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Research Article

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

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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 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, H_2O_2), and Fenton-like reaction conditions were created.

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

Nano bakırın çevre dostu sentezi ve metilen mavisinin bozunması için fenton benzeri reaksiyonlarda kullanımı

ÖZ

Bakır oksit nanopartiküller (CuO NP'ler), Cimin üzüm ekstresi (*Vitis vinifera cv.*) ile yeşil sentez metodu kullanılarak üretildi. Üretilen CuO NP'ler, Fenton benzeri reaksiyonlarla metilen mavisinin (MB) degradasyonla sudan uzaklaştırılması için kullanıldı. CuO NP'lerin yüzey özelikleri FT-IR, SEM ve XRD teknikleri ile belirlendi. MB uzaklaştırılması için deneysel parametreler pH: 3 - 11, sıcaklık: 20 - 80°C, başlangıç MB konsantrasyonu (15 - 50 mg ml^{-1}) ve CuO NP'lerin konsantrasyonu (25 - 800 mg ml^{-1}) olarak seçildi. En iyi reaksiyon şartlarının pH: 7-11, sıcaklık: 40 - 45°C, etkileşim süresi: 120 dak., başlangıç MB konsantrasyonu: 3,125 mg ml^{-1} ve CuO NP'lerin konsantrasyonu: 25 mg ml^{-1} olduğu bulundu. Bu koşullar altında CuO NP'ler, Fenton benzeri işlemle atık sudan MB'nin ortadan kaldırılması için% 97,80'lik bir etkinlik gösterdi. Ayrıca bu çalışma, reaktiflerin tekrar kullanılabilir, ucuz, biyouyumlu, kolay hazırlanabilir, zararsız (CuO NPs, H_2O_2) ve Fenton benzeri reaksiyon şartlarının oluşturulduğunu göstermiştir.

Anahtar Kelimeler: Bakır oksit nanopartiküller, Fenton benzeri, metilen mavisi, bozulma, uzaklaştırma.

1. 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 $C_{16}H_{18}ClN_3S.H_2O$. Its structure and some general characteristics are shown in Table 1.[1]

It has various harmful effects. In case of inhalation, it

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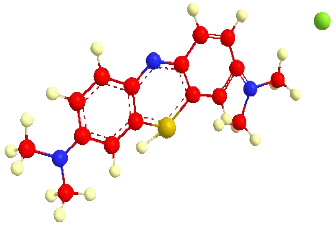
may cause difficulty in breathing in short periods. It creates a flammable sensation in the mouth, and also may cause nausea, stomach, vomiting, gastritis, cyanosis, jaundice, quadriplegia, human cell necrosis and an increment in heart beats.

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, urolene blue
Molecular formula	$C_{16}H_{18}ClN_3S$
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
3D conformer	

On the other hand, some information about *Vitis vinifera L.* used in this study where green nanoparticle production is aimed is given. *Vitis vinifera* L. (common grape) belonging to Vitaceae family has been presented for their therapeutic and dietary worth for thousands of years. Egyptians had consumed grapes for more than 6,000 years in the past, and the first Greek philosophers had praised the medicinal strength of grapes. Phenolic compounds present in nearly all parts of grape are increasingly believed to exhibit antioxidants and antimicrobial efficiency. Grape leaves contain many compounds such as polyphenols, anthocyanins, flavonoids and organic acids (malic, fumaric, oxalic, tartaric, citric and succinic acid).[2,3]

Metal nanoparticles have been considered widely since of their exclusive physicochemical features with optical, electronic, magnetic properties, and catalytic and antimicrobial activities.[4-6] Today, many synthesis methods are being investigated due to these properties of nanoparticles.[7] In general, metal nanoparticles are produced by some chemical means, such as chemical reduction[8] and photochemical reactions[9], and recently by green chemistry.

Usage of fungi, bacteria and plant extracts[10-11] for the green chemistry which offers benefits to chemical and physical techniques is more economical and ecological. Roy and co-workers have defined the Green synthesis of silver nanoparticles using fruit extract of grapes, and also their antibacterial activity.[12]

Disposed dyes create a real danger to health and ecosystems and cause cancer formation. Nowadays, removal of dyes in wastewater by degradation is extremely important and create a striking work due to their dangerous effects.[13,14] In sectors such as fabric production, water containing large amounts of waste dye used for coloring is discharged into the sewage system without being cleaned. Since they are structurally aromatic and complex, it is difficult to remove such dyes by microbial, chemical and biological methods.[15-16] It is not possible to maintain a biological and biodegradation based wastewater management against azo dyes, which are widely used in numerous productions of artificial dyes and is one of the main classes with its wide variety of colors. Widespread wastewater management by chemical and physical methods (adsorption, chemical conversion, firing, photo catalyst or ozonation) used to remove dyes is effective but relatively expensive.[17,18]

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 (H_2O_2), ultraviolet (UV) light, or combined both are amoung the most commonly used oxidation processes. The heterogeneous photocatalytic oxidation combined with Fenton (H_2O_2) and photo-Fenton (H_2O_2/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

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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 inexpensive 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

$CuCl_2.2H_2O$, Na_2HPO_4, CH_3COONa, methylene blue (MB) and hydrogen peroxide (H_2O_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_2O_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_2O_2 solution (v/v) was prepared from a standard 30.0 % H_2O_2 solution with distilled water.

