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Green synthesis of copper oxide nanoparticles using black, green and tarragon tea and investigation of their photocatalytic activity for methylene blue

Siyah çay, yeşil çay ve tarhun çayı kullanarak bakır oksit nanoparçacıkların yeşil sentezi ve metilen mavisi için fotokatalitik aktivitelerinin araştırılması

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Abstract

In this study, copper oxide nanoparticles (CuO-NPs) were obtained by biosynthesis using aqueous extracts of black tea (BT), green tea (GT) and tarragon tea (TT). The effect of extracts from leaves of plants on the reduction mechanism has been investigated. The amount of polyphenol as using reducing agent in the extracts from the plants was determined according to the Folin-Ciocalteu's method. Total phenolic acid amounts of the extracts of BT, GT and TT were found as 59.18, 42.81 and 49.83 mg/L, respectively. Properties of synthesized CuO-NPs using these extracts were examined by UV-visible spectroscopy, Fourier infrared transformation spectroscopy (FTIR), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray spectroscopy (EDX) and Atomic Force Microscopy (AFM) analysis. In addition, prepared CuO-NPs were used in methylene blue (MB) removal as a photocatalyst. According to AFM results, average size of CuO-NPs was determined ranging from 10 to 12 nm. Regarding photocatalytic activity, prepared CuO-NPs from BT, GT and TT removed 89%, 87% and 90% of dye in 360 min, respectively. In the photocatalytic removal study, the reaction kinetics were investigated with zero, first and second order kinetics.

Keywords: Copper oxide nanoparticles, Green synthesis, Polyphenol, Methylene blue, Photocatalytic degradation.

Öz

Bu çalışmada, bakır oksit nanopartiküller (CuO-NP'ler), siyah çay (BT), yeşil çay (GT) ve tarhun çayı (TT) sulu ekstraktları kullanılarak biyosentez yoluyla elde edildi. Bitkilerin yapraklarından elde edilen ekstrelerin indirgeme mekanizmasına etkisi araştırılmıştır. Bitkilerden elde edilen ekstraktlarda indirgeyici ajan olarak kullanılan polifenol miktarı Folin-Ciocalteu'nun yöntemine göre belirlendi. BT, GT ve TT ekstrelerinin toplam fenolik asit miktarları sırasıyla 59.18, 42.81 ve 49.83 mg/L olarak bulundu. Bu özütler kullanılarak sentezlenen CuO-NP'lerin özellikleri UV-görünür spektroskopi, Fourier kızılötesi dönüşüm spektroskopisi (FTIR), Taramalı Elektron Mikroskobu (SEM), Enerji Dağıtıcı X-ışını spektroskopisi (EDX) ve Atomik Kuvvet Mikroskobu (AFM) analizi ile incelenmiştir. Ayrıca hazırlanan CuO-NP'ler metilen mavisi (MB) gideriminde fotokatalizör olarak kullanılmıştır. AFM sonuçlarına göre, CuO-NP'lerin ortalama boyutu 10 ila 12 nm arasında belirlendi. Fotokatalitik aktivite ile ilgili olarak, BT, GT ve TT'den hazırlanan CuO-NP'ler sırasıyla 360 dk. da % 89, % 87 ve %90 oranında boyayı giderdi. Fotokatalitik giderim çalışmasında reaksiyon kinetiği sıfır, birinci ve ikinci dereceden kinetik ile incelendi.

Anahtar kelimeler: Bakır oksit nanoparçacıklar, Yeşil sentez, Polifenol, Metilen mavisi, Fotokatalitik bozunum

1 Introduction

With the growth of various sectors in the industry such as textile, paper, plastic, cosmetics, leather tanning and food, there has been a significant increase in organic dyes in wastewater. These dyes are toxic and carcinogenic as well as damage the water flora by reducing photosynthetic activity. Polluted water from dyeing and processing textile products threatens nature. Methylene blue is known synthetic aromatic compound, toxic and harmful to the environment. It is a dye used to color textiles such as cotton, silk and wood [1]-[4]. Methylene blue which causes water pollution has been reported to cause irritation on the skin as well as harmful effects such as tachycardia, shortness of breath, vomiting, nausea and diarrhea [5]. Different methods such as oxidation, chemical reduction, adsorption, ion exchange, UV radiation, reverse osmosis, ozonation, and coagulation have been used to treat wastewater containing dyes [4],[6]. In recent years, the usage of photocatalysts has attracted great attention due to the reduction of toxicity, prevention of environmental pollution and energy saving [7]. Many metal and metal oxide nanoparticles, as well as various nanocomposites, have been reported to be used as photocatalysts [8].

Metal oxide nanoparticles are promising candidates for various applications such as optoelectronics, magnetic, thermal, sensoric devices, information storages, catalysis, biomedical, waste and dye degradation [9],[10]. Chemical, physical, electrochemical, sonochemical and biological methods are used in nanoparticle synthesis [11],[12]. Green synthesis is an easier, environmentally friendly, non-toxic, easy, cheap and efficient method compared to other methods. Therefore, it is suitable for use in biological applications. In recent studies, it has been reported that nanoparticles such as silver, copper oxide, titanium oxide, iron oxide, zinc oxide, platinum, palladium, cobalt have been synthesized with plant extracts [3],[10],[12],[13]. In green synthesis, dry leaves and branches of many plants, fruit and vegetable extracts and bacteria are used for nanoparticle synthesis [3],[14]. Green tea and black

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tea, which are frequently consumed in daily life, contain high amounts of polyphenols [15]. Phytochemicals such as polyphenol found in plant extracts reduce metal ions to form nanoparticles [16]. Thanks to their antioxidants, BT and GT extracts have chain breaking activity and active oxygen removal [17]. Tarragon (Artemisia dracunculus) is an aromatic plant from the Asteraceae (Compositae) family. It has been reported that tarragon extract contains phenolic acid, coumarins, flavonoid compounds, as well as caffeic acid, chlorogenic acid, caffeoyltaric acid [18],[19].

