Efficient reduction of methylene blue in aqueous solution using a Fenton-like catalyst of Fe$_3$O$_4$/Cu

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Abstract. This work aimed to investigate the efficient reduction of methylene blue (MB) by a heterogeneous magnetic nanoparticles/copper (MNs/Cu) Fenton-like catalyst. The MNs/Cu was successfully synthesized in the presence of Citrus aurantifolia extract. The characterizations showed an effective fabrication of Cu onto the surface of MNs. The reduction of MB by the MNs/Cu Fenton-like catalyst presented an efficiency of 99.5% at the optimum conditions, including MNs/Cu dose of 0.1 mg, temperature of 25°C, contact time of 75 min, pH 4.0, and 20 mL H$_2$O$_2$ 30%, MB initial concentration of 25 mg/L. The reduction kinetics was well fitted to pseudo-second-order with reaction rate constant of 0.0029 g/mg.min. The main mechanism of the MB reduction due to active oxygen species was pointed out. The decrease of reduction yield at high pH, catalyst dose and MB concentration was elucidated in this study.

1. Introduction

Methylene blue (MB) is an organic dye that can have disastrous effects on both the balanced ecosystems and the health of the human being. There are huge amounts of organic dyes released to the environment from industry yearly [1]. It is not the main cause of carcinogenicity and mutagenic also harmful to fauna and flora [2]. MB is used as a viral dye in some industrial fields such as cosmetic, medicine, paper, plastic, leather and textiles [3]. Hence, the scientists give their best shot to find out the best way to remove MB in aqueous solution.

Many kinds of methods for removal of MB have been investigated. In these traditional methods, adsorption is by far the most commonly used one for removal of organic dyes in wastewater. In addition to ease of operation, the adsorbent materials also are able to be reused, so they save the cost for removal processes [4]. One of great adsorbent materials is magnetic nanoparticles (MNs) Fe$_3$O$_4$ which are potentially used in environmental treatment, in which degradation of aqueous organic solutes is no exception. There are several reports about some applications of MNs for removal of toxic and carcinogen heavy metal ions in wastewater such as: As(V) [5], Hg(II) [6], Cr(VI) [7, 8]. MNs contain a strong adsorption ability because of their magnetic properties, superparamagnetism, high
chemical stability and low toxicity [9]. Besides, some degradation of organic dyes using MNs were investigated [10,11]. However, it is not able to completely remove dyes in water by using adsorption or ion exchange, and advanced chemical oxidation shows a great concern to degrade the dyes almost completely [12]. The organic dyes can be oxidized absolutely based on Fenton reaction which created reactive oxygen species (OH$^\cdot$), these refractory organics will be interacted with OH$^\cdot$ by oxidants in Fenton system, in which the catalysts play a crucial role [13].

In previous works, they showed that several transition metal copper-based catalysts performed a strong removal of organic dyes such as CuFe$_2$O$_4$ [14], CuS [15], and yolk-sell structured Fe$_3$O$_4$@copper silicate [16]. Copper (Cu) nanoparticles are inexpensive and easy to synthesize in the laboratory compared to traditional catalysts [17]. Using natural stabilizers or fruit extract to create catalyst fabricated Cu nanoparticles is trending [18,19]. Citrus aurantifolia is popular in Vietnam; this work, therefore, used Citrus aurantifolia fruit extract and NaBH$_4$ as a reducing agent to investigate the synthesis of a Fenton-like catalyst of Fe$_3$O$_4$/Cu connected by lysine. This approach is not only less harmful to the environment but also is low-cost, and confirms the trend of sustainable development. This work also applied the as-synthesized catalyst to degrade MB in water efficiently.

2. Materials and methods

2.1. Materials
The following reagents and chemicals were needed in ferromagnetic synthesis and adsorption experiments: sodium borohydride (NaBH$_4$, 98%), polyethylene glycol (PEG), Poly(vinylpyrrolidinone) (PVP), hexadecyltrimethylammonium bromide (CTAB, 98%), and ethanol (96%) were purchased from Sigma Aldrich. Copper (II) sulfate pentahydrate (CuSO$_4$.5H$_2$O, 98%), ferrous chloride tetrahydrate (FeCl$_2$.4H$_2$O, 98%), L-Lysine (L-Lys) (98%), and methylene blue (MB) trihydrate were purchased from Xilong Chemical Co. Ltd. The chemicals are directly used without further purification. Limes were collected from the local markets in Can Tho city, Vietnam. Freshly prepared deionized (DI) water was used throughout the experiments.

