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Green Synthesis of CuO Nanoparticles Using *Tragopogon porrifolius* and Their Antioxidant and Photocatalytic Applications

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ABSTRACT

Copper oxide nanoparticles (CuO NPs) were produced by green synthesis method which is a cheap, easy and effective method using Tragopogon porrifolius extract. The shape, bond and crystal structure of the nanoparticles were determined by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), energy dispersive X-ray (EDX) and X-ray diffractometer (XRD) analysis methods. SEM analysis showed that the particles were spherical and EDX analysis showed the elemental composition of Cu and O as Cu 58.17 % and O 32.73 %. Cu-O bond structure was identified in FTIR analysis. In XRD analysis, peaks defining CuO NPs were observed. The antioxidant and photocatalytic activity of the synthesized CuO NPs were investigated. Antioxidant capacities were examined in the range of 50-500 µg/mL. The free radical scavenging activity of the nanoparticles was determined as 70.75 % at a concentration of 500 µg/mL. In photocatalytic studies, Reactive Red 120 (RR 120) dye degradation was investigated. The degradation time was calculated as 76 % in 30 min.

Keywords: Copper oxide nanoparticles, Tragopogon porrifolius, Biogenic synthesis, Antioxidant, Photocatalytic.

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Introduction

One of the most significant areas of study in material science is nanotechnology. As significant research is done, this sector of science and engineering is noted for its quick growth [1]. The fact that it takes place in most of human life in daily life has made it one of the leading research areas of our age [2]. Nanotechnology produces and studies materials in the range of 1-100 nm, either by increasing the size of atoms/molecules to nano-size (bottom-up methods) or by size reduction of macroscopic materials (top-down methods) [3]. Among nanostructured materials, nanoparticles provide the link between macroscopic materials and atomic structures. While macroscopic materials show constant properties independent of their size and mass, the properties of nanoparticles depend on their size [4]. Due to their thermal characteristics, surface areas, particle sizes, and electrical conductivity, nanomaterials play a significant role in many different fields [5].There is an increasing interest in the production of nanomaterials, which have many applications in industry such as biomedical [6], pharmaceutical [7], cosmetic [8], food [9] and catalyst [10].

Most of the methods applied for nanoparticle synthesis are physical and chemical methods. Most of these methods are expensive and often require the use of toxic solvents. This is potentially dangerous for the environment and living organisms. These negative effects in the synthesis of nanoparticles have led researchers to use environmentally friendly methods. For this purpose, a green synthesis method has emerged that aims to produce nanoparticles that are economical, easily applicable and of high purity. In comparison to chemical and physical synthesis methods, biosynthesis of nanoparticles utilizing bio-green technologies has a lot of advantages in terms of effectiveness, cleanliness, simplicity, non-toxicity, low cost, and sustainability [11]. Environmentally safe fungi [12], bacteria [13] and plants [14] are used as reductants in green synthesis to produce nanoparticles. Synthesis using microorganisms is slower, more expensive and more complex than synthesis using plant extracts. Furthermore, aseptic conditions are required during the process and the waste products that can be generated are hazardous to the environment.

Recently, studies on CuO NPs are available in the literature due to their widespread applications in different scientific fields. The use of CuO NPs in many application areas has increased due to their cheap and abundant compared to gold and silver metals [15]. CuO NPs have been used in the production of optical[16], electronic [17], catalytic [1], medical [18], dental [19], nanofluid [20], antibacterial [18] and antioxidant [21] agents.

In this study, CuO NPs were synthesized by green synthesis method. In the biosynthesis of nanoparticles, Tragopogon porrifolius plant extract, which is consumed raw or cooked as food, was used as a reductant. As far as we know, this plant has not been used in particle synthesis before. The structure and morphology of the particles were determined by characterization analysis. The antioxidant activity of the synthesized CuO NPs and their photocatalytic activity for the azo class toxic Reactive Red 120 dye were investigated.

Materials and Methods

Materials

"Tragopogon porrifolius" plant was collected from Sivas Cumhuriyet University campus. $CuSO_4.5H_2O$ (Sigma-Aldrich) was used as starting metal and Reactive Red 120 (Sigma-Aldrich, CAS No: 61951-82-4) was used in photocatalytic experiments. pH adjustments were made with concentrated and dilute H_2SO_4 and NaOH.