Copper oxide nanoparticles (CuO-NPs) are very important materials due to their low production cost, high surface area, antibacterial and antifungal potency, heat transfer, catalytic activity and unique electrical, thermal, magnetic and mechanical properties. There are many methods for producing semiconductor copper oxide nanoparticles such as sol-gel, precipitation, gas phase oxidation, hydrolysis, chemical reduction, sonochemical method, micro-emulsion, self-catalytic growth and green synthesis [20]-[23]. The biosynthesis of nanoparticles and their subsequent use in photocatalytic removal has attracted attention. It has been reported that in the production of copper oxide by green synthesis has been used various plant extracts such as clove (Syzygium aromaticum), pomegranate peel (Punica Granatum), Calotropis gigantea, Gundelia tournefortii, Thymus vulgaris L., mint leaves, Delonix elata, lemon and curcumin extract [10],[14],[22],[24]-[28]. Copper oxide nanoparticles (CuO-NPs) are cheaper than other metal oxide nanoparticles and that's why widely used [29]. The application areas of CuO-NPs include pesticide formulation, decomposition, gas sensors, photovoltaic cells, photovoltaic cells, photocatalytic activity, drug delivery, fungicidal and nematicidal applications and antibacterial agents [1],[20]-[22],[30]-[33]. It can also be used to remove dye, heavy metals or agricultural chemicals as it has reducing properties [29]. Some researchers have used CuO-NPs to remove many dyes such as methyl red, methyl orange, methylene blue, Congo red, and Coomassie bright blue [1],[29],[31]. Studies on the use of CuO-NPs in dye removal have shown successful results, but are limited [3]. The primary aim of this study is to investigate the synthesis and characterization of CuO-NPs with different plant extracts in a simple, fast and environmentally friendly way. For this purpose, the total phenolic content of three different extracts was determined. Secondly, the synthesized CuO-NPs were used in the photocatalytic degradation studies of MB. The relationship between the degradation degree of MB and the polyphenol content of plants used in NPs synthesis was investigated. To date, there is no report comparing the effect of CuO-NPs synthesized with different plant extracts on photocatalytic removal.

2 Experimental

2.1 Materials

The copper(II) acetate monohydrate salt ($Cu(CH_3COO)_2{\cdot}H_2O$) was obtained from Merck. Methylene blue was purchased from Isolab. The Folin-Cioceltau reagent was purchased from Carlo Erba. Gallic acid ($C_7H_6O_5$) and sodium carbonate (Na_2CO_3, 99%) were purchased from Sigma Aldrich. Hydrogen peroxide (H_2O_2) was purchased from Tekkim. Dry leaves of black, green and tea were obtained from local markets.

2.2 Preparation of extracts

One gram of dry leaves of black, green and tarragon tea was allowed to steep for 15 min. in 100 mL (70 °C) distilled water. Obtained extracts were filtered on filter paper and separated from the dry leaves.

2.3 Folin-Cioceltau methodology

The total amount of phenolic matter in black, green and tarragon teas was determined according to the Folin-Cioceltau method. In alkaline medium provided with 10 mL Na_2CO_3, 1 mL extract is mixed with 5 mL Folin reagent. Then distilled water is added and the solution is prepared. The solution is kept in the dark for about 1 hour. The absorbance value of the obtained blue solution was determined at 720 nm with a UV-vis spectrophotometer (Shimadzu).

2.4 Green synthesis of CuO-NPs

0.1 M $Cu(CH_3COO)_2.H_2O$ solution was prepared with distilled water. 50 ml of copper acetate solution and 50 ml of extract (individually for each, v/v; (1/1)) were mixed in a 250 ml flask on a magnetic stirrer at 60 °C for 1 hour. Similarly in all formulations, the color of the solution turned green, showing the formation of CuO-NPs at the time of mixing. Then the obtained precipitate from the filtered solution was washed with distilled water. The sample was dried at 60 ^{0}C for about 15 hours. The obtained CuO-NPs from BT, GT and TT were coded as BT-CuO-NPs, GT-CuO-NPs and TT-CuO-NPs respectively.

2.5 Characterization of CuO-NPs

Absorption spectra (range of 200-600 nm) of the synthesized CuO-NPs and photocatalytic studies were determined using the Shimadzu (UV-2600) UV-vis spectrometer. Analysis of FTIR spectra (4000-400 cm^{-1}), CuO-NPs and interactions between the reducing agent, black tea, green tea, tarragon and copper acetate were analyzed by Bruker (Tensor II) FTIR spectroscopy. Morphology of the CuO-NPs was investigated by SEM-EDX (Tescan Mira3 XMU) and AFM (Park System XE-10).

