Iron Carbon Catalyst Initiated the Generation of Active Free Radicals without Oxidants for Decontamination of Methylene Blue from Waters

Yan Liu 1, Guangyu Xie 1,2, Guoyu Li 1, Jingye Cui 1, Chuang Li 1,3, Hao Xu 1, Yating Lu 1,3, Qi Jin 1, Daixi Zhou 1 and Xinjiang Hu 1,*

1 College of Environmental Science and Engineering, Central South University of Forestry and Technology, Changsha 410004, China; yanliu0102@126.com (Y.L.); anyuxie@126.com (G.X.); gylee1221@163.com (G.L.); jingyecui0595@126.com (J.C.); lc302864860@163.com (C.L.); liuyan624909376@163.com (H.X.); luca_18163.com (Y.L.); jq305745239@126.com (Q.J.); daixizhou07@126.com (D.Z.)
2 College of Environmental Science and Engineering, Beijing Forestry University, Beijing 100083, China
3 College of Environmental Science and Engineering, Hunan University, Changsha 410082, China
* Correspondence: xjhu@csuft.edu.cn

Abstract: In conventional oxidation technologies for treatment of contaminated waters, secondary pollution of the aqueous environment often occurs because of the additional oxidants generated during the process. To avoid this problem, Fe/NG catalyst composites without additives were developed in this study for decontamination of methylene blue (MB) from waters. The Fe/NG catalyst, composed of carbon nitride and iron chloride (FeCl$_3$, 6H$_2$O), was prepared by high temperature pyrolysis. It is an exceptionally efficient, recoverable, and sustainable catalyst for degradation of organic matter. The morphological characteristics, chemical structure, and surface properties of the catalyst composites were investigated. The catalyst exhibited high MB removal efficiency (100%) within 30 min under ambient temperature and dark conditions. The experiments indicated that an MB degradation effect was also applicable under most acid–base conditions (pH = 2–10). The characterization results using electron spin resonance and analysis of intermediate products demonstrated that free radicals such as -OH and -O$_2$· were produced from the Fe/NG composites in the heterogeneous system, which resulted in the high MB degradation efficiency. Moreover, the catalysis reaction generated reducing substances, triggering iron carbon micro-electrolysis to spontaneously develop a microcurrent, which assisted the degradation of MB. This study demonstrates the feasibility of Fe/NG catalysts that spontaneously generate active species for degrading pollutants in an aqueous environment at normal temperature, providing an attractive approach for treating organic-contaminated waters.

Keywords: catalytic degradation; iron-carbon; micro-electrolysis; radical mechanism

1. Introduction

Various industries—such as dyeing, printing, textiles, medical treatment, and personal care products—indirectly discharge organic pollutants, which have harmful effects on the aquatic ecosystem [1]. Among the wastewater generated from these sources, dye-contaminated wastewater has been recognized as an emerging environmental issue with chemically stable organic components that can be readily transferred to the aqueous environment through aquacultural aspects and effluent discharge. Most existing dyes have a complex internal structure, exhibiting high stability and poor natural degradability. Organic dyes pose teratogenic, carcinogenic, and mutagenic hazards to most animals [2–4].

Therefore, new technologies must be developed and applied to treat organic dyes in the wastewater. This can reduce the extent of water pollution, promote sustainable regeneration, and is of high significance to human health as well as environmental governance [2,5]. Therefore, many researchers have applied physical adsorption, chemical precipitation,
and biological reduction for treatment of organic-contaminated wastewater [6–8]. These methods and techniques pose some challenges that require further investigation. For example, dosing dyeing wastewater with a quantitieative adsorbent to remove organic matter can rapidly reduce the concentration of organic pollutants, but the adsorbent material is consumed readily and difficult to regenerate. However, chemical methods are often used to add some reagents to enhance the catalytic oxidation activity of the adsorbent. Although they are highly effective, these additives can cause secondary pollution to the environment. Considering the use of organisms or microorganisms to degrade organic wastewater, the biological treatment methods primarily simulate the natural degradation process occurring in the environment and prevent secondary pollution during removal of organic matter. However, different microorganisms require different growth environments, which are cost-intensive and difficult to control during the treatment process. Therefore, scaling up these technologies can be difficult when handling such industrial dyes with highly reducing properties.

Advanced oxidation processes (AOPs) are new environmental remediation technologies, which exhibit numerous advantages in the treatment of stable and toxic wastewater with high organic concentrations. Common AOPs include ozone oxidation, ultrasonic degradation, photocatalysis, and Fenton reaction [6,8]. Active free radicals generated by the oxidants (O$_2$, O$_3$, H$_2$O$_2$, etc.) in AOPs can induce the degradation of organic compounds under externally controlled conditions. However, conventional AOPs require additional oxidants such as hydrogen peroxide to stimulate these free radicals that act as active substances in the removal of pollutants from waters. These additives can cause secondary pollution of the aqueous environment. In addition, a common disadvantage of the Fenton process is that most reactions can only show high activity under acidic environments, which limits its practical application. To solve the abovementioned problems, this paper proposes a catalyst that can generate active free radicals without requiring additional oxidants, to effectively remove organic pollutants such as methylene blue (MB) and purify contaminated waters.

