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## Green synthesis of iron nanoparticles by various tea extracts: Comparative study of the reactivity



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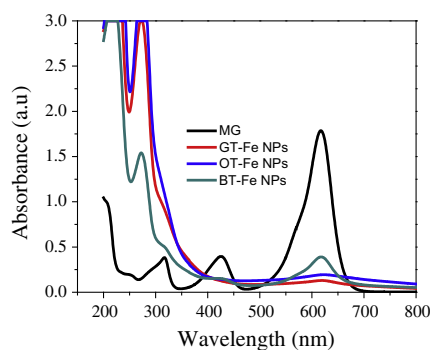
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### HIGHLIGHTS

- Iron nanoparticles (Fe NPs) were synthesized by 3 tea extracts.
- Differences in Fe NPs synthesized were observed by characterization.
- The removal of malachite green was 81.2%, 75.6% and 67.1%.
- Degradation mechanism of MG using Fe NPs were proposed.

### GRAPHICAL ABSTRACT

UV–vis images of degradation of malachite green using various Fe NPs.



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### ABSTRACT

Iron nanoparticles (Fe NPs) are often synthesized using sodium borohydride with aggregation, which is a high cost process and environmentally toxic. To address these issues, Fe NPs were synthesized using green methods based on tea extracts, including green, oolong and black teas. The best method for degrading malachite green (MG) was Fe NPs synthesized by green tea extracts because it contains a high concentration of caffeine/polyphenols which act as both reducing and capping agents in the synthesis of Fe NPs. These characteristics were confirmed by a scanning electron microscope (SEM), UV–visible (UV–vis) and specific surface area (BET). To understand the formation of Fe NPs using various tea extracts, the synthesized Fe NPs were characterized by SEM, X-ray energy-dispersive spectrometer (EDS), and X-ray diffraction (XRD). What emerged were different sizes and concentrations of Fe NPs being synthesized by tea extracts, leading to various degradations of MG. Furthermore, kinetics for the degradation of MG using these Fe NPs fitted well to the pseudo first-order reaction kinetics model with more than 20 kJ/mol activation energy, suggesting a chemically diffusion-controlled reaction. The degradation mechanism using these Fe NPs included adsorption of MG to Fe NPs, oxidation of iron, and cleaving the bond that was connected to the benzene ring.

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## Introduction

Malachite green (MG) is a cationic triphenylmethane dye widely used in the dyeing of cotton, silk, paper, leather and in the manufacture of paints and inks and aquaculture as a biocide [1,2]. MG is toxic and therefore has to be removed from wastewater prior to its discharge into aquatic environments. Various conventional methods such as adsorption [1], photo-catalytic degradation [3,4] and biological degradation [5,6] are often employed to remove MG from wastewater [3,4]. While to some extent these approaches have succeeded, the high cost and low efficiency of these processes limit their applicability [7]. Therefore, the development of innovative remediation techniques is required.

In recent years, zero-valent iron (nZVI) has received great attention from researchers examining groundwater treatment and site remediation due to the higher intrinsic reactivity of its surface sites [7]. Various physical and chemical methods have been developed for the synthesis of nZVI. Physical methods are thermal decomposition [8] and ultraviolet radiation and aerosol [9], but they are limited by the energy consumption required to maintain high pressure and temperature. Sodium borohydride ( $\text{NaBH}_4$ ) as a reducing agent is often used in chemical synthesis of nZVI [10,11]. The drawbacks include chemical substances such as  $\text{NaBH}_4$ , organic solvents, stabilizing and dispersing agents being toxic and very expensive. Furthermore while the electrochemical method has been used to compose iron nanoparticles, its disadvantage lies in the fact that aggregation of nanoparticles often occurs in the cathode's motor [12].

The green synthesis of nZVI has been recently proposed as a cost effective, environmental friendly alternative to chemical and physical methods since a variety of materials from biorenewable natural sources can be employed [13–15]. The components in the synthesis of nZVI such as polyphenols from coffee and tea, protein, vitamins and wine polyphenols are available [13–15]. Consequently, these components have emerged as replacements for the established chemical synthesis of nZVI. Furthermore, these components are extracted from natural sources that are non-toxic, biodegradable and the green material acts as both a dispersive and capping agent, helping to minimize the oxidation and agglomeration of nZVI [14]. The synthesis of nZVI using tea polyphenols has been recently examined in the context of in vitro biocompatibility [11], and used for degrading bromothymol blue by Fenton oxidation [16]. More recently, the synthesis of the membrane Fe/Pd using a green tea extract has been used to degrade trichloroethylene (TCE) [14]. The green synthesis of iron nanoparticles (Fe NPs) using the extract of green tea leaves a Fenton-like catalyst. This has been also reported in the degradation of aqueous cationic and anionic dyes [15]. The size and reactivity of the synthesized Fe NPs depend on significant factors such the reducing and capping agents [17], and different tea extracts indicate differences in the reducing and capping agents. From this it can be concluded that the size and reactivity, as well as the concentration of the synthesized Fe NPs, refer to different tea extracts. However, to date, few studies have been published on the synthesis of iron nanoparticles using different tea extracts.