2.6 Photocatalytic degradation

To initiate photocatalytic degradation, 50 mg photocatalysts (CuO-NPs) were first added to a 200 ml MB solution at a concentration of 10 ppm, then 2 mL H_2O_2 (%30) was added to the suspension and mixed. Before irradiation, it was first stirred for 30 min. in the dark to achieve an adsorption/desorption balance between the MB molecule and the catalyst. The UV lights were then turned on and the solution was irradiated with UV light for 360 min. during which time a 4 mL sample was taken every 30 min. Photocatalytic degradation studies were performed using a 366 nm UV lamp (Merck). The absorption intensity was measured with a UV/vis Lamp 2600 spectrophotometer to determine the MB concentration. The wavelength at which methylene blue gives maximum absorbance is 664 nm. Percent degradation was calculated according to Equation 1.

$$Degradation\ (\%) = \frac{Co - C}{Co}\ x\ 100 \qquad (1)$$

Co is the initial dye concentration (t=0) and C is the dye concentration after irradiation for the selected time point. Photocatalytic degradation studies were carried out at room temperature (25 °C).

3 Result and discussion

3.1 Total phenolic matter determination

In this study, the amount of total phenolics in extracts (BT, GT and TT) was determined with the Folin- Ciocalteu method. Tea

polyphenols are water-soluble, biodegradable and biocompatible [15]. Apart from polyphenols, caffeine and theophylline components are also available in tea extracts [33]. Phenolic compounds are antioxidants that can be used as free radical terminators. Folin-Ciocalteu reagent produces a blue color upon reaction as polyphenols are sensitive to reducing compounds [34]. The calibration graph was obtained using gallic acid as standard and the total amount of phenolic matter was expressed as gallic acid (mg gallic acid/L) equivalents (GAE). 10 ml of standard solution of concentration at 10, 20, 100, 150, 250 and 375 mg/L of gallic acid were prepared in ethanol. Absorbance measurements of prepared standards were done in UV spectroscopy at 720 nm and shown in Figure 1. The total amount of phenolic substance was calculated according to the equation ($y=0.0048x+0.1124$, $R^2=0.9907$) obtained from the gallic acid calibration graph. According to Table 1, the highest total phenolic amount (59.18 mg/L) was calculated in black tea extract. In literature studies, it was determined that the antioxidant properties of black tea were higher than green tea in vivo studies. The antioxidant activity of tea is due to the total phenolic substances it has [17].

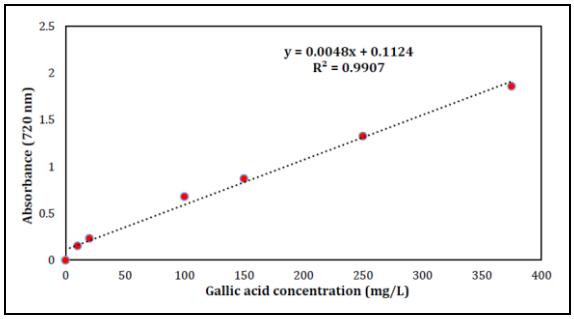


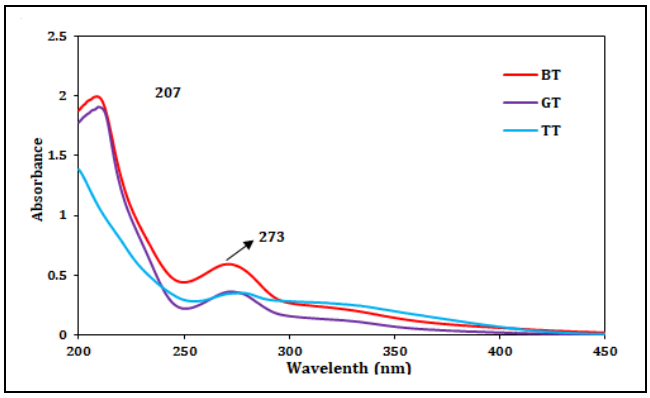
Figure 1. Gallic acid calibration graph.

Table 1. Total phenolic acid content of extracts.

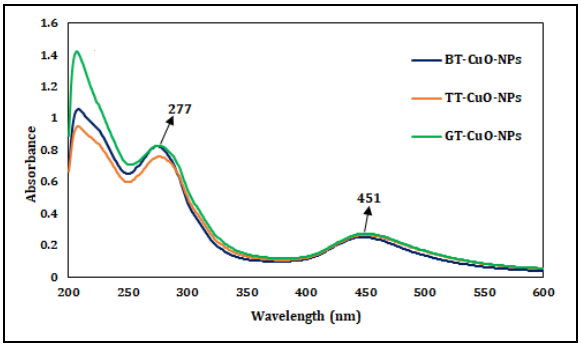
Plant Extract	Total Phenolic acid content (mg/L)
Black Tea (BT)	59.18
Green Tea (GT)	42.81
Tarragon Tea (TT)	49.83

3.2 Characterization of CuO-NPs

In Figure 2, the extracts and synthesized CuO-NPs were first examined by UV-vis absorption spectroscopy. When the black, green and tarragon tea extracts have been separately added to the copper acetate solution, the color of the solutions changes into different tones of green due to the stimulation of surface plasmon vibrations [30],[33],[35]. The density of the plasmon resonance band can vary according to the particle size, shape, property and surrounding environment of the metallic material [33]. According to UV-vis results, the maximum absorbance of the synthesized nanoparticles was revealed at 207, 277 and 451 nm Figure 2(b). The peak occurring at 207 nm expresses the formation of CuO-NPs and is compatible with the literature [36]. The peak at 277 nm indicates the formation of CuO-NPs and the polyphenol structure [31],[37]. The absorption peak at 277 nm from the extracts was also seen in the CuO-NPs structure. This may be because it forms a complex structure between polyphenols and Cu ions [37]. The small peak at 451 nm shows the formation of Cu^+ ions [38]. The color change in the reaction mixture was due to the surface plasmon resonances during reduction and formation of CuO-NPs [25],[30].