In this study, a novel Fe/NG catalyst was developed that can spontaneously generate active substances, such as $\cdot$OH and $\cdot$O$_2^-$, in the absence of oxidants and visible or ultraviolet light. These radicals can naturally decrease the excitation energies of the organic matter and act as reducing agents at ambient temperature. The degradation mechanism of MB is discussed in detail in the following section. The process can not only minimize secondary pollution, but also promote clean production and sustainable development. Therefore, based on the principle that pyrolytic carbon can generate free radicals from other substances, the main objectives of this study are as follows: (1) to investigate the degradation of an organic dye, MB, by free radicals generated from Fe/NG catalyst composites; and (2) to explore the generation mechanism of $\cdot$OH and $\cdot$O$_2^-$ in suspension [9].

2. Results and Discussions

2.1. Characterization of the Catalyst

2.1.1. Morphological Characteristics of the Catalyst

According to the morphological characterization shown in Figure 1, carbon nitride (CN) presents an agglomerated structure (Figure 1a) and n-CN has a layered structure with a smooth surface (Figure 1b). The composite material of Fe/NG has more flower-like structures attached to its surface (Figure 1c), indicating that Fe has been successfully loaded onto n-CN. This can be confirmed by the energy dispersive X-ray spectroscopy (EDX) images (Figure 1d). Analysis showed that the Fe content increased to 12.32 wt %. In addition, a higher number of microscopic pores implies that more active sites are available, improving the MB degradation performance of the catalyst. Moreover, high-resolution-transmission electron microscopy (HR-TEM) revealed that Fe nanoparticles appear uniformly on n-CN (red circle in Figure 1e), with a particle size of about 2–20 nm. Furthermore, clear lattice fringes with a pitch of 0.21 nm can be observed in the HR-TEM image in Figure 1f, indicating the presence of Fe$_3$C structures in the catalyst [10,11].
Figure 1. SEM images of (a) CN, (b) n-CN, (c) Fe/NG; (d) EDX image; and (e,f) HR-TEM images of Fe/NG.

2.1.2. Surface Structure of the Catalyst

X-ray diffraction (XRD) analyses of both of the samples revealed a typical g-C₃N₄ diffraction pattern (Figure 2). As illustrated in Figure 2a, the peak observed at approximately 13.1° is attributed to the structure stacked on and indexed to the (100) plane, which corresponds to the in-plane tri-s-trizine units. The sharpest peak at approximately 27.5° is indexed to the (002) plane, which indicates the graphite-like stacking of the conjugated aromatic unit [12,13]. Two typical peaks were retained in both CN and n-CN. However, the XRD of CN and n-CN did not show any peak shift, which indicates the existence of van der Waals forces between the layers in CN and n-CN. The intensity of the (002) diffraction peak in Fe/NG was observed to decrease rapidly, which suggested that the effect of the high temperature from an additional heat treatment possibly overcame the van der Waals forces between the layers. In addition, the effective exfoliation of CN into nanosheets contributed to the Fe nanoparticles loaded on it, which might be because the material was treated with FeCl₃ [14]. Moreover, a slight shift to a higher diffraction angle and a weak intensity of the main peak for Fe/NG were observed, indicating that Fe was successfully incorporated into the framework of n-CN [12,15,16]. Comparing the XRD results, no evident shift in the spectra was observed for the fresh and degraded Fe/NG catalysts. This implies a feasible preparation of Fe/NG catalyst, effective Fe loading, stable catalyst operation, and absence of secondary contamination of the water that may result from an unstable catalyst structure.
Figure 2. (a) XRD pattern of CN, n-CN and Fe/NG; (b) enlarged view of XRD pattern of Fe/NG.

Figure 2b shows an enlarged view of the XRD pattern for Fe/NG. The strongest peak at approximately 45.8° is indexed to the (211) plane corresponding to Fe₃C [17], which is consistent with the result of HR-TEM. Iron carbide (Fe₃C) has been utilized recently owing to its superior performance in terms of excellent reactivity and high specific surface area. During the degradation of MB, Fe₃C can act as a source of Fe(II) and promote the regeneration of Fe(II) [18]. Nonetheless, the high surface energy and natural magnetic properties of Fe₃C particles can lead to their aggregation and hinder activation activity. The selection of n-CN as a carrier is an efficacious approach to prevent the aggregation of Fe₃C. Carbon nitride (CN) materials are considered to be promising carriers that not only prevent the aggregation of Fe₃C particles, but also increase the electron transfer rate through its graphitic structure [19,20]. In addition, Fe-C solid catalyst consists of redox-active metal ions such as Fe²⁺/Fe³⁺, which is not only a catalyst, but also a powerful reducing agent involved in the catalytic process [21]. This is conducive to fully and effectively degrading contaminants in water [20].

