Decolorization of direct scarlet 4BS dye using biosynthesized iron nanoparticles as effective heterogeneous Fenton-like catalyst

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Decolorization of direct scarlet 4BS dye using biosynthesized iron nanoparticles as effective heterogeneous Fenton-like catalyst

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Abstract

In the present study, the iron nanoparticles (Fe-NPs) were synthesized using extracts of green tea leaves as a reducing and capping agents under atmospheric conditions. The Fe-NPs were characterized using scanning electron microscope (SEM), energy dispersive spectrometer (EDS), transmission electron microscopy (TEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The obtained nanoparticles were mostly spherical and uniform in size with diameters ranging from 50 to 70 nm and then utilized as a Fenton-like catalyst for the decolorization of Direct scarlet 4BS (4BS) in solution. About 85% of the dye was successfully removed in 30 min using 1 g/L of catalyst in the presence of 15 mM of H₂O₂ at lower acidic pH (pH 2-4) at room temperature.

Keywords: green synthesis, iron nanoparticles, direct scarlet 4BS, Fenton-like catalyst

1. Introduction

Nowadays, the pollution of water sources by dyes from many industries such as textile, paper, plastic, food and pharmaceutical are still a major threat to the
environment (Forgacs, Cserháti & Oros, 2004). The release of dye effluent into water sources cause serious impact on aquatic organisms by hindering the infiltration of sunlight into the water because of the mutagen and carcinogen from dyes. Therefore, it is necessary to treat the water containing these dyes. Conventional water treatment methods include chemical coagulation, flocculation, chemical oxidation, photochemical degradation, membrane filtration, aerobic and anaerobic biological degradation (Robinson, McMullan, Marchant, & Nigam, 2011; Khehra, Saini, Sharma, Chadha, & Chimni, 2006; Lin & Peng, 1994; Tisa, Abdul Raman, & Ashri Wan Daud, 2014). All of these methods are known to be effective, however, their techniques have one or limitations and none of them are successful in completely removing the colors from wastewater. In recent years, nanocatalysis has emerged as an alternative to conventional water treatment methods. The high effectiveness of nanocatalyst is due to its high surface area and surface reactivity. Among metal nanoparticles, iron nanoparticles (Fe-NPs) are widely used for the effective removal of dye contaminants. Fe-NPs can be synthesized by chemical and biogenic methods. Chemical methods involve the use of toxic chemicals and severe reaction conditions which lead to chemical toxicity and environmental pollution. The biogenic methods are considered to be safer alternative to chemical methods of nanosynthesis due to its ease, eco-friendly nature and cost effectiveness (Wang, Jin, Chen, Megharaj, & Naidu, 2014; Shahwan et al., 2011; Smuleac, Varma, Sikdar & Bhattacharyya, 2011; Machado et al., 2013; Kumar, Mandal, Kumar, Reddy & Sreedhar, 2013). The components in plant extracts such as polyphenols, flavonoids and alkaloids which serve as reducing and capping agents may assist in designing nanomaterials (Iravani, 2011).
Polyphenols are the major component of green tea extract (Truskewycz, Shukla & Ball, 2016). Polyphenols from the green tea reduce the iron salts to form iron nanoparticles and also cap the metal, protecting it from oxidation. The use of green tea polyphenols to generate iron nanoparticles has been examined in the context of in vitro biocompatibility (Nadagouda, Castle, Murdock, Hussain & Varma, 2010). Recently, the synthesized iron nanoparticle using green tea extract has been utilized as a Fenton-like catalyst for the oxidation of bromothylmol blue (Hoag et al., 2009), cationic (methylene blue) and anionic (methyl orange) dyes (Shahwan et al., 2011), azo (DR80, Direct Red 80) and anthraquinone (RBB-R, Ramazol Brilliant Blue R) dye mixtures (Truskewycz et al., 2016) and monochlorobenzene (Kuang, Wang, Chen, Megharaj, & Naidu, 2013).

The objectives of this research were to study the synthesis of Fe-NPs in green tea leaf extract, and to investigate the effectiveness of Fe-NPs as Fenton like catalyst for decolorizing direct scarlet 4BS from synthetic wastewater.

2. Materials and Methods

2.1 Chemicals

Direct scarlet 4BS dye (4BS) was received from PKS chemical Co. Ltd., Thailand. Green tea leaves were obtained from Baichachokchamroen Co. Ltd., Thailand. The chemical structures are illustrated in Figure 1. All chemical, such as hydrogen peroxide (H$_2$O$_2$, 35% w/v), sulfuric acid (H$_2$SO$_4$) and ferrous sulfate heptahydrate (FeSO$_4$·7H$_2$O) were analytical reagent grade.