2.2. Green and facile synthesis of Fe$_3$O$_4$/Cu

2.2.1. Fe$_3$O$_4$ synthesis. Using Citrus aurantifolia (lime) extract and NaBH$_4$ to synthesize Fe$_3$O$_4$ nanoparticles from FeCl$_2$.4H$_2$O followed the report of Luong et al. (2021) [20]. The synthesis was briefly presented in the following steps. The Citrus aurantifolia extract was freshly prepared for each experiment to minimize oxidation. Then, a desired amount of FeCl$_2$.4H$_2$O solution (0.2 M) and PEG surfactant solution 1% was speedily stirred at room temperature for 60 min before adding 10 mL of the prepared Citrus aurantifolia extract. After 15 min, the color of the solution changed from light green to lemon yellow and then to black by adding 20 mL of NaBH$_4$ 0.3 M solution, indicating the formation of Fe$_3$O$_4$. The precipitates were collected by applying an external magnet, and then washed with DI water and ethanol 96% until neutral pH. The nanoparticles were dried at 60°C until the mass was constant.

2.2.2. Fe$_3$O$_4$/Cu synthesis. The MNs/Cu catalyst was prepared according to a literature method [21]. The synthesis process was summarized as follows: the amount of 0.5 g as-synthesized Fe$_3$O$_4$ was dispersed in 50 mL of DI water. Then, 0.5 g L-Lys was added and constantly stirred for 30 min until
L-Lys powder dissolved entirely. The volume of 30 mL CuSO\textsubscript{4} 0.1 M was then dropped into the solution under the same stirring condition. After that, 15 mL NaBH\textsubscript{4} 0.2 M used as reducing agent was added and reacted during 1 h under a rapid stirring. The magnetic nanoparticle/copper (MNs/Cu) material was collected by using an outward magnet. The MNs/Cu was washed several times with DI water and ethanol 96%. It was then dried at 60°C until the unchanged mass.

2.2.3. Characterization of magnetic nanoparticles
The as-synthesized MNs/Cu was characterized by using different advanced techniques. Its structure was determined by using X-ray diffraction (XRD) (D8 Advance instrument, Bruker) performed with CuK radiation (λ=1.54056 Å) scanned at 7.0000 degree/min, accelerating voltage of 40 kV and applied current of 30 mA. Field emission scanning electron microscopy (FE-SEM) measurements (Hitachi S-4800) and energy dispersive X-ray spectroscopy module ADAX (EDX) were taken at accelerating voltage of 10 kV, working distance of 1.8 mm, low magnification mode to evaluate the morphology and atomic percent of the catalyst. Transmission electron microscopy (TEM) (JEOL-1010, Japan Electron Co.) was operated at an operating voltage of 80 kV, magnification of 60,000x to 100,000x to illustrate the formation of MNs/Cu. The magnetic properties of the sample were investigated using a vibrating sample magnetometer (VSM) (Microsense EZ9, USA) operated with maximum field of 22.5 kOe, field resolution of 0.001 Oe and at room temperature.

2.2.4. Removal of MB experiments
A stock of MB solution (100 mg/L) was firstly prepared by dissolving MB in DI water. All working solutions at the desired concentration were prepared from this stock solution by diluting with DI water. The initial pH was adjusted to between 2.0 and 6.0 with HCl 0.05 M or NaOH 0.05 M solution. The concentrations of MB and MNs/Cu dose were varied from 10–70 mg/L and 0.02–0.2 mg, respectively. Contact time of the catalyst and the solution was changed from 30 to 120 min. Concentrations of MB were determined by using an ultraviolet-visible (UV-Vis) spectrophotometer (V730 Jasco) at λ= 664 nm. The removal capacity of MB (H%) was calculated using the following equation:

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H(\%) = \frac{(C_0 - C_e)}{C_0} \times 100
\]

where \(C_0\) (mg/L) and \(C_e\) (mg/L) are the initial concentration and the equilibrium concentration of MB solution, respectively.