The Fourier transform infrared (FT-IR) spectroscopy results (Figure 3a) show that the sharp absorption peak at 810 cm⁻¹ is attributed to the vibration caused by the bending of the S-triazine ring in n-CN. The peaks observed in the range of 1200–1600 cm⁻¹ correspond to N = C-N hetero-rings in the “melon” skeleton [22]. The multiple broad peaks in the 3000–3500 cm⁻¹ wavelength range are attributed to the N-H expansion vibration or O-H vibration of n-CN [23]. This implies that both CN and n-CN nanosheets exhibit very close FT-IR spectral data. Compared with CN nanosheets, the n-CN nanosheets undergo no increase or decrease in their organic functional groups, which indicates that the structure and composition of the catalyst was unchanged after further pyrolysis.

Figure 3. FT-IR spectrum (a) of CN and n-CN, spectrum (b) of Fe/NG and after the degradation.
The FT-IR spectra of the Fe/NG sample are illustrated in Figure 3b. A strong peak was detected at approximately 3431.4 cm$^{-1}$ corresponding to O-H originating from the sample material or water. Subsequently, distinct peaks occurred at 2937.6, 1735.4, and 1620.8 cm$^{-1}$, which were correlated to C-H, C-O tensile vibrations, and aromatic C=C or C=N bond vibrations, respectively, based on previous investigations. The absorption band in the 987–1236 cm$^{-1}$ region is ascribed to the stretching ring vibration of the C-N and C-C bonds. In the Fe/NG spectra, an apparent peak was also observed at approximately 560 cm$^{-1}$ attributed to Fe-O formation, which has an essential role in the subsequent research. The presence of Fe-C (1395.7 cm$^{-1}$) proves that melamine has an essential contribution in the formation of Fe/NG [24].

To further explore the changes before and after the degradation of the catalyst, we examined the X-ray photoelectron spectra to analyze the chemical properties of the material surface, such as the elemental composition of the material and the morphology of the element. Figure 4a shows the X-ray photoelectron spectroscopy (XPS) wide-scan spectra of Fe/NG, composed of C 1s, N 1s, O 1s, and Fe 2p orbitals [25], which indicates the homogeneous distribution of these four elements. These findings are consistent with the EDX results. In the C 1s region of the fresh and degraded catalysts, four distinctive peaks at 283.9, 285, 286, and 288.6 eV were observed (Figure 4b), which corresponded to Fe-C, C-C, C-OH, and O-C = O, respectively. The analysis revealed that electrons can escape from the C-C bonds of the graphitized carbon structure, thus enhancing the ability to conduct Fe/NG [26]. The high-resolution spectrum peaks of O 1s correspond to the surface hydroxyl groups (533.1 eV), adsorbed hydroxyl groups (531.2 eV) [13], and Fe-O (529.9 eV) (Figure 4c) [27]. The peaks were shifted after degradation, implying that these functional groups interacted with Fe/NG during the degradation process. The peak near 533 eV increased significantly, indicating that water is produced from the conversion of an organic to inorganic substance during the MB degradation process. Among the peaks, the appearance of iron oxide compounds is also consistent with the previous characterization results [19,20]. Figure 4d describes the Fe 2p XPS spectra of fresh and degraded Fe/NG. The distinctive peaks at 706.5 and 719.6 eV belong to Fe$^0$ nanoparticles on the Fe/NG layer, which is consistent with the previous characterization results. Similarly, the presence of distinct peaks at 710.7 and 723.4 eV suggest the presence of Fe(II) and the peaks corresponding to 713.3 and 716.1 eV confirmed the presence of Fe(III) [23,28,29]. Compared with the morphology of the catalyst before and after degradation, a decrease in the peak value of high-resolution Fe 2p spectra was observed at Fe 2p$_{1/2}$ and Fe 2p$_{3/2}$ before and after the reaction. Furthermore, these weakened peaks indirectly indicate that iron ions of different valence states also interact with each other during the degradation of MB by Fe/NG, which may suggest that the change of valence states and electron migration occurred during the degradation process of the catalyst.