2.2 Preparation of Fe-NPs

The green tea extract was prepared by heating 60.0 g/L green tea leaves until boiling. After settling for 1.0 h, the extract was filtered. Finally, the tea extract was
obtained. Separately, a solution of 0.10 M FeSO$_4$·7H$_2$O was added to the green tea extract in 2:1 volume ratio at room temperature. The immediate appearance of black color indicated the reduction of Fe$^{2+}$ ions. These precipitates were then filtered and centrifuged. The resulting Fe-NPs were washed with distilled water at least 3 times and then dried in a vacuum oven. Finally, the solid Fe-NPs were collected.

### 2.3 Characterization of Fe-NPs

The synthesized Fe-NPs were characterized using XRD, TEM, SEM/EDS, and FTIR techniques. The morphology of Fe-NPs was observed using a scanning electron microscopy (SEM-JEOL-JSM-7800F) and elements in Fe-NPs were determined by using an energy dispersive X-ray (EDS) spectroscopy (Oxford ED2000). Transmission electron microscopy images were obtained on JEOL, JEM-2010 equipment. The crystalline structure of Fe-NPs was analyzed by an X-Ray diffractometer (Bruker D2 PHASER) using CuK$_\alpha$ radiation at 30 kV and 10 mA. Data were collected from 10° to 80° with a step size of 0.02. Fourier transform infrared spectroscopy spectra were obtained using a Perkin Elmer Spectrum 100 FT-IR spectrometer. Thermogravimetric analysis (TGA) of the produced nanoparticles was done on a thermogravimetric analyzer (STA 6000, Perkin Elmer) under nitrogen atmosphere at the heating rate of 10 °C/min in the range of 30 -700 °C.

### 2.4 Decolorization experiments

All experiments were carried out in 125 mL-Erlenmeyer flasks with 50 mL of 50 mg/L 4BS. The pH of the solutions was adjusted to the desired values by using 2.0 M H$_2$SO$_4$ and after that the Fe-NPs was added. The reactions were initiated by adding a predetermined amount of H$_2$O$_2$ solution to the flask. The mixture solution was stirred with a magnetic stirrer. At a regular interval of time, 1 mL of the reaction mixture was
withdrawn and centrifuged immediately to remove the catalyst. The concentrations of
4BS were measured using a double beam UV-vis spectrophotometer (Shimadzu, model
UV 1601, Japan) at 504 nm. The decolorization efficiency of 4BS was calculated using
the following equation:

\[
\text{Decolorization efficiency (\%) } = \frac{C_0 - C_t}{C_0} \times 100
\]

where, \(C_0\) (mg/L) is the initial concentration of 4BS and \(C_t\) (mg/L) is the concentration
of 4BS at the time, \(t\) (min).

3. Results and Discussion

3.1 Characterization of Fe-NPs

The SEM and TEM image of the synthesized Fe-NPs are shown in Figure 2(a)-(b). It can clearly be seen that the Fe-NPs has a spherical shape. TEM image as seen in
the polyphenol capping agent indicated successful production of the Fe-NPs
nanohybrids. From the histogram the size distribution of particles (Figure 2(c)), the
average size of the particles was found to be about 63 nm and the size of the
nanoparticles varied in the range of 30-100 nm.

Figure 3 shows a representative EDX spectrum of the iron nanoparticles. The
iron nanoparticles are primarily composed of C, N, O, P and Fe. The C and O elements
originated predominantly from phytochemicals (phenolic and flavonoids compound)
(Kuang et al., 2013; Quideau, Deffieux, Douat-Casassus, & Pouysegu, 2011).