3. Results and discussion
3.1. \(\text{Fe}_3\text{O}_4/\text{Cu}\) synthesis
The \(\text{Fe}_3\text{O}_4/\text{Cu}\) formation mechanism is described by the schematic illustration in figure 1. Firstly, the hydroxyl groups (-OH) in MNs surfaces were generated when the MNs were dispersed in DI water. The -OH groups were then bonded with L-Lys in order to present -NH\textsubscript{2} groups onto the surface of the MNs. Cu (II) metal ions were dissociated from CuSO\textsubscript{4} salt to link with -NH\textsubscript{2} groups of L-Lys by generating -NH\textsubscript{2}…Cu\textsuperscript{2+} complex. These NH\textsubscript{2}…Cu\textsuperscript{2+} complexations were then reacted with a strong base (NaBH\textsubscript{4}) to generate Cu particles by reducing the Cu (II) ions. The MNs/Cu particles were finally formed by L-Lys bridge [21,22].
Figure 1. A formation mechanism diagram of Fe$_3$O$_4$/Cu.
The Fe$_3$O$_4$ nanoparticles were prepared from 10 mL extract combined with 20 mL NaBH$_4$ 0.3 M with the presence of PEG at room temperature for 60 min. The crystalline structure of MNs was determined by using X-Ray diffraction analysis and presented in figure 2. The peaks at 20 = 30.1°, 35.4°, 43.1°, 53.4°, 56.9° and 62.5° refer to (220), (311), (400), (422), (511) and (440) lactic planes, respectively. This observation matched well with the inverse spinel structure of Fe$_3$O$_4$ (JCPDS card no. 75–1610) according to the reflection peak positions and relative intensities. These peaks also observed in the report of Hu et al. (2013), confirming that the nanoparticles synthesized in this study were the Fe$_3$O$_4$ nanoparticles [23].

Figure 2. XRD analysis of MNs/Cu and Fe$_3$O$_4$ nanoparticles.
To determine crystallinity of Cu on MNs, XRD pattern of MNs/Cu was presented in figure 2 to compare and recognize the appearance of Cu particles onto MNs. Apart from the aforementioned usual peaks of MNs, typical peaks of Cu nanoparticles were discovered at $2\theta = 50.4^\circ$ from the (200) lattice plane [24]. In addition, the peaks at $2\theta = 43.3^\circ$ and $73.9^\circ$ also belong to the metallic Cu nanoparticles [25]. However, the previous two peaks practically coincide with MNs peaks, the bases of the MNs/Cu diffraction peaks are larger and the intensity is also higher than solitary MNs diffraction patterns [21].

The morphologies of MNs and MNs/Cu were observed in figure 3a and 3b. The TEM images of both MNs and MNs/Cu showed that the particles were formed in the average diameter of 20 and 40 nm, respectively. In addition, figure 3b displayed the as-synthesized materials that prefer to stick together, so the TEM image revealed the overlap of materials.

The EDX spectrum of the MNs in figure 3c showed that the atomic composition of C, O, and Fe elements accounted for 10.38%, 65.62%, and 24%, respectively. The strong peaks of Fe observed at
around 0.8, 6.2 and 6.9 keV, and the intensive peaks of O at 0.6 keV were related to the binding energies of O. Therefore, these peaks correspond to the presence of Fe$_3$O$_4$. However, the impurity peak of C was found at 0.4 keV due to the presence of bio-organic components as flavonoids, limonoids and carboxylic acids, which were determined to be the main elements in Citrus aurantifolia extract adsorbed on the surface of MNs [26]. From the EDX spectrum of MNs/Cu materials in figure 3d, the appearance of the main elements as Fe, O, and Cu was observed. The atomic percentage of MNs/Cu were O (49.94%), Fe (11.75%) and Cu (38.31%). Besides the spectrum peaks of Fe and O were observed, the intensive peaks of Cu were recorded at 1.1, 8.1 and 8.9 keV positions. In addition, the disappearance of C peaks from the bio-organic compounds was confirmed that these organic components were decomposed and washed out during the synthesis process of MNs/Cu. Finally, it concluded that Cu nanoparticles were fabricated on the MNs surface.

**Figure 4.** Magnetization curve of MNs and MNs/Cu.

The magnetization curves measured for the as-synthesized MNs and MNs/Cu nanoparticles in this study were presented in figure 4. The measured specific saturation magnetization value of MNs and MNs/Cu were respectively at 40.1 and 15.2 emu/g. The existence of a non-magnetic layer on the particle surface as a bio-organic component in Citrus aurantifolia extract might explain the low specific saturation magnetization in MNs with particle sizes of some tens of nanometers. However, the negligible coercivity Hc of hysteresis loop (195.7 Oe) and consequently low remanence Mr (5 emu/g) indicated the superparamagnetic nature of the MNs. Besides, the magnetization reduction of MNs/Cu to 15.2 emu/g was attributed to decrease in the ratio of Fe$_3$O$_4$ in the MNs/Cu compared to MNs. Another reason for the MNs/Cu magnetization reduction is that Cu nanoparticles is an antiferromagnetic metal, so its appearance on the surface of the MNs causes considerable reduce in saturation magnetization value of the MNs/Cu [27]. The fabrication of Cu nanoparticles onto surface of MNs was also illustrated by the shift of pH$_{pzc}$ 9.04 (MNs) to pH$_{pzc}$ 7.54 (MNs/Cu) in figure 7.