The N$_2$ adsorption–desorption isotherms are shown at 77 K in Figure 5a, revealing typical Type-III isothermal curves. Notably, the specific surface area of the Fe/NG catalyst was approximately 4.5 times larger than that of bulk CN, and approximately 3.5 times larger than that of nanosheet n-CN, as interpreted from the isotherms. Moreover, the process is also a typical adsorption of metal oxides [30]. The pore size distribution plot reveals that Fe/NG has a larger pore volume than other catalysts. In addition, the desorption and adsorption curves do not coincide, demonstrating a hysteresis loop. This phenomenon is caused by the condensation of N$_2$ at pressures lower than the saturation vapor pressure of N$_2$ in porous mediators, which releases energy during adsorption and desorption and more energy is required for the formation of N$_2$ molecules. This process is known as capillary condensation and is observed in adsorbents that support mesoporous structures [31]. These findings clarify the reason for the rapid increase in the degradation rate of Fe/NG catalyst. Table 1 presents the specific surface area, pore volume, and pore diameter parameters of these three materials. These data also indicate that high-performance catalysts have high specific surface areas and low pore diameters.
Figure 4. (a) XPS survey spectra of Fe/NG and after the degradation. High-resolution spectra of (b) C 1s, (c) O 1s, (d) Fe 2p of Fe/NG and after the degradation.

Figure 5. (a) Nitrogen adsorption–desorption isotherms of CN, n-CN, and Fe/NG. (b) Magnetic hysteresis loops of Fe/NG at 298 K.

Table 1. BET analysis of synthesized product.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface Area (m² g⁻¹)</th>
<th>Pore Volume (cc g⁻¹)</th>
<th>Pore Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN</td>
<td>16.49</td>
<td>0.0769</td>
<td>18.65</td>
</tr>
<tr>
<td>n-CN</td>
<td>21.36</td>
<td>0.09094</td>
<td>17.03</td>
</tr>
<tr>
<td>Fe/NG</td>
<td>73.90</td>
<td>0.1691</td>
<td>9.125</td>
</tr>
</tbody>
</table>
2.1.3. Magnetic Properties

The magnetic properties of the catalyst were analyzed, as shown in Figure 5b. Previous studies have reported that Fe₃C is magnetic at ambient temperature [10]. The measured saturation magnetization value of Fe/NG catalyst reached approximately 16.1 emu g⁻¹. It exhibits strong magnetic properties, and the material can be reused after separating it from the reaction solution by applying an external magnetic field.

2.2. Catalyst Activity

Different materials were used to degrade 40 mg L⁻¹ MB (Figure 6a). All experiments were performed at ambient temperature. The experimental results showed that during the reaction of CN, n-CN, and Fe/NG with MB, the solutions reached removal equilibria in 30 min and their degradation rates were approximately 12%, 37%, and 100%, respectively. Notably, the degradation rates of MB (40 mg L⁻¹) with 1 g L⁻¹ CN, n-CN, and Fe/NG within 5 min were 7%, 21%, and 84%, respectively. This shows that Fe-doping of the composite material is essential for degrading MB rapidly. The highest degradation rates occurred during the first 5 min. The Brunauer–Emmett–Teller (BET) surface area of Fe/NG was found to be 73.90 cm² g⁻¹. This is because many active sites occur on the surface of Fe/NG at the initial stage of removal. Therefore, MB promptly occupies these active sites, considerably improving the degradation rate. To clarify the MB degradation efficiency of Fe/NG, the degradation effects for different dosages were studied, and the results are shown in Figure 6b. As the dosage increases, the degradation efficiency of the composite material on MB is evidently enhanced. Indeed, the higher the dose of catalyst added to the solution, the higher the number of active sites present during MB degradation. However, saturation of the maximum active sites also occurs, implying that the degradation efficiency for the same concentration of MB does not increase if more than the necessary amount of catalyst is added.

Figure 6. (a) Degradation of MB by CN, n-CN, and Fe/NG: CₐMB = 40 mg L⁻¹, m/V = 1 g L⁻¹. (b) Degradation of MB by different dosage of Fe/NG: CₐMB = 40 mg L⁻¹.

To calculate the tolerance and practicability of Fe/NG to acid–base environments, the degradation effect of this material on MB (50 mg L⁻¹) in solution was investigated under pH = 2–10. As a reference, we chose the same pH range to analyze the removal effects of CN and n-CN catalysts on 50 mg L⁻¹ MB. As shown in Figure 7a, these two catalysts (CN and n-CN) can only exhibit high degradation activity in a strong alkaline solution, which is also reflected in the zeta potential evaluation data (Figure 7b). Because MB is a weakly basic cationic dye, the Zeta potential in the solution gradually decreases with the increase in pH. Accordingly, the number of negative charges on the surface increases and electrostatic attraction may occur, leading to the removal of cationic MB molecules. Notably, the Fe/NG catalyst can degrade MB with slight variations in the efficiencies under different acid–base environments. This implies that the Fe/NG catalyst has a broader application over a wide
range of pH than other materials in degrading organic pollutants. Therefore, the catalytic degradation process of Fe/NG cannot be solely explained by the zeta potential, which was much higher than the elimination of MB by other modified catalysts (Table 2). This catalyst effectively overcomes the drawback that AOP technologies exhibit high activity only under acidic conditions (pH < 4) [32,33], and eliminates one of the factors limiting the application of materials in actual wastewater treatment.

