Synthesis of iron-based nanoparticles by green tea extract and their degradation of malachite

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ABSTRACT

In this paper, green tea extract was used to synthesize iron nanoparticles (GT-Fe NPs) and degrade malachite green (MG) in aqueous solution. The results show that the damage to morphology and increase in size of GT-Fe NPs after reaction with MG were observed by SEM and EDS. XRD shows that there are few changes in the characteristic peaks of GT-Fe NPs before and after reaction. UV–vis spectroscopy shows that the absorption peak of MG decreased, while FTIR shows that the band at 1585 cm^{-1} corresponded to the phenyl after reaction. The factors impacting on the removal efficiency of MG, including the initial solution pH, the initial concentration of MG, the dosage of GT-Fe NPs, and the reaction temperature, was also investigated. It emerged that 96% of MG was removed with a 50 mg/L at 298 K. Kinetics studies showed that the removal of MG fitted well to the pseudo first-order mode.

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1. Introduction

In recent years, iron-based nanoparticles have been successfully used in the field of environmental remediation and toxic waste treatment (He et al., 2012; Lin et al., 2012). Due to their high specific surface area size and high reactivity, iron-based nanoparticles can remove various dyes contaminants including malachite green (He et al., 2012), methyl orange (Chen et al., 2011), scarlet 4BS (Chen et al., 2011), and orange G (Bokare et al., 2008). This is despite dyes being quite difficult to remove from aqueous solutions (Gao et al., 2008). Many reports have been published on the development of synthesis methods to prepare iron-based nanoparticles, for example, inert gas condensation (Sanchez-Lopez et al., 1997), high-energy ball milling (Bianco et al., 1998), liquid-phase reduction (He et al., 2012;), and reverse micelle (Carpenter, 2001). Liquid-phase reduction has been widely used to prepare iron-based nanoparticles (He et al., 2012), but many chemicals are consumed and it is expensive and results in toxic byproducts, which are often potentially dangerous to the environment (Shahwan et al., 2011). Furthermore, recent studies have

proposed that iron-based nanoparticles do have shortcomings, such as aggregating into chain-like structures, and oxidation by non-target compounds. To address these issues, support materials such as bentonite (Chen et al., 2011), and surface stabilizers such as Tween-20 (Kanel et al., 2007), starch (Alidokht et al., 2011), and chitosan (Geng et al., 2009) have been used to disperse iron-based nanoparticles.

As one of the alternatives, green synthesis of metal nanoparticles (NPs) has received considerable attention due to its eco-friendly nanomaterial synthesis strategy (Shahwan et al., 2011). For instance, using plants or plant material could represent an alternative to chemical and physical methods for the synthesis of NPs (Nadagouda et al., 2010). The formation gold nanoparticles using live *alfalfa plants* have been reported (Gardea-Torresdey et al., 2002). Recently, metallic NPs have been synthesized using various plant extracts such as *hibiscus rosa sinensis* for Au and Ag NPs (Philip, 2010), *terminalia chebula* aqueous extract for Pd and Fe NPs (Kumar et al., 2013), *sorghum bran* for Fe and Ag NPs (Njagi et al., 2011), and *green tea* extract for Fe NPs (Shahwan et al., 2011; Smuleac et al., 2011; Hoag et al., 2009). These plant extracts have proven to be non-toxic to living organisms, a reproducible resource and environmental friendly material containing polyphenols and caffeine. These act as both reducing and stabilizing agents when they are used to green synthesize metal NPs. In addition, plant extracts as both reducing agent and capping/stabilizing agent are generating much interest.

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Recently, nanoscale zero-valent iron (GT-Fe NPs) synthesized by green tea extracts as a Fenton catalyst for the oxidation of bromothylmol blue (Hoag et al., 2009) and cationic (methylene blue) and anionic (methyl orange) model dyes (Shahwan et al., 2011) have been reported. The previous studies (Hoag et al., 2009; Shahwan et al., 2011) indicated that GT-Fe NPs as Fenton-like catalyst with high efficiency in the removal of dyes, but the removal mechanism using GT-Fe NPs was limited. In addition, the changes on surface and chemical species between GT-Fe NPs before and after reaction with contaminants were not provided since these were importance to understand the degradation. The aim of this study is to investigate the degradation mechanism of MG using Fe NPs synthesized by green tea extracts (GTE) to provide the insight of applications of GT-Fe NPs. Thus, the following experiments were performed: (1) characterization of GT-Fe NPs to understand their changes on surface and chemical species before and after reaction with MG; (2) batch degradation experiments in various conditions; and (3) proposing a model for the degradation kinetics of MG from aqueous solution by GT-Fe NPs.

2. Experimental

2.1. Preparation of GT-Fe NPs using green tea extract

The synthesis of Fe NPs using green tea extracts has been described previously (Shahwan et al., 2011). Aqueous extract of green tea was prepared by extracting 60 g of the green tea in 1000 mL deionized water in a temperature controlled water bath at 353 K for 1 h. These extracts were then vacuum-filtered after cooling to room temperature. 0.10 mol/L $FeSO_4$ was added to the tea extracts with a ratio volume of $FeSO_4$:tea extract = 1:2. After completing the reduction, this mixture was used to degrade MG.

