Eco-friendly synthesis of nano copper and its use in fenton-like reactions for methylene blue degradation

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Received: 20 April 2020; Revised: 16 May 2020; Accepted: 20 May 2020

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Citation: Demirci Gültekin, D.; Alaylı, A.; Nadaroğlu, H. Int. J. Chem. Technol. 2020, 4 (1), 71-78.

ABSTRACT

Copper oxide nanoparticles (CuO NPs) were produced using green synthesis method with Cimin grape extract (Vitis vinifera cv.). The produced CuO NPs were used to remove methylene blue (MB) from water by degradation with Fenton-like reactions. The surface properties of the CuO NPs were determined by FT-IR, SEM and XRD techniques. Experimental parameters for MB removal were selected as: pH: 3 – 11; Temp: 20 - 80°C; initial MB concentration (15 - 50 mg ml⁻¹), and CuO NPs concentrations (25 - 800 mg ml⁻¹). The best reaction conditions were found to be pH: 7 - 11, temperature: 40 - 45°C, interaction time: 120 min, initial MB concentration: 3.125 mg ml⁻¹ and CuO NPs concentration: 25 mg ml⁻¹. Under these conditions, CuO NPs showed a 97.80% efficacy for the removal of MB from wastewater with Fenton-like process. Moreover, this study showed that reagents were reusable, inexpensive, biocompatible, easy to prepare, harmless (CuO NPs, H₂O₂), and Fenton-like reaction conditions were created.

Keywords: Copper oxide nanoparticles, fenton-like, methylene blue, degradation, removal.

I. INTRODUCTION

Methylene blue (MB) is a cationic dye. It consists of dark green powder crystals and is odorless. MB is a stain material widely used in the textile industry due to its adsorbable feature. MB is frequently used in paper, hair and cotton fabric dyeing. MB is a substance with a molecular mass of 319.86 g mol⁻¹ and its formula is C₁₆H₁₃ClN₃S·H₂O. Its structure and some general characteristics are shown in Table 1.¹

It has various harmful effects. In case of inhalation, it...
may cause difficulty in breathing in short periods. It creates a flammable sensation in the mouth, and also may cause nausea, stomach, vomiting, gastritis, cyanosis, jaundice, quadriplegia, human cell necrosis and an increment in heart beats.

Table 1. General characteristics of MB dye

| Synonyms                  | Blue N, methylene blue, Swiss chromosmon methylene blue, methylene blue N, methylthionine chloride, methylthioninium chloride, Swiss blue, urole blue |
|---------------------------|-----------------------------------------------------------------------------------------------------------------------------|
| Molecular formula         | C₁₆H₁₄ClN₃S                                                                                                                   |
| Molecular weight          | 319.851 g/mol                                                                                                                 |
| Safety and Hazard         | - Damaging if swallowed serious toxicity, - Bases skin irritation, - Effects severe eye irritation, - Might reason breathing irritation, - Reasons injury to tissues through lengthy or recurrent contact |

As a result, great attention has been paid to the development of water cleaning methods that will completely remove the dye molecules. Due to the high oxidative power of the hydroxyl radical, a large number of processes based on this type of removal have been called oxidation processes. Oxidation processes have shown moderate processes in reducing organic and inorganic pollutants in water or wastewater. Hydrogen peroxide (H₂O₂), ultraviolet (UV) light, or combined both are among the most commonly used oxidation processes. The heterogeneous photocatalytic oxidation combined with Fenton (H₂O₂) and photo-Fenton (H₂O₂/UV) are also effective oxidation processes.¹⁹⁻²⁴ The removal of organic pollutants and dyes that cannot be biodegradable can be removed successfully with Fenton reactions.²⁵ In recent years, Fenton and Fenton-like reactions have attracted great attention. In various Fenton reactions, the iron species attach to the surface of the catalysts in a suitable aqueous medium, and the redox reactions between Fe (II)/(III) occur in the presence of hydrogen peroxide, which enables the formation of reactive mechanisms such as (•OH) and hydroperoxyl (•OOH) radicals.²⁶⁻²⁸ In Fenton-like reactions, the metal ions that resemble iron and hydrogen peroxide are separated. The metal ions play an important role in a series of consecutive chemical and biological events. Many applications of Fenton chemistry are used in wastewater management. Iron or iron-like copper ions also separate hydrogen peroxide in the Fenton reaction. Therefore, such recreations have technical and biological importance. However, the optimization of this reaction is difficult. Copper
concentration, ligand and/or organic substrate formation, pH of the solution and buffer composition significantly affect the dissociation kinetics and mechanism of hydrogen peroxide.\(^{29}\)