Preparation of Tragopogon Porrifolius Extract

Tragopogon porrifolius plant was washed to remove dust and impurities and dried until the moisture was completely removed. After drying, 5 g of dry plant was extracted by boiling in 100 ml of water for 15 minutes. The extract cooled to room temperature was filtered with Whatman No. 1 filter paper and stored at + 4 °C for use in metal nanoparticle synthesis.

Determination of Total Phenolic Compounds by Folin-Ciocelteau Method

The total phenolic compounds of the extracts was determined according to the described method using 2 N Folin-Ciocalteu phenol reagent [22]. 2 N 100 µL Folin-Ciocalteu phenol reagent, 100 µL extract, 100 µL standard gallic acid solutions, 2.3 mL distilled water and 1 mL 7 % aqueous sodium carbonate solution were mixed and kept at room temperature for 2 h. Absorbance at 750 nm wavelength was measured in a spectrophotometer. The results are expressed as gallic acid equivalent (GAE).

CuO NPs synthesis

Tragopogon porrifolius extract was used as a reducing agent to produce CuO NPs by green synthesis method. $CuSO_4.5H_2O$ was used to prepare the metal solution. 10 mL of plant extract was added dropwise to 50 mL of 0.2 M $CuSO_4.5H_2O$ solution and stirred in a magnetic stirrer for 2 hours. The pH of the resulting solution was adjusted to 10. After 2 hours of stirring, a color change was observed indicating the formation of CuO NPs and CuO NPs were separated by centrifugation at 10,000 rpm for 15 minutes. The synthesized CuO NPs were dried in an oven at 50°C.

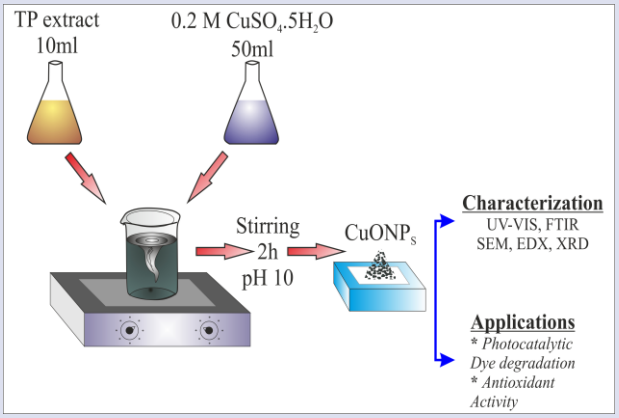


Figure 1. Schematic diagram of the green synthesis of CuO NPs

CuO NPs characterization

Using Tragopogon porrifolius extract as the starting material, CuO NPs were synthesized and then characterized using UV-Vis, FTIR, XRD, SEM and EDX.

FT-IR analysis in the range of 400–4000 cm^{-1} was performed to determine the possible functional groups present in the structure of CuO NPs. The crystal structure of CuO NPs was determined by XRD. SEM analysis was performed for the morphology of the particles and EDX analysis was performed to determine the elemental composition.

Antioxidant Assay

In vitro DPPH radical scavenging assay

Using the method given by Sathiskumar [23] the ability of CuO NPs, an extract of Tragopogon porrifolius, to scavenge free radicals, was evaluated.

Ascorbic acid (as a positive control) and different quantities (50-500 g/mL) of CuONPs, Tragopogon porrifolius extract, and DPPH % solution in ethanol (0.1 mM) were also combined. 30 minutes were given for the mixtures to sit in the dark before the absorbance at 517 nm was determined.

The following equation 1 was used to determine the DPPH% inhibition percentage:

$$\%\text{Inhibition} = \left[(A_{control} - A_{sample}) / A_{control} \right] \times 100 \qquad [1]$$

where A_{sample} is the absorbance of DPPH/ sample solution and $A_{control}$ is the absorbance of DPPH % solution without including the sample.