(a)



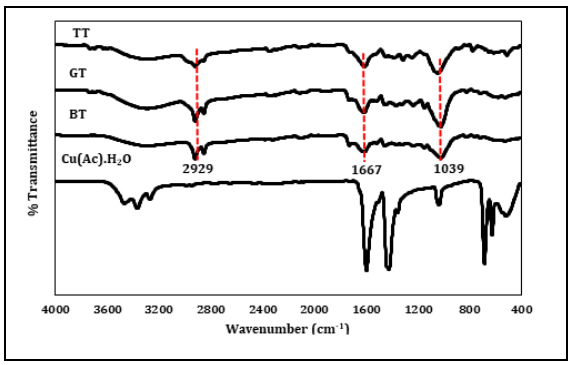
(b)

Figure 2. UV–vis absorption spectrums of (a): BT, GT and TT, (b): BT-CuO-NPs, GT-CuO-NPs, TT-CuO-NPs.

The chemical structure of the phytochemical compounds in the plant extract was examined by FTIR. In Figure 3(a), FTIR spectra of TT, GT, BT and copper acetate salt are given. Peaks at 2929 cm^{-1} are attributed to stretching modes CH_2 and C-H. The peak occurring at 1667 cm^{-1} refers to the amide conjugated C=O and C=C stretch vibration. It is also dedicated to the group of proteins that enable nanoparticles to be reduced and remain stable. The presence of carboxylic acid and amino groups may indicate the stretching vibration of the peak at 1039 cm^{-1} [22]. Functional groups found in tea extracts indicate the presence of phenolic compounds. The phenolics compounds found in the extract have been reported to be responsible for reducing metal ions and obtaining nanoparticles [25]. FTIR spectra for BT-CuO-NPs, GT-CuO-NPs and TT-CuO-NPs are shown in Figure 3(b). Table 2 gives information about the bond structures of CuO-NPs. Bands below 1000 cm^{-1} are attributed as metal-oxygen bonds [39]. The peak occurring at 443 cm^{-1} expresses Cu-O vibrations that confirm the formation of copper oxide nanoparticles [22],[30],[31]. Peaks occurring around 1071 cm^{-1} express the stretching vibration of C-OH [21]. C=C stretching expressing peak in 1587 cm^{-1}, represents the coordination of copper nanoparticles [29]. The peaks occurring at 1587 cm^{-1} and 1342 cm^{-1} represent the aromatic C=C and C=O (carbonyl group) vibration bands, respectively [25],[40]. The band in 2092 cm^{-1} refers to the $-CH_2$ and C-H tensile bands from alkanes [22]. The peak seen at 3314 cm^{-1} refers to the hydroxyl functional group O-H vibration due to the vibration band of molecular water [40],[41]. Lattice vibration modes of functional biomolecule groups adsorbed to synthesized nanoparticles are seen in all spectra [25].

Figure 4 shows 3D topographic images of BT-CuO-NPs, GT-CuO-NPs and TT-CuO-NPs. According to AFM results, the size of

particles within the area of 500nmx500nm was measured as maximum 10, 12 and 10 nm for BT-CuO-NPs, GT-CuO-NPs and TT-CuO-NPs samples, respectively. The high peaks in the AFM images of the synthesized nanoparticles may be due to agglomerated particles in that measurement area. Figure 4(a) shows that BT-CuO-NPs have less agglomerate in 3D AFM images.



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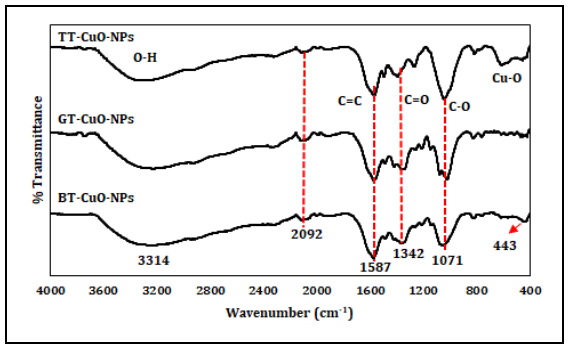


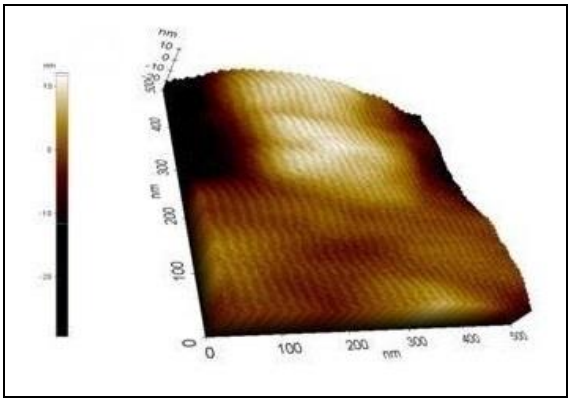
(b)

Figure 3. FTIR spectrums of (a): TT, GT, BT and $Cu(Ac)_2H_2O$. (b): TT-CuO-NPs, GT-CuO-NPs, BT-CuO-NPs.

Table 2. Absorption peaks of the CuO-NPs and corresponding functional groups.