![Figure 7](image-url) (a) Effect of pH values on the degradation of MB with Fe/NG: $C_{0\text{MB}} = 50 \text{ mg L}^{-1}$, $m/\text{V} = 1 \text{ g L}^{-1}$. Zeta potentials (b) of CN, n-CN, and Fe/NG.

**Table 2.** Comparison of various modified materials for MB removal.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>MB Removal (mg/L)</th>
<th>pH</th>
<th>Conditions</th>
<th>Time (h)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnNb$_2$O$_6$</td>
<td>37.5</td>
<td>5</td>
<td>$\text{H}_2\text{O}_2$</td>
<td>3</td>
<td>[34]</td>
</tr>
<tr>
<td>Co-BiVO$_4$</td>
<td>15</td>
<td>10</td>
<td>Visible-light</td>
<td>5</td>
<td>[35]</td>
</tr>
<tr>
<td>npg-C$_3$N$_4$</td>
<td>20</td>
<td>11</td>
<td>Visible-light</td>
<td>0.5</td>
<td>[36]</td>
</tr>
<tr>
<td>MIL-53 (Fe)</td>
<td>15</td>
<td>7</td>
<td>Visible-light</td>
<td>1.5</td>
<td>[37]</td>
</tr>
<tr>
<td>Fe/NG</td>
<td>40</td>
<td>2–10</td>
<td>-</td>
<td>0.5</td>
<td>In this study</td>
</tr>
</tbody>
</table>

Recovery and Reuse of Catalyst

The feasibility of recovering and reusing Fe/NG catalysts is also explored. The material can be recovered by utilizing its magnetic properties and directly reused after washing and drying with deionized water at approximately 60–80 °C. However, the reuse of the material was found to be ineffective. After four cycles, the removal rate did not reach 30%. This might be attributed to the limited life-span of the active species appearing in the reaction process, and therefore, the catalyst cannot be continuously reused with satisfactory performance. Therefore, we added 100 mM of hydrogen peroxide ($\text{H}_2\text{O}_2$) before the third cycle to remove unreacted MB and incompletely degraded organic matter adsorbed onto the catalyst surface. Figure 8 reveals that the reusability of the material was enhanced and the degradation rate was maintained at 82% after four cycles.

2.3. Possible Degradation Mechanisms

2.3.1. Active Species

Kinetic and thermodynamic models were adopted to explore the interaction mechanism of Fe/NG and MB. Figure 9a demonstrates that the linear correlation coefficient ($R^2$) of both the pseudo-first-order and pseudo-second-order kinetic models exhibited exceptional performance. The experimental results show that the removal capacities of adsorbates increased rapidly during the initial 5 min and became almost constant after 10 min. Compared to the pseudo-first-order model, the pseudo-second-order model with a higher $R^2$...
value (>0.999) is more appropriate to depict the degradation process, demonstrating that chemisorption might be the main rate limiting step [38].

![Figure 8. Cycling runs for the degradation of MB (40 mg L\(^{-1}\), 100 mL) over Fe/NG.](image)

Figure 8. Cycling runs for the degradation of MB (40 mg L\(^{-1}\), 100 mL) over Fe/NG.

![Figure 9. (a) Pseudo-first-order and pseudo-second-order for MB adsorption onto Fe/NG: \(C_{0\text{MB}} = 40\) mg L\(^{-1}\), \(m/V = 1\) g L\(^{-1}\). (b) Adsorption isotherms for MB adsorption onto Fe/NG at different equilibrium concentration.](image)

Figure 9. (a) Pseudo-first-order and pseudo-second-order for MB adsorption onto Fe/NG: \(C_{0\text{MB}} = 40\) mg L\(^{-1}\), \(m/V = 1\) g L\(^{-1}\). (b) Adsorption isotherms for MB adsorption onto Fe/NG at different equilibrium concentration.

Equilibrium data were obtained after 48 h, to ensure sufficient removal. Figure 9b presents the Langmuir and Freundlich isotherm plots for MB removal by Fe/NG. The Langmuir model simulates monolayer adsorption, which assumes that the degradation proceeds uniformly at a homogeneous energy level at the surface of the adsorbent [38]. Freundlich model is associated with multilayer adsorption and assumes that the degradation process occurs at non-homogeneous locations on the adsorbent surface [39,40]. In this experimental study, the \(R^2\) of the Freundlich model was found to be superior to that of the Langmuir model, suggesting that the degradation of MB was dominated by multilayer adsorption. These results demonstrated that chemical adsorption was the primary mechanism of MB degradation by Fe/NG catalyst, which also implied that the Fe/NG in the MB degradation system might have undergone some changes in the valence states, involving processes such as electron exchange between the material and the pollutant [41].