Photocatalytic Degradation

The photocatalytic activity of CuO NPs produced by green synthesis method was evaluated by analyzing the degradation of Reactive Red 120 dye. Photocatalytic activity experiments were carried out under UV-C (254 nm) lamp in dark environment. The studies were carried out in a reactor with constant stirring speed to ensure homogeneous dispersion of the nanoparticles. The samples obtained from the photocatalytic reactions were analyzed by UV-vis spectroscopy (Shimadzu UV-2600) at λ= 530 nm [24].

The photodegradation efficiency of RR 120 dye was determined using the following equation (Eq. 2):

$$\%\text{Degradation} = \left[\left(C_o - C_t \right) / C_o \right] x100 \qquad [2]$$

where C_o: The initial concentration of the RR 120 dye. C_t: The residual concentration of the RR 120 dye.

Results and Discussion

Determination of Total Phenolic Compound

The total amount of phenolic compounds in Tragopogon porrifolius extract was determined according to Folin-Ciocalteu method. In this method, when a marker is added to the extract, the color of the extract turns blue, indicating the presence of polyphenols in it.

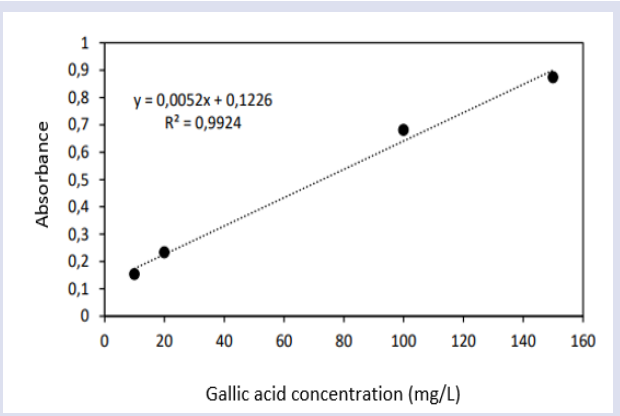


Figure 2. Gallic acid calibration curve

The amount of phenolic compounds in the extract was determined with the help of the standard curve, which is the equivalent of the absorbance value read at 750 nm in terms of gallic acid. With the help of the gallic acid standard curve given in Figure 2 the total amount of phenolic compound in Tragopogon porrifolius was determined as 43.27 mg/L.

UV-Vis Result

UV-Vis spectroscopy is among the analyses used to characterize and validate metal nanoparticles. Since the method is easily applicable, it is used as the first step in the verification of nanoparticle synthesis. UV-Vis absorption spectroscopy of the synthesized CuO NPs was examined in the range of 400-800 nm. UV-Vis absorption spectroscopy of CuO NPs synthesized by green synthesis method using TP extract and extract is given in Figure 3. No peak was observed in the absorption spectroscopy of TP extract. The absorption band of CuO nanoparticles observed at 461 nm confirms the synthesis of CuO NPs. The obtained results show that the UV-Vis absorption results are in agreement with the literature [25].

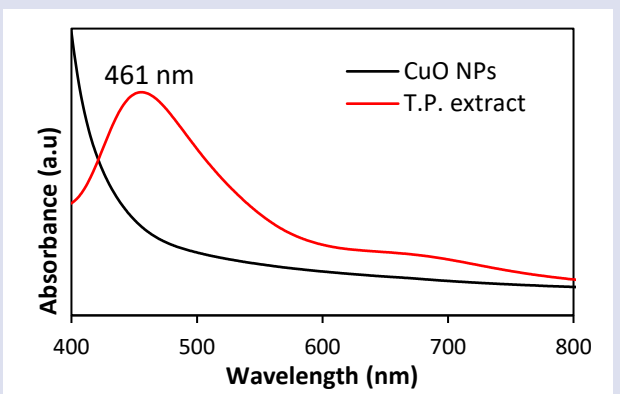


Figure 3. UV-Vis UV-vis spectroscopy absorbance results of TP extract and CuO NPs

The optical energy band gap of CuO NPs synthesized by green synthesis method was determined by Tauc plot obtained by plotting $(\alpha h\nu)^2$ versus hν [26–28] .

$$(\alpha h\nu)^2 = B(h\nu - Eg) \quad [3]$$

α : absorption coefficient
h : Planck's constant
ν : frequency of the photon
Eg : optical enetgy band gap
B : constant

Figure 4 shows the data obtained from the transmittance values and the plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$). The optical band gap of CuO NPs was found to be 2.25 eV.