2.3. Preparation of CuO NPs

The production of gold nanoparticles using cimin grape extracts has been reported previously.[30] In this work, the cimin grape extracts was prepared by mixing 60.0 g l^{-1} cimin grape with distilled water. Subsequently settle down for 1.0 h, the extract was vacuum-filtered. Individually, a solution of 0.10 M $CuCl_2{\cdot}2H_2O$ was prepared by addition 19.9 g of solid $CuCl_2{\cdot}2H_2O$ in 1.0 l of deionized water. As a result, 0.10 $CuCl_2{\cdot}2H_2O$ solution was added to the grape extract of 60.0 g 1^{-1} cimin 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 CuKα ($\lambda = 0.154$ nm) with 2θ, 5° - 100°) 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°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_2O_2 solution (w/w) 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 λ_{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_2O_2 solution under only equal conditions and the ability of H_2O_2 alone to degrade without CuO NPs was measured. Percentage values of MB removed by degradation were calculated from Eq. (1).

$$\% \text{ MB removal} = \frac{Ci - Ce}{Ci} \; x \; 100 \qquad (1)$$

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_2O_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°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.

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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 $CuCl_2.2H_2O$ at room temperature is shown in Figure 1.

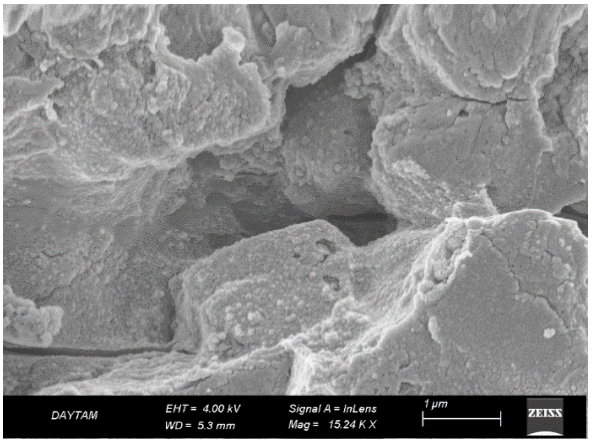


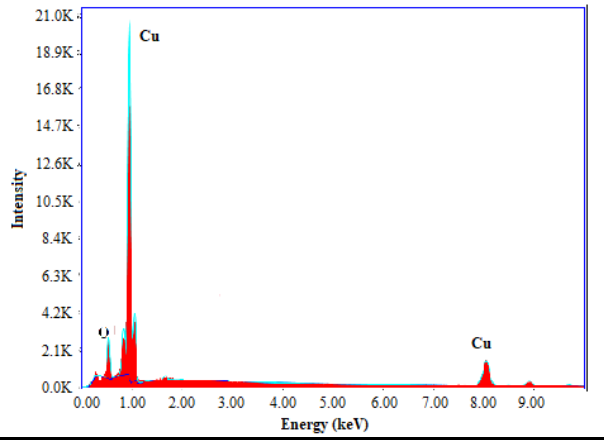
Figure 1. SEM image of CuO NPs.

As seen from Figure 1, the shape of the nanoparticles is spherical on the accumulated extract concentration.[31-33] 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 nanoparticular 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.[34] The XRD spectrum of CuO NPs is shown in Fgure 3.



Element	Weight %	Atomic %
O K	6.2	15.4
Na K	18.2	31.8
Au M	5.1	1
Cl K	14.7	16.7
Cu K	55.7	35.1

Figure 2. EDX spectrum of CuO NPs.

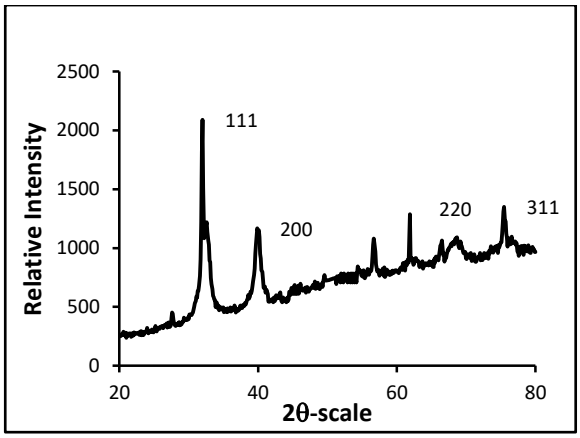


Figure 3. XRD spectrum of CuO NPs.

