Fenton-like reaction-induced degradation of Methylene Blue by using supermacroporous ferrimagnetic nanorings

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Abstract. The removal and/or degradation of methylene blue (MB) from dyestuff wastewater has attracted widespread attention. Utilization of environmental purification nanomaterials is an effective means in the field of environmental remediation, and degradation efficiency under different circumstances is always a high priority for the nanoagents. In this study, uniform supermacroporous ferrimagnetic Fe₃O₄ nanorings (sFe₃O₄-NRs) were fabricated for high-efficiency MB degradation. Typically, the sFe₃O₄-NRs were prepared by a convenient hydrothermal method. Subsequently, the morphology structure of the sFe₃O₄-NRs was characterized by scanning electron microscope (SEM), transmission electron microscope (TEM) and high-resolution transmission electron microscopy (HRTEM), respectively. Next, a Fenton-like reaction-induced MB degradation was performed in the present of sFe₃O₄-NR nanocatalysator and hydrogen peroxide (H₂O₂). Meanwhile, the sFe₃O₄-NRs showed excellent Fenton-catalytic activity for degradation of MB in a wide range of pH (3-11). Moreover, because of the magnetic property of the sFe₃O₄-NRs (saturation magnetization of 34.26 emu/g), the used sFe₃O₄-NR could be rapidly separated from the reaction medium by using a magnet, the sFe₃O₄-NR resented relative high catalytic activity even after 10 times reuse. The main conclusion from this work was that the as-synthesized sFe₃O₄-NRs nanoagent was a type of desirable Fenton catalyst to degenerate MB from wastewater.

1. Introduction
During the past several decades, with the fast developing on chemical industry, organic dyes have been extensively used in the industrial production of textiles, paper, plastics, leather, food, printing, cosmetics, pharmaceuticals, and other industries [1, 2]. Most of organic dyes are harmful, toxic, carcinogenic, or even fatal [3, 4]. However, the organic dyes in general are exceptionally stable and resistant to biodegradation and photolysis [5]. What's more, as hypertoxic and carcinogenic pollutants, most of dyes pose a grave threat to water ecological security and human health, some water-soluble dyes are harmful under even minute quantities (e.g., less than 1 ppm) [6]. Wherein, Methylene blue (MB), is one of the most often utilized basic dyes in industry which could cause serious public health issues, including vomiting, tissue death, limb paralysis, and even death when released into the drinking
water [7]. Furthermore, because of the stable and complex aromatic molecular structure, MB is hard to be removal or degraded under natural conditions. Therefore, there is an urgent need for efficient treatment of the MB effluent.

According to previous reports, multifarious physical and/or chemical techniques have been exploited for the treatment of dyestuff wastewater containing MB, such as membrane separation, physical adsorption, biological degradation, chemical oxidation, electrocatalytic/photocatalytic degradation, and Fenton-like catalytic degradation [8], and so on. Among these purification techniques, the Fenton-like catalytic degradation is demonstrated to be a preferred method for degradation of dyes to harmless products by using hydrogen peroxide (H2O2) as a pro-oxidant. Typically, by using Fenton-like agents, such as iron oxides nanomaterials, the Fenton-like catalytic degradation reactions have been revealed to produce free radicals (•OH) via catalyzing H2O2 with ferrous ions (Fe2+/Fe3+) [9]. In previous studies, the accepted mechanism of •OH generated in Fenton-like reaction includes a series of cyclic reactions, which can be described by the classical Haber-Weiss cycle (Eqs. (1) - (7)) [10].