To further clarify the MB degradation mechanism of the catalyst, electron spin resonance (ESR) tests were performed on Fe/NG with 5, 5-dimethyl-1-pyrroline N-oxide (DMPO) and 2,2,6,6-tetramethylpiperidinoxy (TEMPO) to determine the production of
free radicals (Figure 10). Figure 10a,b shows that superoxide and hydroxyl radicals have strong peaks at 30 s and 60 s under dark conditions. This also implies that the catalyst can generate active free radicals to participate in the catalytic reaction [42]. In addition, we tested whether free radicals are generated under anaerobic conditions (Figure 10c,d). The experimental results revealed that no free radicals were generated in the absence of oxygen, indicating that oxygen supply is an essential requirement in the process of MB degradation by Fe/NG.

![ESR spectra of radical adducts in Fe/NG](image1)

![ESR spectra of radical adducts in Fe/NG without O₂](image2)

![Inhibition effect of SOD and CAT on the Fe/NG solution](image3)

**Figure 10.** ESR spectra of radical adducts in Fe/NG (a,b,e); ESR spectra of radical adducts in Fe/NG without O₂ (c,d); Inhibition effect of 8 mg mL⁻¹ SOD and 8 mg mL⁻¹ CAT on the Fe/NG solution (f).

The prerequisite is that electrons are released from TEMPO, decreasing its peak intensity. Thus, the weak intensity of TEMPO indicates a high amount of released e⁻. After 60 s, more e⁻ gradually appear in the Fe/NG composites (Figure 10e), which indicates that the catalyst exhibits superior e⁻ removal performance to promote the conversion between Fe⁰, Fe²⁺, and Fe³⁺, thereby contributing to the degradation of MB. Existing literature reports that superoxide dismutase (SOD) can be used as a significant indicator of superoxide participate and that catalase (CAT) can transform hydrogen peroxide into water and oxygen [43]. Therefore, to validate the existence of superoxide radicals and hydrogen
peroxide molecules in the present study, both CAT and SOD were added to the solution systems. Figure 10f shows the introduction of CAT (8 mg mL\(^{-1}\)) and SOD (8 mg mL\(^{-1}\)) to 5 mg mL\(^{-1}\) Fe/NG solution. We observed the decrease \(\cdot \)OH concentration in the solution, which indicated that both SOD and CAT inhibited the formation of hydroxyl radicals. Simultaneously, this verified that the catalyst could complete the catalytic degradation of MB in the absence of light or oxidant.

Based on the above results, we suggest the following possible reaction processes: (1) In the Fe-C micro-electrolysis system, Fe\(^0\) acts as the anode and releases two electrons to form Fe(II) \([44]\), while carbon acts as the cathode in the reaction. Moreover, electrons are released from the solution during the reactions to form [H], which is highly reactive and readily reacts with MB \([45]\); (2) Except for the pathway of [H] production, e\(^-\) can also react with oxygen to generate \(\cdot \)O\(_2\)\(^-\), and thereby H\(_2\)O\(_2\) is produced as an intermediate material. This induces the Fenton reaction, and the Fe\(_2^+\) derived from the oxidation reaction reacts with H\(_2\)O\(_2\) to produce \(\cdot \)OH. Finally, the generated O\(_2\)\(^-\) and OH act as the main reactive substances to degrade MB. Herein, to explain the possible mechanism of the catalyst degradation of MB \([6]\), the major reactions between Fe-C and the degradation of MB are expressed in Equations (1)–(7) \([45–47]\).

\[
\begin{align*}
\text{Fe}^0 + 2e^- & \rightarrow \text{Fe}^{2^+} \\
2\text{H}^+ + 2e^- & \leftrightarrow 2[H] \\
e^- + \text{O}_2 & \rightarrow \cdot \text{O}_2^- \\
\cdot \text{O}_2^- + \text{H}^+ + e^- & \rightarrow \text{H}_2\text{O}_2 \\
\text{H}_2\text{O}_2 + \text{Fe}^{2^+} & \rightarrow \cdot \text{OH} + \text{OH}^- + \text{Fe}^{2^+} \\
\cdot \text{O}_2^- + \text{MB} & \rightarrow \text{degradation} \\
\cdot \text{OH} + \text{MB} & \rightarrow \text{degradation}
\end{align*}
\]

The g-factor of carbon-centered radicals is reported to be less than 2.0030, while the g-factor of oxygen-centered radicals is greater than 2.0040 \([48]\). We performed the room temperature electron paramagnetic resonance (EPR) test. The Fe/NG composite exhibited an EPR signal intensity with a g-factor of 2.00169, as shown in Figure S2a. Thus, the substance is a carbon-centered radical because it has a g-factor of less than 2.0030. This may be caused by the unpaired electrons of the sp\(^2\) carbon atom in the \(\pi\)-conjugated aromatic ring \([49]\). In addition, we also measured the quantity of environmentally persistent free radicals (EPFRs) in the material at ambient temperature. The experimental results (Figure S2b) showed that the content of EPFRs in the catalyst increased with time, which indicated that these active free radicals could be used to promote the degradation of MB.