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 631cm^{-1} indicates Cu–O vibration in CuO NPs.[35]

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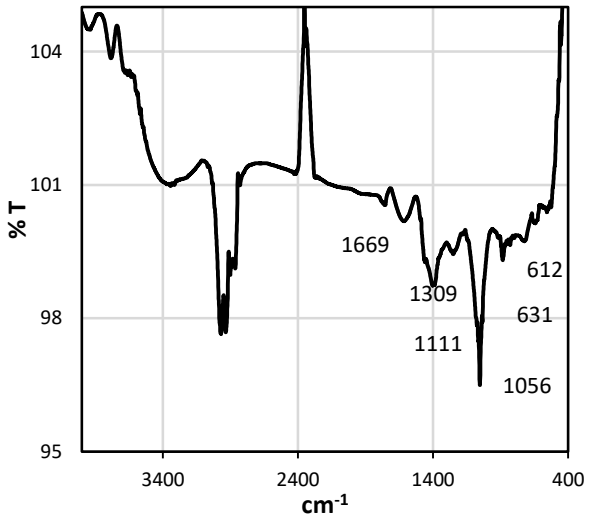

Figure 4. FT-IR spectrum of CuO NPs.

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.

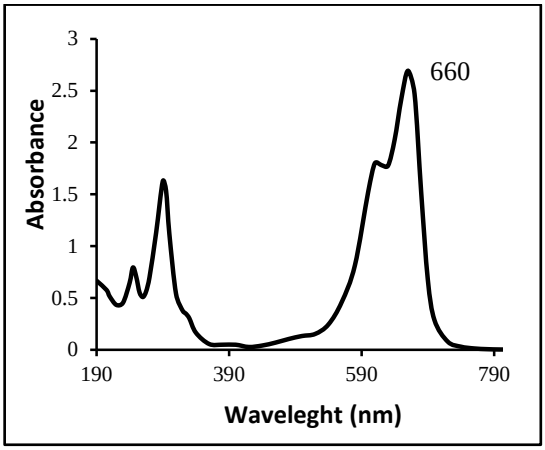

Figure 5. Absorption spectrum of MB (Initial dye concentration: 25 mg l^{-1}, pH: 10, Temperature: 40 °C).

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.

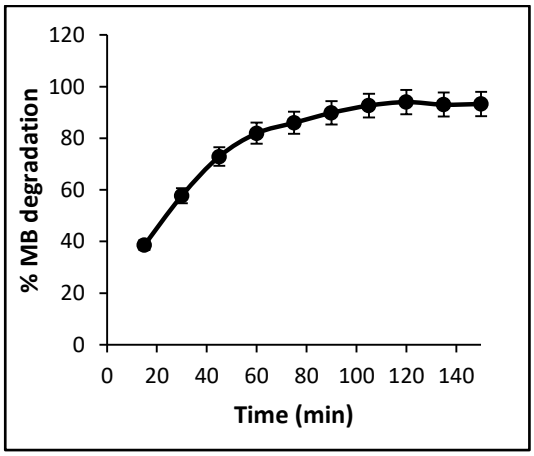

Figure 6. Effect of contact time on MB degradation by CuO NPs (Initial dye concentration: 25 mg l^{-1}, Temperature: 40 °C, pH: 10, CuO NPs concdentration: 25 mg l^{-1}).

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.[36-40]

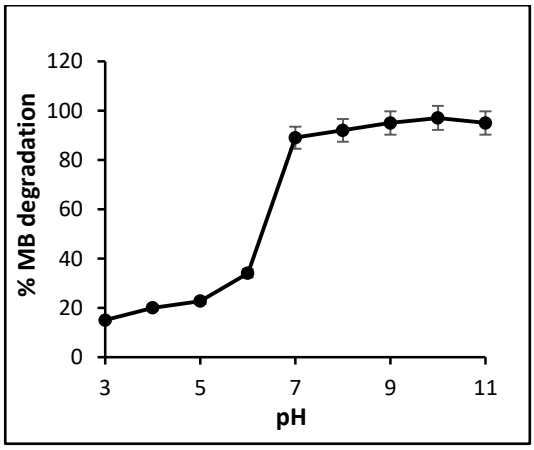

Figure 7. Effect of pH on MB degradation by CuO NPs (Initial dye concentration: 25 mg l^{-1}, Temperature: 40°C, CuO NPs concentration: 25 mg ml^{-1}).