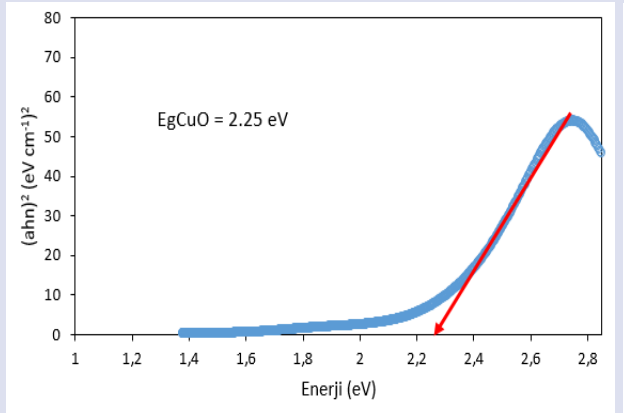


Figure 4. Optical energy band gap of CuO NPs

FTIR Result

FTIR analysis was performed to characterize the chemical composition and bond structure of CuO NPs. FTIR analysis was performed by ATR method in the range of 400-4000 cm^{-1} (Fig. 5).

CuO exhibits a characteristic peak in the IR spectrum between 400 and 600 cm^{-1} [14, 29]. The peaks at 599 cm^{-1} and 424 cm^{-1} observed in the spectrum define the Cu-O bond structure.

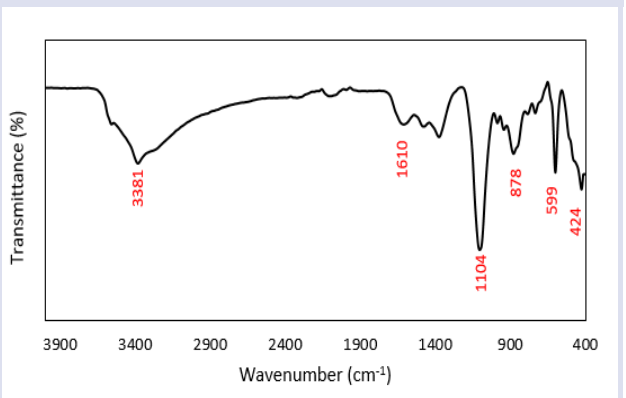


Figure 5. FTIR spectra of CuO NPs

Peaks between 900-700 cm^{-1} define the aromatic bending vibration of the C-H group and the peak observed at 878 cm-1 in the spectrum corresponds to the aromatic bending vibration of the C-H group [30]. The peak observed at 1104 cm^{-1} corresponds to O-H bending of

phenol and alcoholic compounds (alcohols) [31]. The peak observed at 3381 cm^{-1} corresponds to amide N-H stretching and the peak observed at 1628 cm^{-1} corresponds to C=C stretching (alkene) [31].

SEM Result

The morphology of the nanoparticles produced by green synthesis method was analyzed by SEM. SEM images were obtained by "Au coating". Images showing the morphological structure of CuO NPs taken with 100 kx are given in Figure 6. It is clearly seen from the SEM image that the particles are spherical in shape. In many studies investigating the production of CuO NPs by green synthesis, it was determined that CuO NPs synthesized with TP extract yielded similarly shaped spherical particles [32–34]. It is seen that the particle sizes in the measured area vary between 235 nm and 350 nm. With the average of 20 measurements taken, the average particle size in the measured area was calculated as 288 nm.