Current research aims to develop an innovative method for the removal of MB in solution medium. Therefore, green CuO NPs was produced using Vitis vinifera L. The produced CuO NPs were used for the removal of MB by degradation. The effects of CuO NPs concentration, pH, contact time, temperature on the degradation were investigated.

2. MATERIALS AND METHODS

2.1. Chemicals and reagents

CuCl\(_2\)·2H\(_2\)O, Na\(_2\)HPO\(_4\), CH\(_3\)COONa, methylene blue (MB) and hydrogen peroxide (H\(_2\)O\(_2\)) (w/w, 30 \%) were provided from Sigma-Aldrich. All of the compounds were used without further purification, as they are of analytical purity.

2.2. Preparation of methylene blue and H\(_2\)O\(_2\) solutions

1000 mg l\(^{-1}\) standard solution of MB was first prepared. Then, the solutions with lower concentration were prepared from this standard solution using distilled water. A 10.0\% H\(_2\)O\(_2\) solution (v/v) was prepared from a standard 30.0 \% H\(_2\)O\(_2\) solution with distilled water.

2.3. Preparation of CuO NPs

The production of gold nanoparticles using cinin grape extracts has been reported previously.\(^{30}\) In this work, the cinin grape extracts was prepared by mixing 60.0 g l\(^{-1}\) cinin grape with distilled water. Subsequently settle down for 1.0 h, the extract was vacuum-filtered. Individually, a solution of 0.10 M CuCl\(_2\)·2H\(_2\)O was prepared by addition 19.9 g of solid CuCl\(_2\)·2H\(_2\)O in 1.0 l of deionized water. As a result, 0.10 CuCl\(_2\)·2H\(_2\)O solution was added to the grape extract of 60.0 g l\(^{-1}\) cinin in a 2:3 volume ratio. Subsequently, when the pH of the medium was adjusted to 6.0, the formation of dark blue mullet showed the formation of CuO NPs. Then, the copper nanoparticles were washed with pure water and alcohol and then dried in an oven for 24 hours.

2.4. Characterization of CuO NPs surface

The chemical structure of CuO NPs was analyzed by scanning electron microscopy (SEM) and other spectral studies. A scanning electron microscope (SEM; Metek, Apollo prime, Active field 10 mm\(^2\), Microscope examination S50, SE detector R580) was used to examine the surface of the metal material covered with metal, which magnifies 5000 times. SEM analysis is done by coating the sample surfaces with a thin layer of gold (20 nm) to obtain a conductive surface and prevent electrostatic charge throughout the investigation. Energy dispersive EDX analysis was used to determine the chemical composition of the synthesized CuO NPs. Fourier Transform Infrared (FT-IR) analysis was used for the analysis of functional groups in the structure. The FT-IR spectrum was recorded in the range of 4000 - 400 cm\(^{-1}\) wavelength by a Mattson 1000 FT-IR. The XRD pattern of CuO NPs was analyzed using XRD (Rigaku D-Max 2000 and CuK\(_\alpha\) (\(\lambda = 0.154 \) nm) with 20, 5\(^0\) - 100\(^0\)) radiation.