EPFRs have been shown to form on the surfaces of particles containing transition metal oxides \([43]\). The high-concentration EPFRs in the Fe/NG composite might act as electron donors to facilitate the reduction of Fe(III), and thus, enhance the catalytic activity.

### 2.3.2. Degradation Mechanism

The Fe/NG catalyst is advantageous over other catalysts because it can spontaneously generate active free radicals in the solution, and does not require excitation by external conditions, such as microwave \([50]\), ultraviolet light, and visible light \([47,51–53]\), or activation of the corresponding oxidant such as hydrogen peroxide (H\(_2\)O\(_2\)) \([54]\), persulfate (PS), and permonosulfate (PMS) to generate free radicals \([55,56]\). Thus, that is the novelty of the catalyst proposed in this study. To determine the degradation routes of MB, high-resolution liquid chromatography-mass spectrometry (LC-MS) was applied. As presented in Figure S3, the MS analysis results indicated that several intermediates were produced during the MB degradation process, which confirmed that MB could be degraded under dark conditions \([57]\). The mass-to-charge ratios (\(m/z\)) and preliminary structures of the intermediates are presented in Figure 11, which revealed the presence of undegraded MB.
and other intermediate products. The process includes common mechanisms associated with MB degradation [31]. Analysis of the products after the reaction revealed that the first step of degradation process involved demethylation and cleavage of N=C double bonds ($m/z = 319$). The second step is the saturation of the two remaining amino bonds by the generated free radicals, thereby resulting in the substitution of aniline with sulfonic acid ($m/z = 230$). Subsequently, hydroxy hydroquinone ($m/z = 110$) was the last aromatic compound detected prior to the benzene ring-opening reaction. This is because the amino-containing compound interacts with the hydroxyl radical to produce the corresponding phenolic compound. Thereafter, Fe/NG catalysts can spontaneously remove MB from aqueous solutions and reduce the burden on the water treatment process.

Figure 11. Pathway of possible for MB degradation over Fe/NG under dark situation.

3. Materials and Methods

3.1. Chemical Reagents

Melamine, FeCl$_3$·6H$_2$O (Alfa Aesar, Haverhill, MA, USA) and ethanol were purchased from China National Pharmaceutical Group Chemical Reagent Co., Ltd. (Shanghai, China). Polyether F127 (98%, Alfa Aesar, Haverhill, MA, USA) was purchased from Shanghai Maclean Biochemical Technology Co., Ltd. (Shanghai, China). All chemicals were analytical grade reagents and deionized water was used throughout the experiment, unless otherwise specified.

3.2. Synthesis of CN

Generally, graphitic CN was prepared by high temperature pyrolysis as follows [58]: 30 g of melamine in a covered alumina crucible was placed in a muffle furnace, which was then closed, and the temperature was set to 550 °C with a ramp rate of 5 °C min$^{-1}$ for 4.5 h. After pyrolysis, the furnace was switched off and the material was allowed to cool. Then, the furnace was opened and the crucible was removed with a clamp. The resultant product was collected and ground into powder for further use.

3.3. Synthesis of n-CN Nanosheet

CN with a nanosheet structure (n-CN) was prepared as follows: 2 g of the above-prepared CN was uniformly dispersed in a crucible without cover to facilitate sufficient contact between CN and air, and then heated to 500 °C in an open system for 3 h at
5 °C min\(^{-1}\) in a muffle furnace. The products were cooled naturally and the obtained white powder was n-CN.

### 3.4. Synthesis of Fe/NG

Fe/NG was synthesized by high temperature pyrolysis as follows [17]: 3 g n-CN was added to 500 mL deionized water in the beaker, which was then placed in an ultrasonic bath and sonicated for 1 h to ensure complete dispersion. Then, 6 g F127 was added to the suspension with continuous stirring for 2 h and sonicated according to the abovementioned method for 2 h. Subsequently, 5 mL aqueous solution (0.3 M) of FeCl\(_3\)-6H\(_2\)O was injected into the mixture with stirring for 12 h. The obtained solution was evaporated in a water bath at 80 °C and dried in an oven at 60 °C for 24 h. The dried precipitate was calcined at 550 °C under a nitrogen atmosphere for 2 h, and then the temperature was increased to 800 °C for another 2 h at a heating rate of 3 °C min\(^{-1}\) in a tube furnace. The carbonization products were soaked in hydrochloric acid (2 M) for 24 h, and then dried in a vacuum oven at 60 °C overnight to obtain the Fe/NG catalyst.