2.2. Characterization

Scanning electron microscopy (SEM) images of GT-Fe NPs before and after reaction with MG were acquired using a JSM-7500F (JEOL Ltd. Co., Tokyo, Japan). The samples were effectively dispersed in aluminum foil so that photographs could be taken. Images of samples were recorded at different magnifications at an operating voltage of 5.0 kV. Localized GT-Fe NPs information from the chosen region was obtained with INCA EDS (Oxford Instruments, UK) in conjunction with SEM.

X-ray diffraction (XRD) patterns of GT-Fe NPs before and after reaction with MG were performed using a Philips-X'Pert Pro MPD (Netherlands) with a high-power Cu-Kα X-ray source (λ = 0.154 nm) at 40 kV/40 mA. All samples were scanned from 5° to 80° 2θ at a scanning rate of 3° 2θ per min.

FTIR analysis of MG, GT-Fe NPs before and after reaction with AMX was obtained with a Fourier transform infrared spectroscopy (FTIR Nicolet 5700, Thermo Corp., USA). Samples were prepared by mixing 1% (w/w) specimen with 100 mg of KBr powder and pressed into a sheer slice. An average of 32 scans was collected for each measurement with a resolution of 2 cm^{-1}.

2.3. Batch experiments

The degradation experiments were carried out using GT-Fe NPs (0.0448 g) added to 8 mL of aqueous solution containing 50.0 mg/L of MG at various conditions. Mixed solutions were stirred on a rotary shaker (250 rpm at 298 K) for 60 min. Then the mixtures were centrifuged at 10,000 rpm by the centrifuge for 10 min and the bottom solid was collected to determine the surface and chemical species after reaction with MG.

The effect of various parameters which affected the degradation of MG in aqueous solution by GT-Fe NPs was investigated.

The initial pH values used in this study were 3–9, the initial concentration of MG was 30–200 mg/L, the dosage of GT-Fe NPs was 0.112–1.12 g/L, and the reaction temperature was 288–308 K. Following this the mixtures were centrifuged at 10,000 rpm by the centrifuge for 10 min and the liquid supernatant collected to measure the residual concentration of MG. All these experiments were carried out in duplicate.

The absorbance of MG solution was measured using a UV-Spectrophotometer (722N, Shanghai, China) at λ_{max} (617 nm). Degradation efficiency of MG by GT-Fe NPs was calculated using the following equation (Chen et al., 2011):

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

where R (%) represented the MG degradation efficiency, and C_0 and C_t (mg/L) represented the concentration of MG at initial and t time, respectively.

3. Results and discussion

3.1. Characterizations

The SEM images of GT-Fe NPs before and after reaction with MG are shown in Fig. 1, where the GT-Fe NPs in the size range from 40–60 nm as shown in Fig. 1(a), and some nanoparticles tend to disperse on the capping agent to form irregular clusters with 40–200 nm. This phenomenon was also observed on the green synthesized iron nanoparticles and used a Fenton-like catalyst to degrade aqueous cationic and anionic dyes (Shahwan et al., 2011). In contrast, Fig. 1(b) shows that the size of GT-Fe NPs partly increased and their surface became scabrous after reacting with MG in aqueous solution, this was due to form the iron oxides, and MG or its degradation products adsorbed on GT-Fe NPs (Giri et al., 2011). This is also attributed to some green tea extracts adsorbed onto the formed iron oxides of GT-Fe NPs (Chen et al., 2011). However, some of the GT-Fe NPs maintained their original shape and size due to green tea extracts acting as both capping and stabilizing agents (Shahwan et al., 2011). This is due to the fact that green tea extracts as capping and stabilizing agents evidently protected Fe^0 from oxidization when GT-Fe NPs contacted with air and consequently a high surface area and reactivity (Hoag et al., 2009) was maintained, which agrees with EDS, XRD, FT-IR and UV–vis analysis.

Table 1 confirms the samples containing Fe, O, C, S, and Al elemental composition before and after GT-Fe NPs reaction with MG. The elemental percentages obtained by EDS were 16.8% Fe, 30.7% C, 34.8% O, 3.6% S, and 14.2% Al of GT-Fe NPs before reaction with MG, respectively. The S composition element may originate from $FeSO_4$ as precursors used in the synthesis of GT-Fe NPs. The Al composition element may derive from aluminum foil which was used as the basis for the samples acquiring by the EDS. The C and O are attributed mainly to the carbonyl groups of polyphenol and other C-containing molecule in green tea extracts (Shahwan et al., 2011). However, after reacting with MG, the Fe, C, O, S and Al percentages were 9.6, 20.9, 50.5, 5.0 and 14.1 wt%, respectively. The O percentages rose from 34.8 to 50.5 wt% while the Fe content fell 16.8 to 9.6 wt%, which can be explained by the Fe^0 in the GT-Fe NPs acting as a reductant being oxidized to form Fe_3O_4, Fe_2O_3 after reacting with the MG (Chen et al., 2011).

The XRD patterns of GT-Fe NPs before and after reaction with MG are shown in Fig. 2. As in Fig. 2a, the XRD patterns of GT-Fe NPs before reaction with MG was deficient at peak (2θ = 44.9°) of Fe^0 since it is amorphous in nature, and the Fe^0 surface was capped with green tea extract working as a capping or stabilizing agent (Kumar et al., 2013). Therefore the diffraction peak (2θ = 44.9°) of Fe^0 was difficult to detect using XRD. Similar results have observed since GT-Fe NPs were amorphous in nature, which were