GC/MS screening of buckthorn phytochemicals and their use to synthesize ZnO nanoparticles for photocatalytic degradation of malachite green dye in water

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ABSTRACT
Zinc oxide nanoparticles (ZnO NPs) were biosynthesized. According to gas chromatography/mass spectrometry analysis, chalcone, the main phytochemical, is probably complexed with Zn ions that are then oxidized to ZnO NPs by atmospheric O2 during heating. The ZnO NPs were characterized by thermogravimetric analysis, Fourier transform infrared spectroscopy, X-ray diffraction, field emission scanning electron microscopy, transmission electron microscopy, energy-dispersive X-ray spectroscopy, and Brunauer–Emmett–Teller surface area analysis. Sphere-like ZnO NPs were formed with 11 nm mean crystallite size, 5.2 m² g⁻¹ surface area, and 0.02 cm³ g⁻¹ total pore volume. The synthesized ZnO showed excellent photocatalytic degradation (96.5 ± 0.24% in 1 hour at 25 °C) of malachite green (MG) in aqueous solutions under ultraviolet light at optimum conditions; pH 10, MG initial concentration of 20 mg L⁻¹, and ZnO dose of 1.5 g L⁻¹. Also, ZnO showed very good reusability (92.9 ± 0.2% after five runs). The experimental data obeyed pseudo-first-order kinetics (R² = 0.92). The photocatalysis process was dependent on the following species in the order: OH⁻, electron/positive hole pairs, O₂. Moreover, photodegradation efficiency decreased in the presence of CO₃²⁻, HCO₃⁻, and Cl⁻, but increased in the presence of NO₃⁻ and SO₄²⁻ ions. Thus, the green synthesized ZnO NPs can be applied as an efficient photocatalyst for the removal of MG from aqueous media.

Key words: buckthorn, GC/MS, malachite green, photocatalytic degradation, ZnO nanoparticles

HIGHLIGHTS
- Phytochemicals in buckthorn leaves were GC/MS screened.
- Phytochemicals were applied to green synthesize mesoporous ZnO nanocatalyst.
- ZnO photocatalytically degraded malachite green.
- Different parameters of the photocatalytic process were studied and optimized.
- Scavenging experiments were done and mechanism of photocatalysis was suggested.

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**1. INTRODUCTION**

Large amounts of dyes have been released into the environment since the last century due to the endless expansion of the dyeing and printing industries (Rafatullah et al. 2010; Olivera et al. 2018). Exposure to dyes results in many health risks, including carcinogenicity, mutagenicity, and dysfunction of human beings' kidneys, liver, brain, reproductive system, and central nervous system. Thus, it is vital to explore an efficient method to remove dyes from industrial effluents. Large numbers of processes have been applied for the treatment of dyes in contaminated water, such as adsorption (Mittal 2006; Inamuddin 2018; Mashkoor & Nasar 2020; Tara et al. 2020), biological treatment (Wang et al. 2011a), and photocatalysis (Sayilkhan et al. 2007; Inamuddin 2019; Fegade et al. 2020), etc. Photocatalysis is of great importance because it can convert organic toxic compounds into harmless chemicals (Lee et al. 2012; Mezni et al. 2017).

