



# Heterogeneous Fenton-like oxidation of malachite green by iron-based nanoparticles synthesized by tea extract as a catalyst



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## ABSTRACT

The green synthesis of functional iron nanoparticles (Fe NPs) by tea extracts was used as a catalyst for the Fenton-like oxidation of malachite green (MG), where more than 85% of MG was removed. The new findings are that the removal of MG by Fe NPs was based on the adsorption of MG onto iron oxide and degradation of MG by iron nanoparticles. This was confirmed by adsorption and degradation kinetics, indicating that: firstly, the adsorption kinetics follows the pseudo-first-order model; and secondly, degradation kinetics fitted well to the pseudo-second-order model. Morphology, size and changes in the Fe NPs surface were characterized using SEM, XRD, and FTIR techniques, showing that Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> was formed and green tea extract contained a high concentration of caffeine/polyphenols. It acted as both reducing and capping agents in the synthesis of Fe NPs. To further confirm the removal mechanism of MG by the functional Fe NPs, the degraded products were identified by FTIR and GC–MS analysis. Finally the mechanism of Fenton-like oxidation of MG based on both adsorption and degradation was proposed.

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## 1. Introduction

Over the past few decades, advanced oxidation technologies (AOTs) have received widespread attention for their effectiveness in destroying organic compounds [1]. Homogeneous Fenton oxidation (Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>) is the most widely used technique for treating organic pollutants in aqueous solution. However, the drawbacks of homogeneous Fenton oxidation restrict its application [2]. Heterogeneous Fenton oxidation provides an alternative to address the drawbacks.

In recent years, iron-supported catalysts have often been used as the catalyst in heterogeneous Fenton oxidation of organic contaminants, including zero-valent iron nanoparticles (nZVI) [3], iron containing clays [4] and iron oxide minerals [5,6]. Recently, nZVI has been used as the heterogeneous catalyst for the oxidation of 4-chloro-3-methyl phenol, demonstrating that complete degradation of 4-chloro-3-methyl phenol was achieved at pH 6.1 [3]. More recently, Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles (MNPs) as the catalyst have also been employed for the Fenton-like degradation of 2,4-dichlorophenol (2,4-DCP) in aqueous solution. Here the degradation and mineralization of 2,4-DCP was achieved

completely, and 51% of TOC was removed after 180 min [7]. Iron-based nanoparticles as the catalyst for oxidation of organic contaminants can have potential nanoremediation properties. However, nZVI is often synthesized using sodium borohydride as a reducing agent [3], and MNPs are synthesized by co-precipitation of Fe(II) and Fe(III) in basic solutions [7]. The drawbacks include chemical substances, organic solvents, stabilizing and dispersing agents being toxic and expensive and hence they are limited to the large-scale field remediation of contaminants [8].

The green synthesis of iron nanoparticles (Fe NPs) using plant extract has been recently developed as a cost effective, environmental friendly alternative to chemical methods [9]. These components extracted from plants are non-toxic, biodegradable and the green material acts as both a dispersive and capping agent, reducing the oxidation and agglomeration of iron-based nanoparticles [8]. However, few reports have been published on the use of green synthesized iron-based nanoparticles as a heterogeneous catalyst for Fenton-like oxidation of organic contaminants. Fe NPs were prepared using green tea extracts and were utilized as a Fenton-like catalyst to decolor methylene blue and methyl orange dyes; Fe NPs used as a Fenton-like catalyst in this context indicate higher dye removal percentages and faster kinetics [10].

Recently, Fe NPs were synthesized using tea extracts as a catalyst for the Fenton-like oxidation of monochlorobenzene, where Fe NPs synthesized using green tea extracts demonstrated the best

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degradation capacity comparing with Fe and bimetallic Fe/Pd nanoparticles synthesized using tea extracts. This is because green tea contains a high concentration of caffeine/polyphenols used as both reducing and capping agents in the synthesis of Fe NPs [11]. These results demonstrate the green synthesis of Fe NPs as the catalyst for the Fenton-like oxidation of organic contaminants has potential as a nanoremediation strategy. However, Fe NPs contains nZVI, iron oxide and iron oxyhydroxide and their functions in the oxidation process were still not well understood [10,11]. In our previous report, Fe NPs synthesized by green tea extract could be used for the degradation of malachite green (MG) [8], where the degraded products still remained. This is usually preceded by the Fe NPs' reduction process involving the removal of color. Subsequently, H<sub>2</sub>O<sub>2</sub> is added to react with the Fe<sup>2+</sup> generated by the Fe NPs' reduction reactions to generate hydroxyl radicals. Consequently, the Fenton-like oxidation process is developed to remove the color and COD in textile wastewaters [12].

For these reasons, this study concerns the functions of Fe NPs in the Fenton-like oxidation of malachite green and their oxidation mechanism, where MG is a triphenylmethane dye and is used extensively in many industries [13]. The objectives here include: (1) investigating the influences of various oxidation parameters on the rate of degradation; (2) to evaluating the removal kinetics, including adsorption and degradation based on nZVI and iron oxide; and (3) analyzing the surface changes of Fe NPs by characterization, and examining degraded products using gas chromatography mass spectrometry (GC–MS). Finally, Fe NPs functions in the Fenton-like oxidation of MG are proposed.