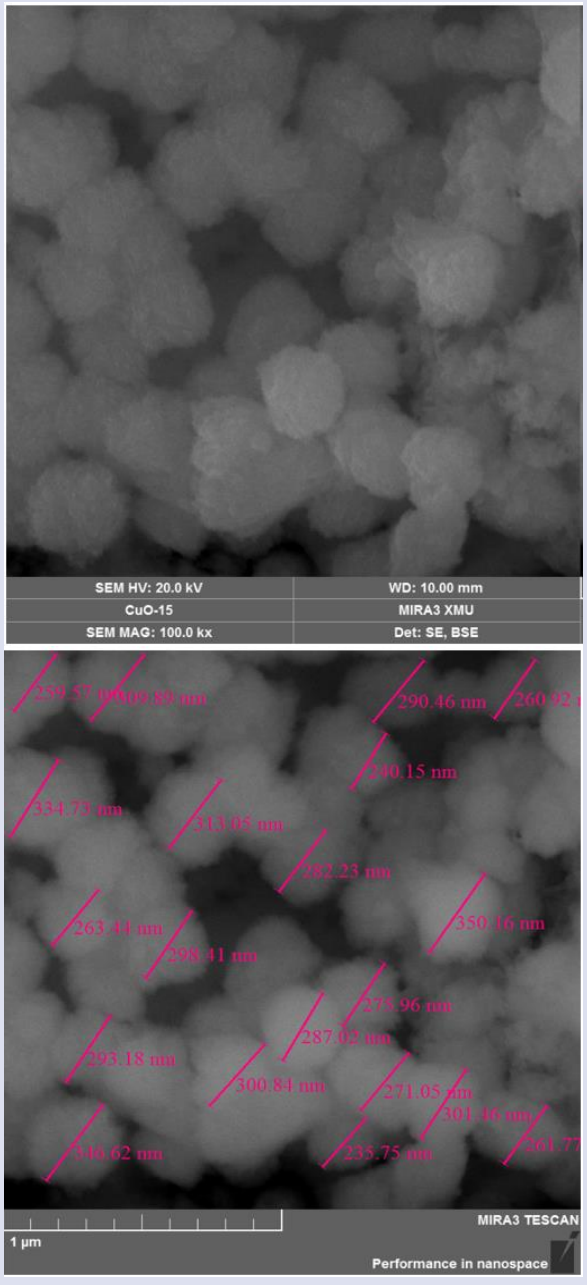


Figure 6. Sem image of CuO NPs

EDX Result

The EDX spectrum of CuO NPs is given in Figure 7. The strong peaks due to Cu and O elements observed in the spectrum prove the CuO structure. Cu and O incorporation ratios were determined as 58.17 % (w.t.) and 32.73 % (w.t.), respectively. There are weak peaks belonging to C and S in the spectrum. C peak is due to the organic compounds in the structure of TP extract and S is due to the metal salt [14, 35].

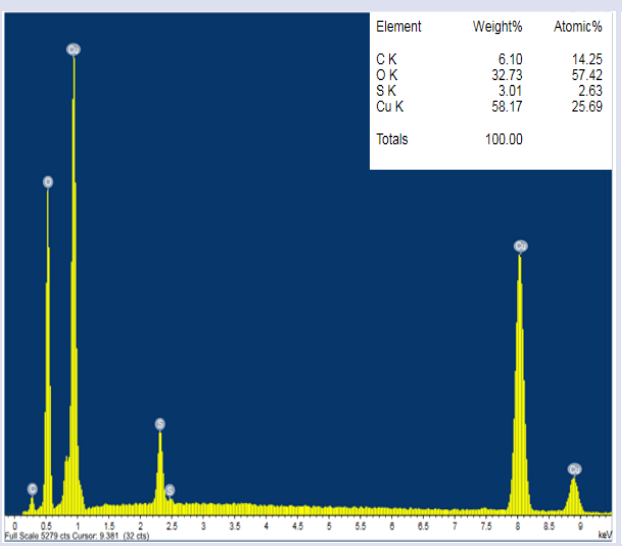


Figure 7. EDX spectrum of the CuO NPs

XRD Result

XRD analysis result of CuO NPs synthesized by green synthesis method using TP extract is given in Figure 8. XRD analysis was performed at a scanning speed of 2°/min. The presence of XRD peaks at 2θ value of 31.92°, 35.7°, 38.6°, 48.82°, 52.84°, 58.06°, 61.4° corresponds to the (1 1 0), (1 1 1), (2 0 0), (2 0 2), (0 2 0), (0 2 1), (1 1 3) crystal planes, respectively. This result confirms the formation of CuO NPs [36, 37]. The obtained XRD pattern clear and well-defined CuO reflections indicate that the produced nanoparticles have a high degree of crystallinity.