Absorption Peak Position (cm^{-1})	Functional Group
3314	O-H streching vibration
2092	C-H, $-CH_2$
1587	C=C
1342	C=O
1071	C-OH
443	Metal-oxygen bonds

Morphological properties of BT-CuO-NPs, GT-CuO-NPs and TT-CuO-NPs samples were examined with SEM measurements. SEM image of three nanoparticles at 500 nm scale with 200 kx magnification is given in Figure 5. The change in the size distribution of the nanoparticles may be due to the various reducing properties of the different (secondary metabolites) compounds usually contained in aqueous extracts of BT, GT and TT. Tea leaves have many phytochemicals and beneficial properties with antioxidant activity. Components found in aqueous tea extracts are used as reductants for the synthesis of metal oxide nanoparticles. Therefore, the extract is highly effective in the structural properties of the nanoparticles obtained [42]. According to SEM images Figure 5(a),(c) and (e), nanoparticles appear to have a spherical, irregular and agglomerated structure [14],[30],[40]. EDX analysis Figure 5(b),(d) and (f) is an important tool to understand the basic composition of synthesized copper oxide nanoparticles. The presence of Cu and O was confirmed by EDX spectroscopy [26]. Spectrum results showed the successful formation of NPs. In addition, it has been observed that there are impurities (carbon) thought to be caused by plant components [42]. According to EDX analysis, elemental Cu and O amounts are close to each other. Therefore, the chemical composition of the synthesized copper oxide nanoparticles can be said to be CuO. Copper and oxygen weight ratio for BT-CuO-NPs, GT-CuO-NPs and TT-CuO-NPs appear to be approximately 1.



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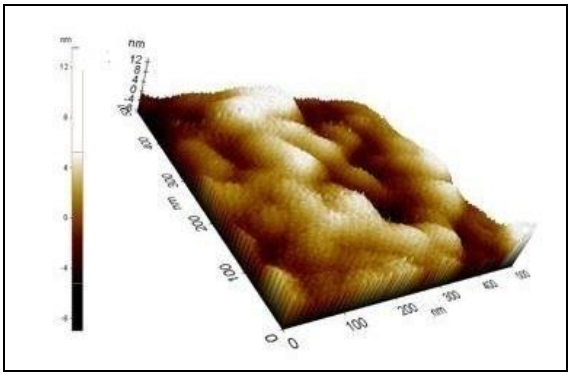

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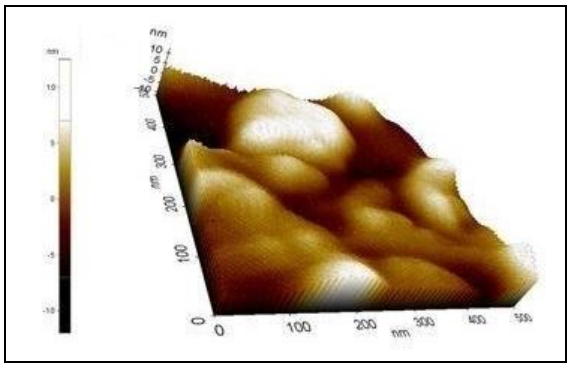


(c)

Figure 4. 3D topographical view of (a): BT-CuO-NPs. (b): GT-CuO-NPs, c)TT-CuO-NPs.

Some plants used in the literature in the green synthesis of CuO-NPs and the parts used in the preparation of the extract are given in Table 3. The characterization results for CuO-NPs obtained by green synthesis show that NPs formation is

successful. The suggested estimated reduction mechanism is as follows (Equation 2 and 3) [43];

$$Cu(CH_3COO)_2.H_2O+2OH^- \rightarrow Cu(OH)_2+2CH_3COO^-+H_2O \quad (2)$$

$$Cu(OH)_2 + (polyphenol) \rightarrow CuO - NPs + H_2O \quad (3)$$

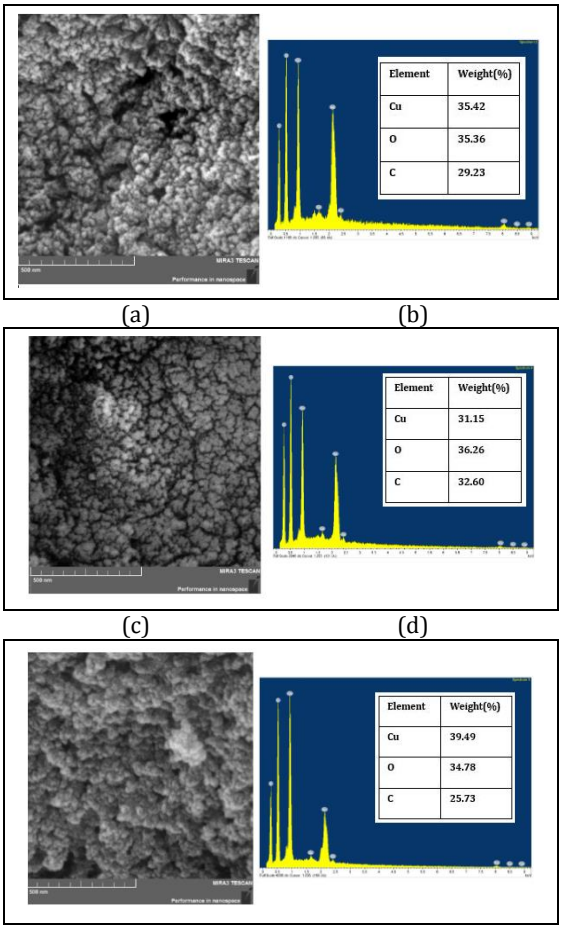


Figure 5. SEM images. (a): BT-CuO-NPs. (c): GT-CuO-NPs, e) TT-CuO-NPs and EDX images. (b): BT-CuO-NPs. (d): GT-CuO-NPs. (f): TT-CuO-NPs.