## 2. Experimental

### 2.1. Materials and chemicals

All chemicals used in this study were analytical reagent grade or higher and used directly without any further pretreatment. Ferrous sulfate (FeSO<sub>4</sub>·7H<sub>2</sub>O, purity over 99%) was obtained from Xilong Chemical Co., Ltd. (China), H<sub>2</sub>O<sub>2</sub> (30%, v/v), ethyl acetate, ethyl alcohol, HCl and NaOH were obtained from Sinopharm Chemical Reagent Co., Ltd., China. All solutions were prepared in distilled water. Green tea purchased from Fuzhou in Fujian Province, China, was used in this work.

### 2.2. Preparation of Fe NPs using green tea leaves extract

Fe NPs can be synthesized by green tea and this has been reported in previous studies [14,15]. Aqueous extract of green tea was prepared by heating 60 g/L green tea leaves in 80 °C water for 1 h. The green tea extract was then cooled down to room temperature and vacuum-filtered. Following this one part a solution of 0.10 mol/L of FeSO<sub>4</sub> was mixed with three parts filtered green tea extracts in a beaker. After the reaction was completed this mixture was utilized to degrade MG.

### 2.3. Characterizations and methods

The oxidative degradation experiments were carried out using Fe NPs (0.185 g) and 7.4 M H<sub>2</sub>O<sub>2</sub> added to a water solution containing 50.0 mg/L MG (250 mL) at various conditions. Mixed solutions were stirred by a blender (250 rpm) for 90 min and the temperature was controlled through the thermostatic water bath. Following the reaction the mixtures were centrifuged at 10,000 rpm for 10 min and the supernatant was collected to determine the effects of removing MG using a UV-Spectrophotometer (722N, Shanghai, China) at λ<sub>max</sub> (617 nm). The influences of various parameters were also investigated, including pH (3–7), the dosage of Fe NPs (0.3–1.1 mg/L) and the reaction temperature (298–318 K).

The oxidative degradation efficiency of MG – whose concentrations were determined by the calibration curves using the Fenton-like system was calculated based on the following equation [11]:

$$R (\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

Here, C<sub>t</sub> and C<sub>0</sub> (mg/L) represented the concentration of MG in *t* time and the initial concentration and *R* (%) is the MG degradation efficiency.

### 2.4. Characterization

Morphology and distribution of Fe NPs before and after reaction with MG were characterized using SEM (JSM 7500F, Japan). The samples of powdered Fe NPs were fixed on the adhesive tapes supported on metallic disks and then coated with an electric conductive gold film. Images of samples were recorded at different magnifications at an operating voltage of 5.0 kV. X-ray diffraction (XRD) patterns of Fe NPs before and after oxidation reactions were obtained using a Philips-X'Pert Pro MPD (Netherlands) with a high-powered Cu Kα radioactive source (*k* = 0.154 nm) at 40 kV/40 mA. FTIR (FTIR Nicolet 5700, Thermo Corp., USA) assisted in detecting the MG and Fe NPs. Samples were prepared by mixing 1% (w/w) specimen with 100 mg of KBr powder and pressing the mixture into a sheer slice.

### 2.5. GC–MS analytic method of MG

An Agilent Technology 5975c GC–MS system used to identify the MG and its reaction intermediates, was equipped with a film thickness of 0.25 μm TR-35MS capillary column with a film thickness of 0.25 μm for the separation. The injector was operated at 250 °C and aliquots of 1.0 μL were injected for analysis. The column oven temperature was initially kept at 50 °C for 1 min, then the temperature was increased from 50 °C to 290 °C at a rate of 15 °C min<sup>-1</sup> and maintained at 290 °C at for 15 min. The GC–MS system was operated in full scan (*m/z* 50–650).

## 3. Results and discussion

### 3.1. Fenton-like oxidation of MG using Fe NPs synthesized from tea extract

To understand the reactivity of the Fenton-like oxidation using Fe NPs synthesized from green tea extract as the catalyst, their efficiency in removing MG from an aqueous solution using H<sub>2</sub>O<sub>2</sub>, green tea extract + H<sub>2</sub>O<sub>2</sub>, and Fe NPs + H<sub>2</sub>O<sub>2</sub> was compared (see Fig. 1). 78.2% of MG was removed by the Fenton-like oxidation system, while only 24.3% and 5.2% of MG was removed using green tea extract + H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>, respectively. It can be clearly seen that Fe NPs synthesized from green tea extract as the catalyst exhibited excellent catalytic activities for the Fenton oxidation of MG, where the MG degradation efficiency was 78.2% (50 mg/L) within 10 min. This indicates that the nZVI was easily oxidized and MG was degraded by reduction reaction firstly as confirmed in our previous report [8].

Consequently, the produced Fe<sup>2+</sup> was further oxidized to Fe<sup>3+</sup> by H<sub>2</sub>O<sub>2</sub> in the Fenton process, and the generated hydroxyl radicals are powerful oxidant species. Then a high reaction rate of the heterogeneous Fenton oxidation using Fe NPs + H<sub>2</sub>O<sub>2</sub> was observed [5]. In addition, 24.3% of MG was removed by green tea extract + H<sub>2</sub>O<sub>2</sub>, which was mainly attributed to the adsorption of MG onto the particles in the tea extract containing polyphenols and caffeine. These particles interacted with MG, which is consistent with a previous study on biosorption of basic orange using on the dried *Azolla*

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