2.5. Degradation study

All the degradation experiments were performed in a 50 ml bottle having 50 mg l\(^{-1}\) MB and 0.1 g CuO NPs with 5 ml distilled water in temperature controlled shaking water bath under atmospheric pressure at 25\(^\circ\)C. The desired pH values were adjusted using 0.1 M NaOH or 0.1 M HCl. The degradation reaction was started by adding 3\% H\(_2\)O\(_2\) solution (w/v) to the previously prepared medium. The reaction medium was placed on a shaker (300 rpm) at room temperature. The reaction mixture samples were centrifuged at 6000 x g for 15 min. Samples were taken from the reaction medium at regular intervals using a micropipette. The supernatant was was passed through a filter. The concentration of MB was determined spectrometrically. The UV–Vis absorbance was measured at \(\lambda_{\text{max}} = 660 \) nm for MB by a spectrophotometer. The final concentrations were obtained using the standardization curves. In addition, similar blank tests were performed with H\(_2\)O\(_2\) solution under only equal conditions and the ability of H\(_2\)O\(_2\) alone to degrade without CuO NPs was measured. Percentage values of MB removed by degradation were calculated from Eq. (1).

\[
\% \text{ MB removal} = \frac{c_i - c_e}{c_i} \times 100
\]  

(1)

Where \(c_i\) is initial concentrations of dye (mg l\(^{-1}\)), \(c_e\) is final (equilibrium) concentrations of dye (mg l\(^{-1}\)).

2.6. Effects of contact time, pH, temperature, H\(_2\)O\(_2\) and adsorbent concentrations

The influence of the amount of CuO NPs was studied by changing metal amount between 0.0125 - 0.20 mg/50 ml, and also the experimental conditions were between pH: 3 - 11, T: 20 - 80\(^\circ\)C, and MB concentration: 3.25 - 50 mg l\(^{-1}\). It is detected that MB degradation increases at first 20 min of interaction with CuO NPs. Essentially, MB degradation is fast at the beginning but it regularly decreases with time until it reaches the equilibrium.

DOI: http://dx.doi.org/10.32571/ijct.724056

E-ISSN:2602-277X
This shows that the concentration of MB in the solution is reduced quickly in 20 min and was nearly finished at 120 min of interaction time.

2.7. Statistical analysis

All of the experiments were repeated three times. Statistics were shown as mean ± standard error. Statistical analysis were achieved by SPSS version 10.0 software (SPSS Inc., Chicago, IL, USA), and the important action changes were founded with a 95% confidence (P ≤0.05) by Tukey’s test.

3. RESULTS AND DISCUSSIONS

3.1. SEM study

The SEM analysis is important to determine the surface structure of CuO NPs. The SEM image of CuO NPs produced with means of grape fruit water extract concentrations with 0.1 M CuCl₂·2H₂O at room temperature is shown in Figure 1.

As seen from Figure 1, the shape of the nanoparticles is spherical on the accumulated extract concentration. CuO NPs have been determined to have a particle size ranging from about 35 nm to 50 nm.

EDX spectrum on the elemental configuration of the CuO NPs is shown in Figure 2. From the EDX results, it is seen that there are present 35.10% Cu and 15.40% O in CuO NPs nanoparticle structure.

3.2. XRD analysis

The stage configuration of crystal buildings of the formed products, taken from dark blue suspensions of CuO NPs, was explored by XRD. The XRD spectrum of CuO NPs is shown in Figure 3.

As seen from Figure 3, XRD peaks obtained for dark blue compound found after two weeks of the synthesis are indexed to CuO with characteristic diffraction indices (111), (200), (220) and (311) at 2 theta value of 32º, 39.8º, 61.6º and 75.3º respectively.

3.3. FT-IR analysis

Fourier transform infrared (FT-IR) spectroscopy was used to describe the functional groups of the synthesized CuO NPs. The FT-IR spectrum of CuO NPs is presented in Figure 4. From Figure 4, the characteristics peaks were observed at 612, 1056, 1111, 1309 and 1669 cm⁻¹. The weak peak at 631 cm⁻¹ indicates Cu–O vibration in CuO NPs.
3.4. Degradation studies

The degradation of MB by CuO NPs was investigated under conditions changed such as pH (3 - 11), temperature (20 - 80°C), initial MB concentration (15 - 50 mg l⁻¹), and nanoparticles concentration (25 - 800 mg ml⁻¹). Dye degradation was determined by a UV-Vis spectrophotometer. Absorption spectrum of MB is shown in Figure 5. As seen from this spectrum, MB has maximum peak at 660 nm.