Table 3. Plants used in the green synthesis of CuO-NPs in the literature.

Plant Extract	Used Part	References
Celastrus paniculatus	leaves	[3]
Aloe vera	leaves	[6]
Carica papaya	leaves	[12]
Seedless dates	fruit	[21]
Punica granatum peels	peels	[22]
Delonix elata	flower	[27]
Lemon	fruit	[28],[30]
Cedrus deodara	leaves	[36]
Black, green and tarragon tea	leaves	This study

3.3 Photocatalytic activity

Studies on MB removal from aqueous solution using CuO-NPs have been carried out over time. For this purpose, a UV lamp (366 nm) was used as the light source. All tests were applied at room temperature and constant mixing speed. Methylene blue ($C_{16}H_{18}N_3SCl$, MB) is known as a cationic dye [44]. Hydrogen peroxide (H_2O_2) was added to the aqueous solution to increase the removal efficiency of the dye in photocatalytic removal studies. H_2O_2 acts as an electron acceptor in the process. After obtaining electrons under UV lamp radiation, it can convert into OH radical [45]. The proposed OH formation mechanism in photocatalytic degradation is shown in Equation 4-7. [3],[32],[45];

$$CuO + hv \rightarrow CuO(h) + CuO(e) \quad (4)$$

$$H_2O_2 \rightarrow 2OH^* \quad (5)$$

$$CuO(e) + O_2 \rightarrow O^{2*} + CuO \quad (6)$$

$$CuO(h) + MB + OH^*/O^{2*} \rightarrow Degradation\ product \quad (7)$$

Experiments were carried out under certain experimental conditions to study the photocatalytic degradation kinetics of MB (methylene blue concentration 10 mg/L, photocatalyst dosage 0.25 mg/mL). In the study, the kinetic study of MB photocatalytic degradation is expressed according to zero, first order and second model. Therefore, the following Equation 8, 9, 10 were used:

$$C - Co = -kt \quad (8)$$

$$Ln\left(\frac{Ct}{Co}\right) = -kt \quad (9)$$

$$\frac{1}{[C]} - \frac{1}{[Co]} = k.t \quad (10)$$

Where t is the time spent by the solution under the UV lamp in minutes, C_0 is the concentration of MB at the starting (t = 0 min), Ct is the final concentration of the reaction at time t and k is the apparent rate constant. In order to calculate the photocatalytic rate constants of the BT-CuO-NPs, GT-CuO-NPs and TT-CuO-NPs photocatalysts, $(C - Co) - t$, $Ln(Co/C) - t$, $(1/C - 1/Co) - t$ change graphs were drawn and their slopes were calculated. All the plots displayed a linear association with good correlation coefficients. The calibration chart prepared to calculate MB removal in experiments is given in Figure 6. Methylene blue aqueous solution was prepared at different concentrations in the range of 1-10 mg/L and absorbance was measured at 664 nm UV-vis spectrometer.

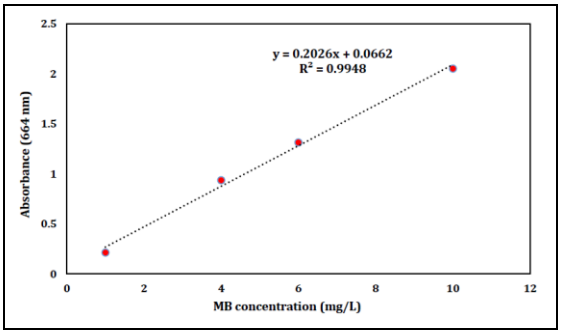
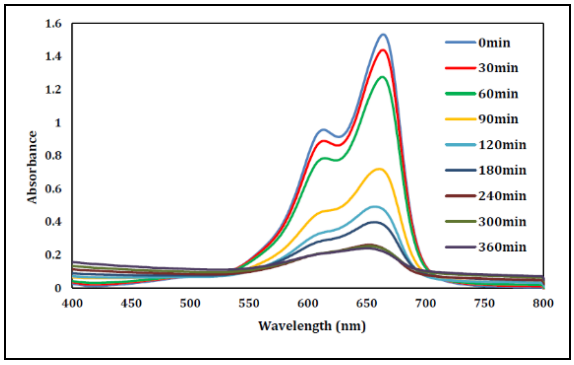


Figure 6. Calibration curve of MB.

Figures 7(a), (b) and (c) show a gradual decrease in MB concentration during photocatalytic removal over 360 min. When the degradation results for MB are examined, it is seen that the decrease in the absorption data in the first 90 min. is fast but then slows down. Especially after 240 min. absorbance values are close to each other. The Cu^{2+} ion can be easily functionalized with polyphenol [46]. Ejima et al. reported that

metal ions and polyphenol can form complexes [47]. In addition, it can also work as a reducing agent capping agent in green synthesis [11].