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\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \cdot \text{OH} + \text{OH}^- \quad k = (63 - 70) \text{ mol}^{-1}\cdot\text{L}^{-1}\cdot\text{s}^{-1} \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{2+} + \cdot \text{HO}_2^- + \text{H}^+ \quad k = (0.001 - 0.01) \text{ mol}^{-1}\cdot\text{L}^{-1}\cdot\text{s}^{-1} \\
\cdot \text{OH} + \text{H}_2\text{O}_2 & \rightarrow \cdot \text{HO}_2^- + \text{H}_2\text{O} \quad k = 3.3 \times 10^7 \text{ mol}^{-1}\cdot\text{L}^{-1}\cdot\text{s}^{-1} \\
\cdot \text{OH} + \text{Fe}^{2+} & \rightarrow \text{Fe}^{3+} + \text{OH}^- \quad k = 3.2 \times 10^8 \text{ mol}^{-1}\cdot\text{L}^{-1}\cdot\text{s}^{-1} \\
\text{Fe}^{2+} + \cdot \text{HO}_2^- + \text{H}^+ & \rightarrow \text{Fe}^{3+} + \cdot \text{H}_2\text{O}_2 \quad k = (1.2 - 1.3) \times 10^6 \text{ mol}^{-1}\cdot\text{L}^{-1}\cdot\text{s}^{-1} \\
\text{Fe}^{3+} + \cdot \text{HO}_2^- & \rightarrow \text{Fe}^{2+} + \text{O}_2 + \text{H}^+ \quad k = (1.3 - 2.0) \times 10^5 \text{ mol}^{-1}\cdot\text{L}^{-1}\cdot\text{s}^{-1} \\
2\cdot \text{HO}_2^- & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad k = 8.3 \times 10^5 \text{ mol}^{-1}\cdot\text{L}^{-1}\cdot\text{s}^{-1}
\end{align*}
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Herein, we presented a feasible one-step hydrothermal method to fabricate supermacroporous ferrimagnetic Fe3O4 nanorings (sFe3O4-NRs). With the assistance of H2O2, Fe2+/Fe3+ released from the sFe3O4-NRs were used as a Fenton-like agents for MB degradation by a Fenton-like catalytic reaction. Moreover, the sFe3O4-NRs could be easily separated from the processed medium with an external magnet for reuse. All characterizations indicate that the sFe3O4-NRs were uniform, well dispersed, supramaximal porous and favourable magnetizable, which make them ideal for use as Fenton-like catalytic degradation. **Scheme 1** shows the Fenton-like degradation mechanism of sFe3O4-NRs.

![Scheme 1. Overview of MB degradation mechanism of sFe3O4-NRs.](image)

2. Materials and Methods

2.1. Materials and Reagents

Chemicals: Methylene blue (AR, 3,7-Bis(dimethylamino)-5-phenothiazinium Chloride, 98%), iron(III) chloride (AR, FeCl3, 99%) were supplied by Alfa Aesar Co., Ltd (Tianjin, China), ammonium dihydrogenophosphate (AR, NH4H2PO4, 99%), anhydrous Sodium sulfate (AR, Na2SO4, 99%) were
bought from J&K Co., Ltd (Beijing, China), other normal reagents were all purchased from Aladdin Co., Ltd (China) without any further purification.

2.2. Synthesis of sFe3O4-NRs
Firstly, supermacroporous α-Fe2O3 nanorings were synthesized via a simple hydrothermal method and then used as a precursor to fabricate sFe3O4-NRs [11]. In this experimental reaction procedure, FeCl₃ (0.03 M), NH₃H₂PO₄ (0.25 mM) and Na₂SO₄ (0.64 mM) were dissolved into 75 mL distilled water. The maple solution was stirred for 30 min under room temperature with N₂ protection. Until the ferric salt is dissolved completely, the mixture solution was then transferred into a 100 mL Teflon-lined stainless-steel autoclave. The hydrothermal reaction was carried at 230 °C for 24 h. Next, the autoclave was cooled down to room temperature, the yellow precipitates were separated and collected by centrifugation at 7500 rpm. The final products (α-Fe₂O₃-NRs) were washed with deionized water and ethanol for eight times and then dried at 60 °C for 10 hours.

To prepare sFe3O4-NRs, a reduction process was taken by using α-Fe₂O₃-NRs as the precursor. In brief, 100 mg α-Fe₂O₃-NRs were annealed in a tube furnace at 400 °C under a continuous reducing gas flow (v/v: H₂/Ar = 5%) for 10h. The resulting sFe₃O₄-NRs was finally collected with an external magnet and washed with distilled water and ethanol each for eight times, respectively.

2.3. Characterization
The morphological of as-prepared sFe₃O₄-NRs were observed by transmission electron microscopy (TEM, JEM-2100, Japan), Scanning Electron Microscope (SEM, JSM-7800F, Japan), and high-resolution transmission electron microscopy (HRTEM, JEM-2100, Japan). The XRD pattern of sFe₃O₄-NRs was measured by a X-ray diffraction diffractometer (XRD, Bruker D8 Advance, America) with Cu Kα radiation (λ = 1.514 Å). The magnetization intensity of sFe₃O₄-NRs was generated by a vibrating sample magnetometer (VSM, Lake Shore 7400, America). The spectra of MB degradation were detected using an UV-Vis spectrophotometer (Thermo Scientific NanoDrop One, America). The free radicals triggered by sFe₃O₄-NRs in H₂O₂ was recorded with an electron paramagnetic resonance spectroscopy (EPR, Bruker EMXnano, Germany).