In our previous studies, oolong tea extract has been used to synthesize iron nanoparticles [18]. To determine whether other tea extracts could be acted as reducing agent to synthesize Fe NPs, green tea extract, oolong tea extract and black tea extract were acted as the reducing agent to synthesize Fe NPs and used for Fenton-like oxidation of monochlorobenzene (MCB), where 69%, 59% and 39% of MCB were removed [19]. As a reductive degradation, the different degradations of MG are obtained using Fe NPs since the Fe NPs are synthesized by various extracts. Therefore, in this study, the synthesis of Fe NPs employs extracts from green

tea, oolong tea and black tea as reducing and capping agents. These can determine whether the synthesized Fe NPs can be used to degrade MG, as well as to examine why differences in using these Fe NPs emerge when the degradation of MG is being considered. To achieve these aims, the following issues are investigated: (1) the synthesis of Fe NPs utilizing various tea extracts and characterization of these Fe NPs by SEM, EDS, XRD, and BET- $\text{N}_2$ ; (2) evaluating the degradation of MG by Fe NPs synthesized from various tea extracts, including their degradation kinetics; (3) the mechanism of degradation of MG being proposed; and (4) demonstrating the application of Fe NPs to remove MG from wastewater.

## Experimental procedure

### Preparation of Fe NPs using tea extracts

The synthesis of Fe NPs using green tea extracts has been described previously [15,16]. The initial concentrations of 60.0 g/L green tea, oolong tea and black tea extracts were prepared by heating them at 80 °C for 1 h. These extracts were then vacuum-filtered and 0.10 mol/L  $\text{FeSO}_4$  solution was added to the tea extracts at a ratio of 1:2 respectively. The Fe NPs were synthesized from green tea, oolong and black tea extracts in the form of GT-Fe, OT-Fe and BT-Fe, respectively. The stock solution of MG with a 100.0 mg/L was first prepared, and the required MG concentration in our experiments was diluted using deionized water.

### Characterization

The synthesized Fe NPs using tea extracts were characterized using Uv-vis, SEM, EDS, BET- $\text{N}_2$  and XRD techniques. Morphology and distribution of Fe NPs were characterized using a scanning electron microscope (SEM) (JSM 7500F, Japan). Images of samples were recorded at different magnifications using an operating voltage of 10 kV. Localized elemental information of Fe NPs was determined by INCA EDS (Oxford Instruments, UK) in conjunction with SEM.

X-ray diffraction (XRD) patterns of Fe NPs before and after reaction with MG were obtained using a Philips-X'Pert Pro MPD (Netherlands) with a high-power Cu  $\text{K}\alpha$  radioactive source ( $\lambda = 0.154 \text{ nm}$ ) at 40 kV/40 mA. All samples were scanned from 10° to 80°  $2\theta$  at a scanning rate of 3°  $2\theta$  per minute.

The specific surface areas (SSA) of Fe NPs were measured using the BET- $\text{N}_2$  adsorption method (Brunauer–Emmett–Teller isotherm), specifically Micromeritics' ASAP 2020 Accelerated Surface Area and Porosimetry Analyzer (Micromeritics Instrument Corp., Georgia, USA).

### Degradation of malachite green

To compare the removal efficiency of MG using various synthesized Fe NPs, batch experiments were carried out using GT-Fe (0.01 g), OT-Fe (0.01 g) and BT-Fe (0.01 g) added to a solution containing 50.0 mg/L MG (8 mL). These were then placed on a rotary shaker at 298 K and 250 r/min. The degraded solutions were then filtered through 0.45  $\mu\text{m}$  membranes to determine the concentration of MG. This concentration was measured using a UV-Spectrophotometer (752N, Shanghai, China) at 617 nm. The removal efficiency of MG using various nanomaterials was calculated using the following equation [17]:

$$\eta = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

where  $\eta$  (%) = the MG removal efficiency,  $C_0$  = the initial MG concentration in the solution ( $\text{mg L}^{-1}$ ),  $C_e$  = the MG concentration after reaction ( $\text{mg L}^{-1}$ ). All experiments were undertaken in duplicate.

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