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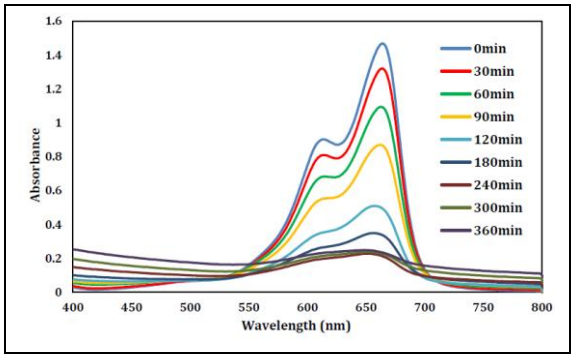

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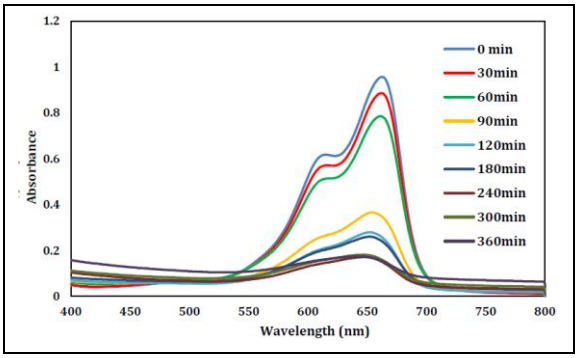


(c)

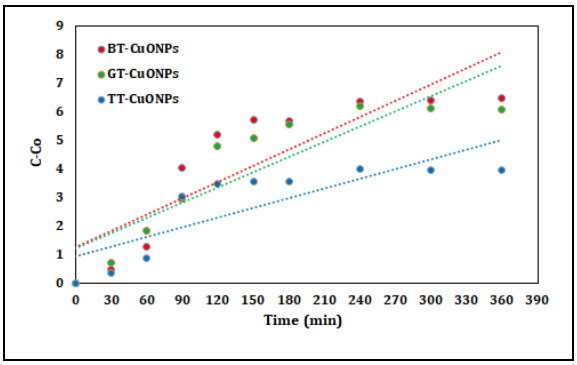
Figure 7. UV-vis spectrum showing degradation of MB solution under UV light irradiation with CuO-NPs (a) BT-CuO-NPs, (b) GT-CuO-NPs, (c) TT-CuO-NPs (10 mg/L MB, 0.25 mg/mL CuO-NPs).

It is thought that there may be a directly proportional relationship between the amount of polyphenol, which is the reducing agent in the extract used in the synthesis of CuO-NPs, and the degradation. Table 4 gives the comparative results of the rate constant values obtained with the zero, first and second order kinetics.

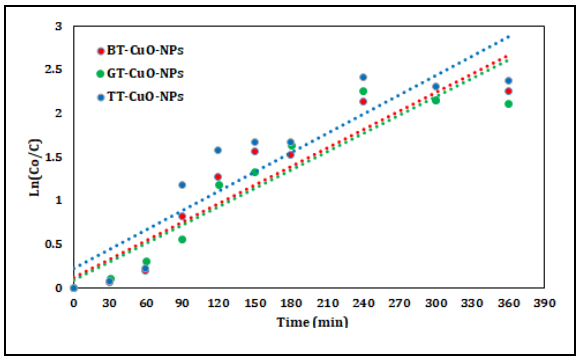
Table 4. Zero- first and second order kinetic parameters for the degradation of MB with CuO-NPs (after 360 min.).

	Zero-Order		First-Order		Second-Order	
NPs	R^2	k_0 (mg/L.min)	R^2	k_1 (min^{-1})	R^2	k_2 (L/mg.min)
BT-CuO	0.74	0.019	0.89	0.0071	0.95	0.0038
GT-CuO	0.78	0.0178	0.88	0.007	0.87	0.0038
TT-CuO	0.68	0.0112	0.84	0.0074	0.9	0.0073

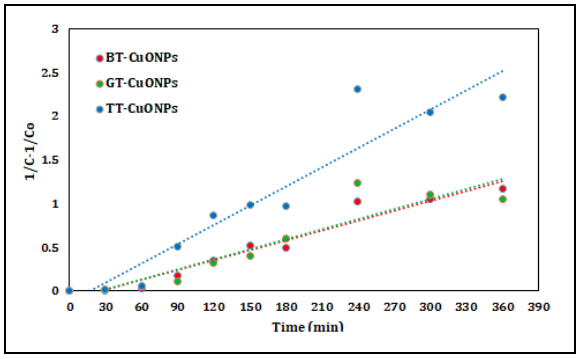
The smallest R^2 values for zero-order reaction kinetics were obtained for all CuO-NPs. In the first order kinetic study, R^2 values increased and k values decreased. Overall, the best kinetic results were obtained with the second-order kinetic datas. The results show that the highest R^2 value (0.95) in the photocatalytic degradation process is obtained with second order reaction kinetics and BT-CuO-NPs photocatalyst. Similarly, the smallest rate constant value was calculated as 0.0038 mg/L.min for BT-CuO-NPs Figure 8. When the R^2 values in all photocatalytic degradation kinetics were examined, it was determined that it was more compatible with the second-order reaction.