2.4. Catalytic activity measurements
Next, the synthesized sFe₃O₄-NRs were evaluated through the oxydic degradation of MB in the presence of H₂O₂. Typically, effects of pH (3.0-11.0) were measured during the degradation process. Meanwhile, initial concentration of MB was investigated for dyes degradation. Typically, sFe₃O₄-NRs (5.0 mg) was firstly dispersed into MB solution that containing 1.0 ml H₂O₂ at room temperature. Then, 1 µL sample was measured in time course by monitoring the absorbance at 665 nm with a UV-vis spectrophotometer.

2.5. Statistical analysis
Significance test was taken by using an analysis of variance and Tukey’s test (OriginPro, version 9.0, OriginLab Corporation, America). Statistical significance was established at p < 0.05.

3. Results

3.1. Morphology of the sFe₃O₄-NRs
The morphology of as-synthesized sFe₃O₄-NRs was observed by SEM (Figure 1) and TEM (Figure 2). It showed that the sFe₃O₄-NRs with a hollow ring structure, rules of the sample morphology and uniformity size distribution. Meanwhile, the sFe₃O₄-NRs’ inner average diameter was determined to be about 77.4 nm. The outer average diameter of the sFe₃O₄-NRs was calculated to be about 157.2 nm (Figure 3, n = 400), the thickness of the sFe₃O₄-NRs was was calculated to be 38.8 nm. Figure 4 showed the HRTEM images of the obtained sFe₃O₄-NRs. These characteristic lattice fringes of
sFe$_3$O$_4$-NRs are 0.290 nm and 0.480 nm, respectively, which indicating the formation of Fe$_3$O$_4$ inverse-spinel type structure.

3.2. Magnetization
To measure the magnetic properties of sFe$_3$O$_4$-NRs, hysteresis loops text was taken under room temperature. As shown in Figure 5, saturation magnetization of the obtained sFe$_3$O$_4$-NRs was about 58.6 emu/g, which revealed that the sFe$_3$O$_4$-NRs have excellent Magnetic strength and can be easily separated by an external magnet.

3.3. X-ray diffraction pattern
Then composition of the magnetic nanorings were further detected by X-ray diffraction (XRD). As shown in Figure 6, the results indicated that all characteristic peaks (30.12 °, 35.51 °, 43.12 °, 53.41 °, and 57.04 °) matched well with pure spinel Fe$_3$O$_4$ (JCPDS NO: 19-0629).
3.4. MB Degradation

The quantitative MB degradation efficiency of the sFe₃O₄-NRs was determined by UV-vis. The decoloration optical image was shown in Figure 7, briefly, after 6 hours Fenton-like catalysis, with the assistance of H₂O₂, sFe₃O₄-NRs exhibited excellent performance in MB degradation under different pH (Figure 8). Finally, the MB molecule was degraded to various inorganic ions (Figure 9) such as SO₄²⁻, NH₄⁺, and NO₃⁻, respectively. Accordingly, with the assistance of H₂O₂, the sFe₃O₄-NRs exhibited excellent Fenton catalytic efficiency for dyes decoloration though a typical Fenton-like reaction. Moreover, the reuse ability is very important for nanomaterials, Figure 10 shows the reuse performance of sFe₃O₄-NRs in MB degradation, the magnetic nanorings can retain above 85% of its original activity after being used for 10 cycles.

4. Conclusion

In summary, sFe₃O₄-NRs were successfully prepared and used as Fenton-like nanoagents for MB degradation. The sFe₃O₄-NRs exhibited excellent Fenton-like catalytic activity under a wide range of pH, and therefore could overcome the shortcoming of traditional Fenton reaction in narrow pH ranges. Moreover, the sFe₃O₄-NRs could be separated from solution for reuse by an external magnetic field.
All results revealed that the sFe$_3$O$_4$-NRs are suitable for Fenton-like reaction-induced dye degradation in wastewater treatment.

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