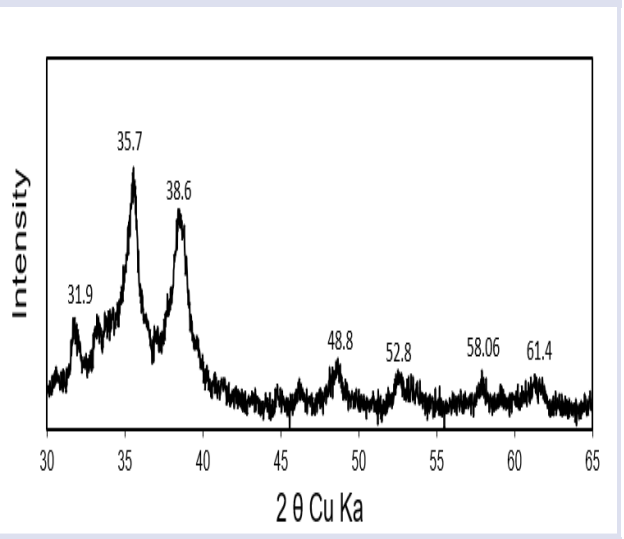


Figure 8. XRD pattern of CuO NPs

Antioxidant Activity

Antioxidants are substances used to reduce the damage caused by free radicals. Different chemical entities known as free radicals have one or more unpaired electrons. These free radicals are very unstable and try to stabilize themselves by attacking other molecules and taking their electrons. They form within the system and are highly reactive. This makes them potentially damaging for short-lived chemical species. These radicals are continuously produced in the human body because they are essential for detoxification, energy supply and immune function [38]. The redox properties of phenolic compounds, which are crucial in absorbing and neutralizing free radicals, are what give them their antioxidant activity [39, 40].

The antioxidant capacity of biosynthesized CuONPs was examined in this study using the DPPH technique. The principle of DPPH analysis is that the intense purple color of a freshly made DPPH solution tends to fade or disappear when an antioxidant sample is present in the solution. As a result, antioxidant molecules aim to quench DPPH free radicals, converting them into a colorless product. Analyses are performed by absorbance measurement at 517 nm.

The antioxidant capacity of CuO NPs synthesized with TP extract was investigated in the concentration range of 50-500 µg/mL (Fig. 9). Ascorbic acid was used as a positive control in the study.

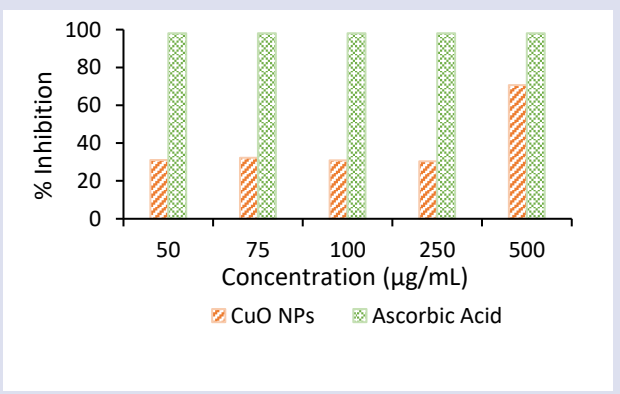


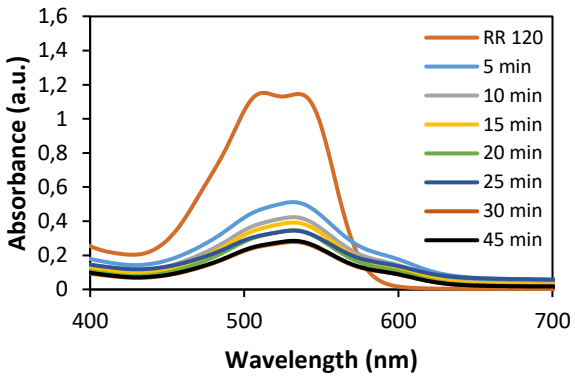
Figure 9. DPPH radical scavenging activity of CuO NPs and ascorbic acid

The results obtained showed that CuO NPs have antioxidant activity. In the concentration range of 50-250 µg/mL, the % inhibition values of CuO NPs ranged between 30-32 %. The % inhibition value of CuO NPs at 500 µg/mL concentration was calculated as 70.75 %. The decrease in the concentration of CuO NPs resulted in a decrease in antiradical capacity.