(a)



(b)

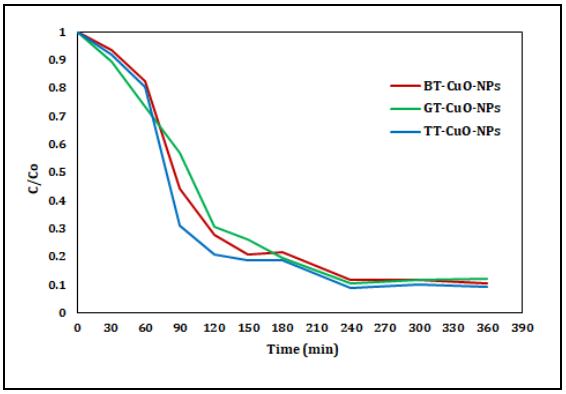


(c)

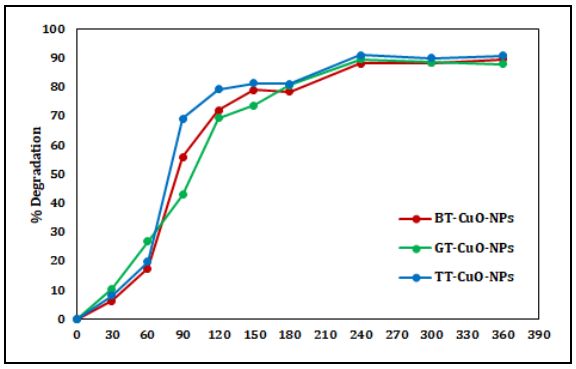
Figure 8(a): Time-(C-Co) plot expressing zero order kinetic reaction between MB and CuO-NPs. (b): Time-Ln (Co/C) for first order. (c): Time-((1/C)-(1/Co)) plot for second order kinetic (10 mg/L MB, 0.25 mg/mL CuO-NPs).

Figure 9(a) and (b) represent the rate of removal of the dye from the water and the percentage of removal. In Figure 9(a) the rate of removal of MB from aqueous solution is fast during the first 120 min, but then slowed down. Using CuO-NPs obtained by green synthesis, it was concluded that the

degradation time of MB was 360 min. Figure 9(b). Dye removal has been found to slow considerably between 240 and 360 min. As a result of photocatalytic removal studies, degradation of MB dye under UV light was determined as 89%, 87% and 90% for BT-CuO-NPs, GT-CuO-NPs and TT-CuO-NPs, respectively. In addition, a control experiment was conducted to examine the effect of hydrogen peroxide on the degradation of MB, and no photocatalyst was added under the same experimental conditions. That is, 2 mL of hydrogen peroxide (%) was added to 200 mL of 10 ppm MB aqueous solution and exposed to UV light. At the end of 360 min it is seen that MB dye provides 7.5% removal. This result reveals the positive effect of CuO-NPs on degradation as a photocatalyst.



(a)



(b)

Figure 9(a): C/Co, degradation rate graph. (b): Graph of MB's removal percentage over 360 min. (10 mg/L MB, 0.25 mg/mL CuO-NPs).

In Table 5, photocatalytic degradation information of MB dyes in the literature against different photocatalysts and irradiation times are given. According to the results, it is noticed that prepared CuO-NPs using the green synthesis method were efficient in the degradation of MB dye.

Table 5. Comparison of MB degradation by different photocatalysts in the literature.

Photocatalsts	Degradation (%)	Irradiation time (min)	References
CuO-NPs	81	80	[48]
PVDF/GO/ZnO	86	100	[49]
rGO/TiO_2	91	30	[50]
ZnO	92	120	[51]
ZnO/$ZnCr_2O_4$	93	120	[52]
CuO-NPs	90	360	This study

4 Conclusions

In this study, the main objective is the preparation of CuO-NPs using green synthesis method by BT, GT and TT extracts as reducing agents. For extracts whose concentrations were prepared equally, the highest amount of polyphenol (59.18 mg/L) was determined to be in BT extract. All CuO-NPs were used in removal of methylene blue in aqueous solution at the same conditions and under UV lamp. According to the results, it is obtained that when the reduction properties of BT, GT and TT extracts are compared, characterization of the nanoparticles gives similar properties. It has been proven to be successfully synthesized of CuO-NPs using green synthesis. The characterization results showed that the nanoparticles have the composition of CuO. AFM results point out that the average size of the particles was between 10-12 nm. SEM images showed that nanoparticles are in a spherical structure. The effect of photocatalyst used, process time, and a kinetic investigation was evaluated. BT-CuO-NPs, GT-CuO-NPs and TT-CuO-NPs were used for the photodegradation of MB. Due to the strong adsorption capacity of CuO-NPs and the presence of UV light, the photodegradation of MB has been successful. As a result of photocatalytic degradation of MB in an aqueous solution, it is seen that TT-CuO-NP reaches 90% degradation at the end of 360 min. The degradation values in BT-CuO-NPs (%89) and GT-CuO-NPs (%87) are close. Considering the effect of polyphenol content in the extracts on MB removal, the amount of polyphenol increased the MB removal rate during the first 90 minutes. However, at the end of 360 min, the dye removal values are very close for the three NPs samples. This indicates that the surface of CuO-NPs is covered by polyphenol and may therefore accelerate the removal of MB. This study proposes that the green method, which has been prominent in recent years, can be considered an effective method in nanoparticle synthesis and possibly nanoparticles can be used as a photocatalyst in the removal of dyes from wastewater.

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6 Author contribution statement

In this study, Nurşah KÜTÜK contributed to the formation of an idea, literature review, experiments, evaluation of data and article writing, while Sevil ÇETİNKAYA contributed to the formation of ideas, evaluation of the data, and article writing and editing.

7 Ethics committee approval and conflict of interest statement

There is no need to obtain ethics committee approval for the article prepared. There is no conflict of interest with any person/institution in the article prepared.

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