### 3.5. Characterization

Transmission electron microscopy (TEM; Tecnai G2 F20, FEI, Hillsboro, OR, USA), high-resolution TEM (HR-TEM; voltage 200 KV), field emission scanning electron microscopy (SEM; Quanta FEG 400, FEI, USA), and X-ray diffraction (XRD; D8 ADVANCE, Bruker, Germany; voltage 40 KV, current 40 mA, step length 0.02°, test speed 0.1 s/step, copper target, and incident radiation wavelength 0.15418 nm) were performed to determine the structure and morphology of the samples. The chemical composition of the catalyst was analyzed using EDX (Genesis Software, EDAX, Mahwah, NJ, USA). The BET specific surface area was measured with a BET instrument (QUADRASORB evo, Quantachrome Instruments, Boynton Beach, FL, USA). The structures of the samples were observed by FT-IR (Nicolet iS5, Thermo Fisher Scientific, Waltham, MA, USA), XPS (ESCALAB 250Xi, Thermo Fisher Scientific; monochrome Al Ka (hv =1486.6 eV), power 150 W, 500 µm beam spot; binding energy at C1s 284.8 calibration). In addition, the magnetic properties were measured using a superconducting quantum interference device (SQUID; MPMS XL7, Quantum Design, San Diego, CA, USA). The ESR signals were detected using an ESR spectrometer (JES-FA200, JEOL, Japan). The intermediate products produced by degradation of MB were detected by high pressure liquid chromatography (HPLC; Waters 2695, Milford, MA, USA) with a mass spectrometer (Waters ZQ2000, Milford, MA, USA, equipped with a UV detector). A C18 column (250 × 4.6 mm, 3 µm) was used; mobile phase A was ultrapure water and mobile phase B was acetonitrile. The gradient of A:B was 95:5, the flow rate was 1 mL min\(^{-1}\), the column temperature was 30 °C, and the operation time was 20 min. The mass spectrometer was also equipped with electrospray ionization.

### 3.6. Catalytic Experiment

All experiments were performed under the same catalyst loading conditions (except for the experiments to determine the influence of pH), with 300 mL solutions. The dosage of the composite material was 1 g L\(^{-1}\) (MB = 40 mg L\(^{-1}\)). 0.3 g catalyst was introduced, and the reaction equilibrium was achieved by magnetic stirring in the dark for 30 min. During the process, 4 mL of solution was collected every 5 min through a 0.45 µm syringe with a filter to monitor the change in the dye in the solution after the catalytic treatment at a given time interval. To study the possible mechanism of MB decolorization, the MB concentration was measured by a UV spectrophotometer at 664 nm. Using the Beer–Lambert law, the degradation rate of MB was determined as

\[
\eta(\%) = \frac{C_0 - C_t}{C_0} \times 100\%
\]

During the reaction, the effect of catalysts on dye degradation under different acid-base conditions was studied. Low-concentration HCl and NaOH were used for pH ad-
justment. In addition, the influence of the dosage of the catalyst on the reaction was investigated. All experiments were conducted in three parallel experiments and all statistical analyses were performed using SPSS software (SPSS Statistics Version 22.0, IBM, Armonk, NY, USA).

4. Conclusions
Considering the existing research and current applications, most catalysts for removing organic pollutants usually require oxidizing agents (such as persulfate), ultrasound, ultraviolet light, visible light, and other technologies. In this study, an Fe/NG catalyst was synthesized and explored to accomplish the degradation of MB without other special conditions. The proposed method can reduce costs to achieve a circular economy and no additional additives are required to achieve cleaner production. Moreover, the degradation process can be completed under most acid–base environments and the structure of the material remains constant after degradation. In addition, the presence of abundant Fe-C configurations in the composite material promotes catalyst activity through the formation of numerous galvanic cells. It also facilitates the generation of surface-bound atomic hydrogen, which plays a crucial role in the degradation process. ESR characterization results demonstrated that free radicals \( \cdot \text{OH}, \text{O}_2^- \), and \( \text{e}^- \) were produced from the Fe/NG composites, which results in a highly efficient MB degradation process. In addition, the catalysts are more readily recyclable because of their inherent magnetic properties. This study provides a novel method for the development of a metal–carbon nanoparticle catalyst, which can have high potential for application in the field of environmental remediation.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal12040388/s1, Figure S1: UV–vis absorption spectra of MB; Figure S2 (a) Room-temperature EPR spectra;(b) EPR spectra of radical adducts in Fe/NG; Figure S3 Degradation intermediates of MB; Figure S4. Toxicological evaluation results of MB degradation intermediates; Table S1: Toxicological assessment of the MB and its intermediates.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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