The XRD patterns of Fe- NPs samples synthesized by green tea plant extracts
are shown in Figure 4(a). The patterns of the Fe- NPs samples lack distinct diffraction
peaks, suggesting that the Fe- NPs are amorphous. The broaden peaks at about \(2\theta = 25^\circ\),
which can be attributed to organic materials from plant extract which are responsible for
capping and stabilizing nanoparticles (Kumar et al., 2013; Wang, 2013; Njagi et al.,
2011). The similar observation was noticed in the green synthesis of Fe-NPs using
extracts of eucalyptus, S. jambos (L.) Alston and sorghum bran (Wang, 2014; Njagi et
al., 2011; Xiao et al., 2016). Figure 4(b) shows the FTIR spectrum of Fe-NPs and green
tea extract. For the extract of green tea, strong bands at 3402 cm\(^{-1}\) is assigned to O-H
stretching vibrations (Kumar et al., 2013). The peak at 2929 cm\(^{-1}\) is characteristic of
aliphatic C-H stretching vibrations. The presence of band attributed to polyphenolic
compounds at 1631 cm\(^{-1}\) is due to C=C aromatic ring stretching vibration, 1367 cm\(^{-1}\)
for C-N stretching vibration for aromatic amines, and 1043 cm\(^{-1}\) for C-N stretching
vibration of aliphatic amines (Das, Borthakur & Bora, 2010). Thus, functional groups
including phenols, amines and carboxyl are confirmed in the green tea. Meanwhile, the
FTIR spectrum of the prepared Fe-NPs also displayed stretching vibrations at 3382 cm\(^{-1}\)
for O-H, at 1630 cm\(^{-1}\) for C=C and 1,068 cm\(^{-1}\) for C-O-C absorption peak (Kumar et
al., 2013). The FTIR analysis observed some minor shifts in the position of various
peaks as compared with that of the green tea extract thus indicating the involvement of
the plant extract in the synthesis and stabilization of nanoparticles. Zero-valent iron
nanoparticles exhibit a typical core-shell structure, zero-valent iron atoms forming the
core which is surrounded by an oxide shell, composed of Fe\(^{2+}\) and Fe\(^{3+}\), is formed as a
result of the oxidation of the metallic iron (Kharisov et al., 2016). The thin iron oxide
shell resulted in the appearance of Fe-O absorption bonds, but in lower intensity than
that usually observed for iron oxide nanoparticles. The Fe-O characteristic peaks of the
iron oxide nanoparticles appear at about 640 cm\(^{-1}\) and 450 cm\(^{-1}\) (Ebrahiminezhad,
Ghasemi, Rasoul-Amini, Barar, & Davara, 2012). These peaks were not observed in the
FTIR spectrum of the prepared Fe-NPs indicated that the absence of iron oxide shell. This confirms the organic coating from leaf extract seems to protect the surface of Fe⁰ atoms from oxidation.

Thermogravimetric analysis of Fe-NPs is shown in Figure 5. The initial weight loss observed prior to 200 °C relates to the presence of volatile (water and carbon) on the surface of the synthesized Fe-NPs. Beyond 200 °C the rapid weight loss at high temperatures could be due to the decomposition of the phytomolecules from the green tea extract, which are present on the surface of the nanoparticles acting as stabilizing agents. (Katithi et al., 2016).

3.2 Decolorization experiments

To investigate their catalytic activity, the iron nanoparticles were employed in the decolorization of 4BS in the presence of H₂O₂. The progress of the catalytic decolorization of 4BS was monitored by the decreasing of the absorbance at the maximum absorbance wavelength of 4BS. Figure 6 shows the UV-Vis spectra of the decolorization of 4BS. 4BS has the maximum absorbance wavelength (λ_max) at 504 nm and the absorbance at 250 and 310 nm confirm the phenyl and naphthyl rings-possessing 4BS structure (He, Hu, & Li, 2004). After 10 min of reaction, the dye structure changed markedly and the absorbance at 504 nm disappeared. This is because of the cleavage of azo bonds (N=N). However, iron nanoparticles were not stable under acidic pH conditions (pH 2-4) or in the presence of 15mM H₂O₂. The solutions became brown-yellow color because the particle size of zero valent iron nanoparticles decreased and were well dispersed in acidic media. The UV-vis spectrum of the solution with brown-yellow color (as shown in Fig.6) showed the peaks at 272 nm, which confirmed
the appearance of iron nanoparticles (Huang, Weng, Chen, Z. Megharaj, & Naidu, 2014).

The reaction is based on the action of hydroxyl radicals (•OH), generated in aqueous solution by the well-known Fenton reagent which is a combination of Fe$^{2+}$ and H$_2$O$_2$ in aqueous solution for oxidation of organic pollutants from contaminated water.

