sustain. Chem. Eng. 4 10588 – 68
[41] Dastgheibi S A, Ren J, Rostam - Abadi M and Chang R 2014 Preparation of functionalized and metal - impregnated activated carbon by a single - activation method: Appl. Surf. Sci. 290 92 – 101
[42] Yang J, Zhao Y, Ma S, Zhu B, Zhang J and Zheng C 2016 Mercury removal by magnetic biochar derived from simultaneous activation and magnetization of sawdust Environ. Sci. Technol. 50 12040 – 7
[43] Yadav B S, Singh R, Vishwasakaram A K and Kumar N 2020 Facile synthesis of substantially magnetic hollow nanospheres of maghemite (γ-Fe2O3) originated from magnetite (Fe3O4) via solvothermal treatment J. Supercond. Nov. Magn. 33 2199 – 208
[44] Wei Y, Han B, Hu X, Lin Y, Wang X and Deng X 2012 Synthesis of Fe3O4 nanoparticles and their magnetic properties Procedia Eng. 27 632 – 7
[45] Sun J, Zhou S, Hou P, Yang Y, Weng J, Li X and Li M 2007 Synthesis and characterization of biocompatible Fe3O4 nanoparticles J. Biomed. Mater. Res. A 80A 333 – 41
[46] Liu N, Liu Y, Zeng G, Gong J, Tan X, JunWen, Liu S, Jiang L, Li M and Yin Z 2020 Adsorption of 17β-estradiol from aqueous solution by raw and direct / pre / post - KOH treated lotus seedpod biochar J. Environ. Sci. 87 10 – 23
[47] Li K, Zhang Y, Yang Y, Wei H and Wang Q 2014 Removal of Cr(VI) from aqueous solutions using buckwheat (Fagopyrum esculentum Moench) hull through adsorption - reduction: affecting factors, isotherm, and mechanisms Clean Soil Air Water 42 1349 – 57
[48] Shi X, Gong B, Liao S, Wang J, Liu Y, Wang T and Shi J 2020 Removal and enrichment of Cr(VI) from aqueous solutions by lotus seed pods Water Environ. Res. 92 84 – 93
[49] Zhang S, Su Y, Zhu S, Zhang H and Zhang Q 2018 Effects of pretreatment and FeCl3 preload of rice husk on synthesis of magnetic carbon composites by pyrolysis for supercapacitor application J. Anal. Appl. Pyrolysis 135 22 – 31
[50] Zeng H, Qi W, Zhai L, Wang F, Zhang J and Li D 2021 Preparation and characterization of sludge-based magnetic biochar by pyrolysis for methylene blue removal Nanomaterials 11 2473
[51] Ghasemi M and Mouss兰nejad N 2014 Study of competitive adsorption of malachite green and sunset yellow dyes on cadmium hydroxide nanowires loaded on activated carbon J. Ind. Eng. Chem. 20 1085 – 96
[52] Xu H - Y, Shi T - N, Wu L - C and Qi S - Y 2013 Discoloreation of methyl orange in the presence of schorl and H2O2: kinetics and mechanism Water Air Soil Pollut. 224 1740
[53] De Laat J and Le T G 2006 Effects of chloride ions on the iron(III)-catalyzed decomposition of hydrogen peroxide and on the efficiency of the Fenton-like oxidation process Appl. Catal. B: Environ. 66 137 – 46
[54] Sun S - P, Li C - J, Sun J - H, Shi S - H, Fan M - H and Zhou Q 2009 Decolorization of an azo dye Orange G in aqueous solution by Fenton oxidation process: Effect of system parameters and kinetic study J. Hazard. Mater. 161 1052 – 7
[55] Yang X, He J, Sun Z, Holmgren A and Wang D 2016 Effect of phosphate on heterogeneous Fenton oxidation of catechol by nano-Fe3O4: inhibitor or stabilizer J. Environ. Sci. 39 69 – 76
[56] Wang W, Zhou S, Li R, Peng Y, Sun C, Vakili M, Yu G and Deng S 2021 Preparation of magnetic powdered carbon/nano-Fe3O4 composite for efficient adsorption and degradation of trichloropropyl phosphate from water J. Hazard. Mater. 416 125765
[57] Ramirez J H, Maldonado - Hódar F J, Pérez - Cadenas A F, Moreno - Castillo G, Costa C A and Madeira L M 2007 Azo-dye Orange II degradation by heterogeneous Fenton-like reaction using carbon-Fe catalysts Appl. Catal. B: Environ. 75 312 – 23
[58] Ou X, Yan J, Zhang F and Zhang C 2018 Accelerated degradation of orange G over a wide pH range in the presence of Fe3O4 J. Environ. Sci. Eng. 12 7
[59] Yousef N A, Shaban S A, Ibrahim F A and Mahmoud A S 2016 Degradation of methyl orange using Fenton catalytic reaction Egypt. J. Pet. 25 317 – 21
[60] Madhavan J, Grieser F and Ashokkumar M 2010 Degradation of orange-G by advanced oxidation processes Ultrason. Sonochem. 17 338–43

[61] Pang Y L, Lim S, Ong H C and Chong W T 2016 Synthesis, characteristics and sonocatalytic activities of calcined γ-Fe$_2$O$_3$ and TiO$_2$ nanotubes/γ-Fe$_2$O$_3$ magnetic catalysts in the degradation of Orange G Ultrason. Sonochem. 29 317–27

[62] Gan G, Liu J, Zhu Z, Yang Z, Zhang C and Hou X 2017 A novel magnetic nanoscaled Fe$_3$O$_4$/CeO$_2$ composite prepared by oxidation-precipitation process and its application for degradation of orange G in aqueous solution as Fenton-like heterogeneous catalyst Chemosphere 168 254–63