3.2. **MB removal process of MNs/Cu**
The value of pH is well-known as one of the most essential parameters, which strongly affects the removal of organic compounds using the Fenton reaction. Hence, the variation of pH from 2.0 to 10.0 in the removal of MB was carried on and the results were shown in figure 5. As can be observed, the pH of the solution had a big impact on the removal capacity. The MB reduction efficiency was at 96.3% at pH 2.0 and moderately dropped to 94.1, 88.4 and 77.4% at pH 4.0, 6.0 and 8.0, respectively. However, the reduction slightly climbed to 81.8% at pH 10.0. From the aforementioned results, MNs/Cu showed a strong MB removal in the acid region. At low pH, the surface of MNs/Cu is strongly protonated in a solution containing more protons [28], which causes an acceleration of the Fe$^{2+}$ ion release from Fe$_3$O$_4$. The positive surface charge of MNs/Cu was also confirmed by pH$_{pzc}$ 7.54 in figure 7. The released Fe$^{2+}$ ions reacted with H$_2$O$_2$ to generate the active oxygen species (OH\(^{-}\), O$_2$\(^{2-}\)) (reaction 1). These OH\(^{-}\) then strongly interacted with MB and degraded its structure into simple compounds, such as CO$_2$ and H$_2$O. In addition, Cu$^0$ on the surface of the catalyst could also enhance the production of Cu$^+$ [29] and these Cu$^+$ ions are then involved in Fenton reactions like Fe$^{2+}$ to reduce MB into minerals (reaction 2 and 3) [30]. The above explanation is the main mechanism of MB reduction by using Fenton-like MNs/Cu catalyst. This explanation was also depicted as figure 6. At alkaline (pH≥7), the surface charge of the catalyst varied to negative and the environment contained a huge amount of OH\(^{-}\) ions. These cause interference in the adsorption of H$_2$O$_2$ due to the electrostatic repulsion and backward interaction of reaction 1, 2, and 3, which decreased the reduction efficiency of MB at pH 8. The slight increase of the reduction efficiency at pH 10 was attributed to the adsorption of positively charged MB and negatively charged surface of the catalyst (figure 7) via electrostatic attraction. Generally, pH presented a great influence on the degradation of MB via the Fenton-like reaction of the MNs/Cu catalyst at acidic pH, and this reaction was less efficient at alkaline condition.

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \text{OH}^+ + \text{OH}^- \quad \text{(Reaction 1)} \\
\text{Cu}^0 + \text{H}_2\text{O}_2 & \rightarrow \text{Cu}^+ + 2\text{OH}^- \quad \text{(Reaction 2)} \\
\text{Cu}^+ + \text{O}_2 & \rightarrow \text{Cu}^{2+} + \text{O}_2^{2-} \quad \text{(Reaction 3)}
\end{align*}
\]

![Figure 5. Effect of pH on MB reduction.](image-url)
(\[\text{MB}\]_0: 20 mg/L, T: 25 °C, MNs/Cu dose: 0.05 mg, contact time: 45 min, 20mL \text{H}_2\text{O}_2 \text{30\%})

Figure 6. Mechanism MB reduction via Fenton-like reaction of MNs/Cu catalyst.

Figure 7. Surface charge of MNs and MNs/Cu nanoparticles as a function of initial pH. Contact time has a significant effect on the MB removal process. In this work, the reaction time varied from 30 to 120 min and the results are presented in figure 8. The MB reduction raised from 88.6% to
96.9% as contact time increased from 30 min to 120 min. From the figure, it is observed that the MB reduction efficiency was directly proportional to contact time. However, at the reaction time range of 75 to 120 min, the efficiency of reduction indicated a negligible change due to the fact that the Fenton-like reaction nearly reached equilibrium [16]. Therefore, the contact time of 75 min was chosen as the optimum condition of MB reduction for further experiments.

Figure 8. Effect of contact time on MB reduction.
([MB]₀: 20 mg/L, T: 25 °C, MNs/Cu dose: 0.05 mg, pH: 4.0, 20 mL H₂O₂ 30%)

Adsorption kinetics are utilized as a critical set of parameters in the use of adsorption procedures to water treatment in order to estimate the MB reduction speed from an aqueous solution. Because it is usual to use formal kinetic equations to calculate rate constants, the kinetic parameters are difficult to determine due to the complexity of the adsorption process. Popular kinetic models including pseudo-first-order and pseudo-second-order were applied in this work and the results were presented in Table 1.