Based on the above results, a possible mechanism for Fenton-like degradation of direct scarlet 4BS dye employing Fe-NPs has been proposed as similarly reported by Kuang et al. (2013), in Eqs. (1)-(6). Firstly, the adsorption of 4BS onto the surface of Fe-NPs (Eq. (1)). Secondly, the process of generating hydroxyl radicals is suggested. In the presence of H$_2$O$_2$, the zero valent iron (Fe$^0$) is transformed into Fe$^{2+}$ (Eq. (2)). Fe$^{2+}$ can then react with H$_2$O$_2$ to form •OH (Eq. (3)). During reaction, Fe$^{3+}$ is formed which can be reacted to produce Fe$^{2+}$ (Eq. (4)). (Bergendahl & Thies, 2004). Finally, the highly oxidative •OH radicals reacted rapidly with the adsorbed 4BS and attacked effectively on the bonds of the dye molecules. A part of 4BS was mineralized on the surface of Fe NPs into CO$_2$ and H$_2$O. In conclusion, the possible oxidation mechanism using Fe-NPs is described below:

(1) Adsorption process:

$$4BS + FeNPs \rightarrow 4BS/FeNPs$$ (1)

(2) The process of generating •OH radicals:

$$Fe^0 + H_2O_2 \rightarrow Fe^{2+} + 2OH^-$$ (2)

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + •OH$$ (3)

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + •OOH$$ (4)

(3) •OH radicals attack the 4BS on the surface of FeNPs:

$$4BS/FeNPs + •OH \rightarrow \text{Reaction intermediates/FeNPs}$$ (5)
Reaction intermediates/FeNPs + •OH → CO₂ + H₂O  \( (6) \)

The decolorization of 4BS were experienced for all solution pHs (Figure 7). The greatest decolorization of 4BS occurred at pH 2.0-4.0 with a decolorization of approximately 85% within 30 min. At pH 5.0, the decolorization was 71% within 30 min and the decolorization was up to approximately 83% with the increasing of the reaction time. It can be concluded that the optimum for the Fenton oxidation mostly fall in the lower acidic pH because a high amount of Fe²⁺ and •OH was generated (He et al., 2004; Bergendahl & Thies, 2004; Chen, Ma & Sun, 2008; Pignatello, Oliveros, & MacKay, 2006). The effect of H₂O₂ dosage on the decolorization of 4BS was examined by varying initial concentration of H₂O₂ from 7 to 28 mM at pH 3.0 (Figure 8). The best initial H₂O₂ concentration was obtained at 15 mM. Decolorization of 4BS increased with increase in the H₂O₂ concentration due to the high concentration of •OH radicals generation to catalyze the organic dye. However, the formation of less reactive species such as hydroperoxyl radicals (•OOH) may be generated due to the scavenging effect of hydroxyl radicals and the inhibition of iron corrosion on the surface of Fe-NPs by hydrogen peroxide (Eq. (7)) with the increase of the reaction time when an initial concentration of 28 mM H₂O₂ (Kuang et al., 2013) was used.

\[ \text{H}_2\text{O}_2 + \cdot\text{OH} \rightarrow \text{H}_2\text{O} + \cdot\text{OOH} \]  \( (7) \)

4. Conclusions

Iron nanoparticles was successfully synthesized using the green tea leaf extract following the green procedure. The phytochemicals in the leaf extract play dual roles as both are reducing and stabilizing agents. The obtained iron nanoparticles (Fe-NPs)
showed a sphere-like morphology. Furthermore, the iron nanoparticles (Fe-NPs) exhibited good catalytic effects on the decolorization of the 4BS dye with H$_2$O$_2$ based on the Fenton-like reaction. The results show that the green synthesis of iron nanoparticle can be an effective technology for treating wastewater containing organic dyes.

**Acknowledgments**

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**References**


Figure 1 Chemical structure of Direct Scarlet 4BS (4BS).

Figure 2 SEM image (a), TEM image (b) and particle size distribution of Fe-NPs (c).
Figure 3 EDX spectrum of Fe-NPs.

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Figure 4 XRD pattern (a) and FTIR spectra of Fe-NPs and green tea extract (b).
Figure 5 The TGA curve (% weight loss) of the Fe-NPs.
Figure 6 UV-vis absorption spectra of Fe-NPs in media acid solution and 4BS before and after the Fenton-like reaction. Reaction conditions: initial concentration of 4BS, $[4BS]_0 = 50$ mg/L, initial concentration of hydrogen peroxide, $[H_2O_2]_0 = 15$ mM, catalyst dosage = 1.0 g/L, initial pH = 3 and temperature = 26 °C.
Figure 7 Effect of pH on the decolorization of 4BS. Reaction conditions: initial concentration of 4BS, $[4BS]_0 = 50$ mg/L, initial concentration of hydrogen peroxide, $[H_2O_2]_0 = 15$ mM, catalyst dosage = 1.0 g/L and temperature = 26°C.
Figure 8 Effect of initial concentration of H$_2$O$_2$ on the decolorization of 4BS.

Reaction conditions: initial concentration of 4BS, [4BS]$_0$ = 50 mg/L, initial pH = 3, catalyst dosage = 1.0 g/L and temperature = 26 °C.