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 withincreasing temperature. It is found that the maximum percent degradation of MB occurrs at 40 - 45°C.

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The degradation efficacy of MB with fenton-like process is found to be more advantageous for industrial discharge at more temperatures.

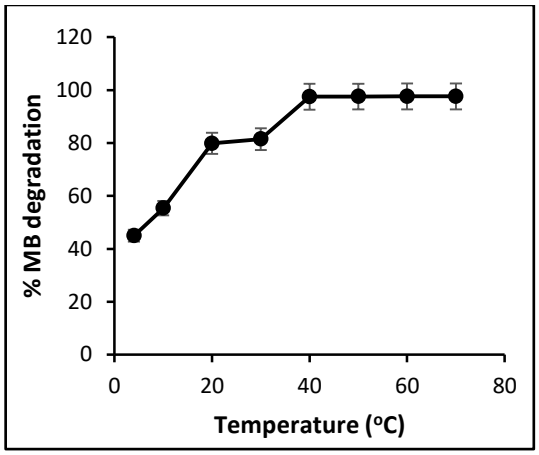

Figure 8. Effect of temperature on MB degradation by CuO NPs (Initial dye concentration: 25 mg l^{-1}, pH: 10, CuO NPs concentration: 25 mg ml^{-1}).

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 percet 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_2O_2 concentration on MB degradation. As seen from Figure 11, the percent degradation of MB significantly increases with increasing H_2O_2 concentration. It is seen that the maximum percent degradation occurs for 0.8 µg ml^{-1} H_2O_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.

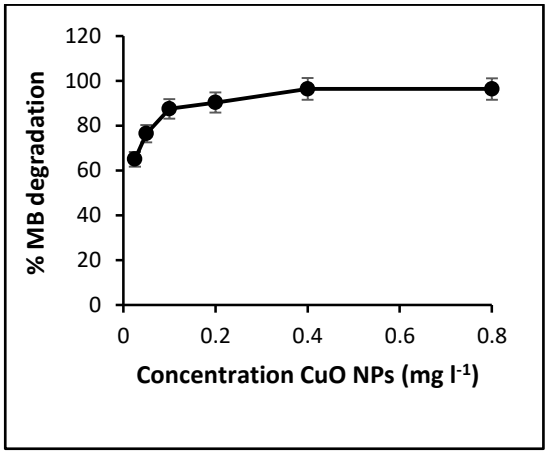

Figure 9. Effect of CuO NPs concentration on MB degradation (Initial dye concentration: 25 mg l^{-1}, pH: 10, Temperature: 40°C).

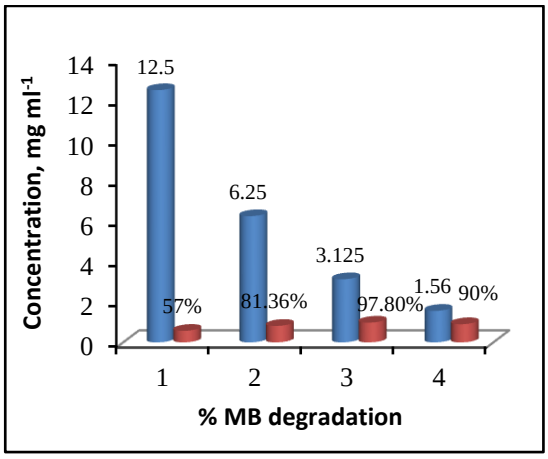

Figure 10. Percent of MB degradation (Blue: Initial dye concentration, Red: Percent of dye removal) (Temperature: 40 °C, pH: 10, CuO NPs concentration: 25 mg ml^{-1}).

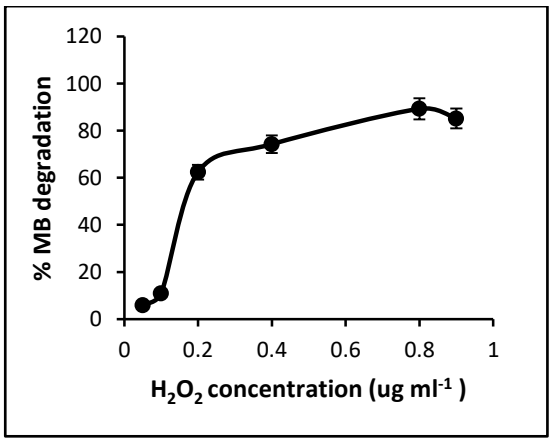

Figure 11. Effect of H_2O_2 concentration on MB degradation (Initial dye concentration: 25 mg l^{-1}, Temperature: 40°C, pH: 10, CuO NPs concentration: 25 mg ml^{-1}).

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Conflict of interests

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

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