The reaction kinetics can be easily observed from the time-dependent efficiency. As can be seen from Table 1, the correlation coefficient \( R^2 \) of pseudo first-order reaction is relatively low \( R^2 = 0.8934 \) and \( q_e \) of 58.79 mg/g was greatly different to the experimental value. Hence, the MB reduction reaction using the MNs/Cu catalyst was not fitted to pseudo-first order model. In the meantime, the reduction reaction of MB was in good agreement to the pseudo second order model with the \( R^2 \) value of 0.9997 and \( q_e \) of 80.68 mg/g. The slope of the pseudo second-order model is quite low \( (a = 0.0124) \), which means the MNs/Cu catalyst was favorable to the reduction reaction of MB.

As can be seen from figure 9, MNs/Cu dose presented a positive impact on the removal yield of MB. As the catalyst dose increased from 0.02 to 0.1 mg, the removal percentage of MB increased from 88.1% to 97.4%. On the other hand, as the catalyst dose continuously increased from 0.1 to 0.2 mg,
the efficiency decreased from 97.4 to 88.8%. The increase in catalyst dose enhanced the number of active sites on catalyst surface leading to accelerate active oxygen species, namely OH$^\cdot$, O$_2$$^\cdot$$^-$, which were the main species to mineralize MB into CO$_2$ and H$_2$O. However, as the catalyst was significant, these particles was likely to cluster together and stack on top of each other, shielding one another and preventing MB from diffusing and reaching the surface of MNs/Cu [30]. In other words, MB molecules did not disperse or adsorb virtually entirely on the surface of the catalyst, so the reduction of MB partially decreased. The catalyst dose of 0.1 mg MNs/Cu, consequently, was the optimum dose and chosen for the rest experiments.

**Table 1.** Set of parameters of pseudo-first-order and pseudo-second-order reaction.

| Model                  | a     | b     | $q_e$ (mg/g) | $k_1$ (1/min) | $k_2$ (g/mg.min) | $R^2$  |
|------------------------|-------|-------|--------------|---------------|------------------|--------|
| Pseudo-first-order     | -0.0627 | 4.0739 | 58.79        | -0.0627       | -                | 0.8934 |
| Pseudo-second-order    | 0.0124 | 0.0524 | 80.65        | -             | 0.0029           | 0.9997 |

**Figure 9.** Effect of MNs/Cu dose on MB reduction. ([MB]$_0$: 20 mg/L, T: 25 °C, contact time: 75 min, pH: 4.0, 20 mL H$_2$O$_2$ 30%)

Initial concentration of contaminants is usually a symmetrical ratio to contact time and reducing agents; the influence of MB concentration, thus, was conducted and presented in figure 10. The results showed that removal efficiency of MB rose as concentration of MB increased, and peaked at 99.5% at initial concentration of 25 mg/L. The efficiency then decreased to 89.6% as MB concentration increased to 70 mg/L. It is known that the removal of contaminants at low concentration normally needs much more time to finish, owing to the fact that it takes time to these molecules diffuse to surface of catalyst or to meet the reducing agents. Hence, at the identical contact time, the low concentration cannot completely be removed. In other words, the efficiency of low concentration
of the contaminants was usually low compared to the higher ones. Nevertheless, at high concentration of MB, the degradation process needs more contact time at the same MNs/Cu dose or more catalyst dose at the identical contact time to complete the reduction reaction. Another reason is that these molecules massively adhered to the surface of MNs/Cu, so the catalyst could not contact H₂O₂ well to generate more active oxygen species, reducing treatment efficiency [30]. Consequently, the optimum concentration of MB reduction with MNs/Cu dose of 0.1 mg, temperature of 25 °C, contact time of 75 min, pH 4.0, and 20 mL H₂O₂ 30% was 25 mg/L.

![Figure 10. Effect of MB concentration on the reduction.](image)

(MNs/Cu dose: 0.1 mg, T: 25 °C, contact time: 75 min, pH: 4.0, 20 mL H₂O₂ 30%)

4. Conclusion
This study synthesized a Fenton-like catalyst of Fe₃O₄/Cu and degraded MB effectively. The MNs/Cu was synthesized in nano sizes with spherical and elliptical shapes. The catalyst activity presented a positive impact at acidic pH and became less at alkaline condition. The efficient reduction was observed at contact time of 75 min and kept almost unchanged until 120 min, while increase in MNs/Cu dose made a decrease in reduction yield of MB. Effect of initial concentration of MB on the removal efficiency presented a similar tendency as that of the catalyst dose. Finally, MNs/Cu dose of 0.1 mg, temperature of 25 °C, contact time of 75 min, pH 4.0, 20 mL H₂O₂ 30%, and initial MB concentration of 25 mg/L were the optimum conditions to reduce MB with the efficiency of 99.5%.

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