Figure 5. Absorption spectrum of MB (Initial dye concentration: 25 mg l⁻¹, pH: 10, Temperature: 40 °C).

Figure 6 shows the effect of contact time on MB degradation by CuO NPs. As seen this figure, the percent degradation of MB increases with increasing contact time. It is seen that maximum dye degradation occurs at 120 min. Therefore, this time has been accepted an equilibrium time.

Figure 6. Effect of contact time on MB degradation by CuO NPs (Initial dye concentration: 25 mg l⁻¹, Temperature: 40 °C, pH: 10, CuO NPs concentration: 25 mg ml⁻¹).

Figure 7 shows the effect of pH on MB degradation by CuO NPs. pH value of solution has a significant effect in the fenton-like reaction because it affects both the solubility of MB and the degree of ionization of CuO NPs. As seen from Figure 7, it is determined that MB degradation significantly increases with increasing pH of the solution. Generally, fenton reactions are more effective at low pH, but our research has shown that pH values higher than 6 are more suitable for dye removal.

Figure 7. Effect of pH on MB degradation by CuO NPs (Initial dye concentration: 25 mg l⁻¹, Temperature: 40°C, CuO NPs concentration: 25 mg ml⁻¹).

Figure 8 illustrates the effect of temperature on MB degradation by CuO NPs. From this figure, it is seen that the percent degradation of MB increase similarly with increasing temperature. It is found that the maximum percent degradation of MB occurs at 40 - 45°C.

Figure 8. Effect of temperature on MB degradation by CuO NPs (Initial dye concentration: 25 mg l⁻¹, Temperature: 40°C, CuO NPs concentration: 25 mg ml⁻¹).
The degradation efficacy of MB with fenton-like process is found to be more advantageous for industrial discharge at more temperatures.

Figure 8. Effect of temperature on MB degradation by CuO NPs (Initial dye concentration: 25 mg l\(^{-1}\), pH: 10, CuO NPs concentration: 25 mg ml\(^{-1}\)).

Figure 9 shows the effect of CuO NPs concentration on MB degradation. As seen from this figure, MB degradation increases with increasing CuO NPs concentration. It is seen that the maximum percent degradation occurs at 0.4 mg l\(^{-1}\) CuO NPs concentration.

Figure 10 demonstrates the percent degradation of MB for various initial MB concentration. As seen from Figure 10, the maximum degradation of 97.80% is obtained for initial MB concentration of 3.125 mg ml\(^{-1}\).

Figure 11 illustrates the effect of H\(_2\)O\(_2\) concentration on MB degradation. As seen from Figure 11, the percent degradation of MB significantly increases with increasing H\(_2\)O\(_2\) concentration. It is seen that the maximum percent degradation occurs for 0.8 \(\mu\)g ml\(^{-1}\) H\(_2\)O\(_2\).

4. CONCLUSION

Metal nanoparticles are widely used commercially to remove dyes in many areas. In this research, firstly, copper nanoparticles (CuO NPs) were manufactured using green synthesis technique. For this aim, Cimin grape seeds water extract was employed as green synthesis intermediate. The synthesized CuO NPs were analyzed by means of different spectroscopy techniques (UV-Vis spectrophotometer, SEM, EDX, XRD and FT-IR). Then CuO NPs were used in the Fenton-like reaction, to eliminate the methylene blue dye from water. It was determined that green CuO NPs could be easily used in removing of MB by degradation method.
ACKNOWLEDGEMENT

The SEM, EDX, XRD and FTIR analyses were performed in the DAYTAM (East Anatolia High Technology Application and Research Centre) in Ataturk University.

Conflict of interests

Authors declare that there is no a conflict of interest with any person, institute, company, etc.

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