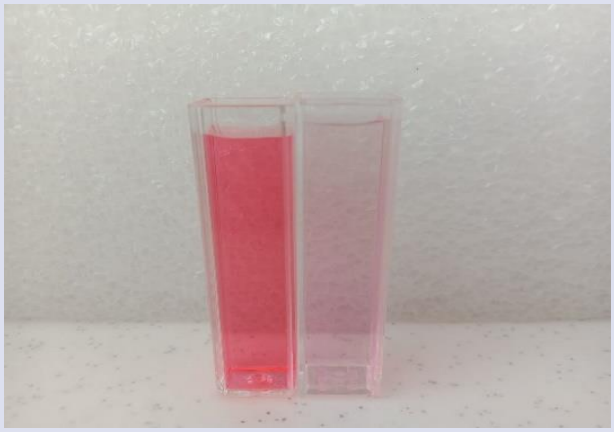
Photocatalytic Activity

The time dependent absorbance spectra and % removal of RR 120 dye as a result of photocatalytic degradation with CuO NPs produced by green synthesis method using TP extract are given in Figure 10 and Figure 11, respectively. In the experiment for the degradation of RR 120 dye, 50 ppm dye concentration, 0.04 g adsorbent amount and natural pH (pH= 7.98) of the dye solution were studied. The degradation of RR 120 was studied for up to 45 minutes and measurements were taken at 5 minute intervals for the first 30 minutes.

As seen in Figure 11, 55 % RR 120 degradation occurred in the first 5 minutes of photocatalytic degradation. RR 120 dye degradation occurred in approximately 30 minutes and the removal efficiency was calculated as 76 %.



(a)



(b)

Figure 10.Time dependent absorbance spectra of RR 120 (a), before and after the UV light induced degradation

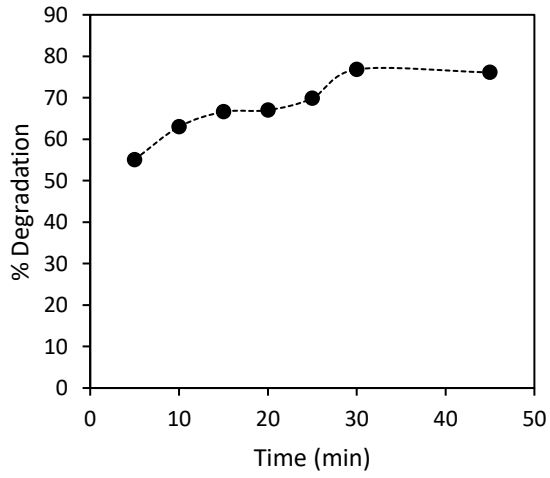


Figure 11. % Degradation-time graph for RR 120

Conclusion

CuO NPs were produced by green synthesis method using Tragopogon porrifolius extract as reducing agent. In the SEM analysis of the nanoparticles, it was determined that the nanoparticles had a spherical structure and the average particle size of the particles within the measured area was 288 nm. In EDX analysis, Cu and O ratios were determined as 58.17 % and 32.73 %, respectively. The synthesis of CuO NPs was confirmed by peaks obtained from XRD and FTIR analysis.

Antioxidant and photocatalytic activity of the synthesized CuO NPs were investigated. The free radical scavenging activity of CuO NPs synthesized with TP extract was investigated in the concentration range of 50-500 µg/mL. Free radical scavenging activity was determined as 70.75 % for 500 µg/mL CuO The free radical scavenging activity of ascorbic acid was calculated as 98 %. In antioxidant activity studies, CuO NPs were found to have antioxidant activity.

In the photocatalytic study, the degradation of azo dye and toxic Reactive Red 120 dye was investigated. The study was carried out at a concentration of 50 ppm and at the natural pH of the solution. The catalyst amount of CuO NPs was used as 2 g/L. RR 120 degradation was calculated as 76 % in about 30 minutes. In the first 5 minutes, 55 % RR 120 degradation was realized. These results showed that CuO NPs synthesized with TP extract were highly effective in RR 120 degradation.

Acknowledgement

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Conflict of interest

The authors declare that they have no competing interests.

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