Zinc oxide (ZnO) is one of the most important photocatalysts. ZnO and its composites with other materials have several industrial and environmental applications, especially as a promising photocatalyst (Nguyen et al. 2018). The high value of the zinc-based catalyst can be attributed to its low cost, high stability, nontoxicity, strong oxidation capacity, considerable surface area, good adsorption capacity, high free excitation binding energies, and significant corrosion resistance (Chankhanittha & Nanan 2018). Recently, researchers synthesized various zinc oxide nanocomposites and doped them with metals and non-metals to narrow the band gap (Mohamed et al. 2016; Babajani & Jamshidi 2019; Arsalani et al. 2020; Dimova et al. 2020; Saad et al. 2020; Yulizar et al. 2020). Physico-chemical synthesis routes have many drawbacks, such as high energy consumption, high cost, onerous procedures, and the generation of hazardous waste. At this time, biosynthesis is the method of choice due to cost-effectiveness, simplicity, and eco-friendliness (El-Belely et al. 2021; Fagier 2021; Gangwar & Sebastian 2021; Huang et al. 2021; Murali et al. 2021; Nityasree et al. 2021; Ramesh et al. 2021; Soltanian et al. 2021; Tran et al. 2021; Thirumoorthy et al. 2021). In addition, the synthesis of ZnO using agricultural waste adds economic and
environmental value to the waste. It also follows green chemistry and an environmental sustainability approach. In this way, waste can be converted from a probable environmental pollutant to a pollution remediator. Thus, we continue to utilize plant waste to green synthesize metal oxide nanostructures with superior properties and use them in environmental and analytical applications (Hasan et al. 2021a, 2021b).

According to phytochemical screening, buckthorn, Christ’s thorn jujube (CTJ), is rich in flavonoids, essential oils, tannins, phytosterols, triterpenoid, vitamin C, saponins, glycosides, and alkaloids (Shahat et al. 2001; Kadioglu et al. 2016). These phytochemicals can act as reductants and stabilizers in the biosynthesis of ZnO, avoiding the use of harmful chemicals and their by-products.

In the present work, phytochemicals in Christ’s thorn jujube leaf extract (CTJLE) were gas chromatography/mass spectrometry (GC/MS) screened and applied for the bioreduction of zinc ions into ZnO NPs. The synthesized ZnO was fully characterized and its photocatalytic performance for MG degradation under ultraviolet (UV) irradiation was examined and optimized. In addition, the mechanisms of ZnO formation and ZnO photocatalytic degradation effect were proposed.

2. MATERIALS AND METHODS

2.1. Materials

Zinc acetate dihydrate ((CH3CO2)2Zn.2H2O) and malachite green (MG) oxalate (C52H54N4O12) were purchased from Merck & Co. (Germany) and used directly without pretreatment. CTJ leaf aqueous extract was used to synthesize ZnO NPs. All other chemicals were of analytical grade and used as received without further purification. At ambient temperature, bidistilled water was employed for the preparation of aqueous solutions.

2.2. Instruments

The thermal stability was investigated by thermogravimetric analysis (TGA) with a 30 °C/min heating rate up to 800 °C under Ar gas flow at 100 mL/min. To evaluate the phytochemicals role in ZnO NP synthesis, Fourier transform infrared (FTIR) spectra were recorded from 400 to 4,000 cm⁻¹ (Shimadzu FTIR, Kyoto, Japan). The phase structure and size of ZnO NPs were investigated using a powder X-ray diffractometer (X’Pert3 Powder, PANalytical, The Netherlands) at 40 kV voltage and 30 mA current, with monochromatic radiation (Cu-K, 1.5406) and a nickel monochromator, and a diffraction angle in the 30–80° range. The Scherrer equation (D = Kβ/λcosθ) was used to determine the crystallite size, where D is the mean crystalline size (nm), K is a dimensionless shape factor, with a value close to unity, λ is the X-ray beam wavelength (nm), β is the full width at half-maximum of the diffraction peak in radians, and θ is the Bragg angle. Field emission scanning electron microscope (FESEM) (QUANTA FEG250) coupled with energy-dispersive X-ray spectroscopy (Inspect S 50, FEI, The Netherlands) operated at a 20-kV accelerating voltage, 10 mm working distance, and 1.0 nA probe current, were conducted to examine the surface morphology, and chemical composition of the synthesized sample. Information about the particle shape and size was obtained utilizing high resolution transmission electron microscopy (HRTEM) (Themis ETEM, Thermo Fisher Scientific Inc., USA). The determination of the surface texture of the sample was carried out on a BEL SORP-MAX analyzer (MicrotracBEL, Japan). The MG concentration was measured using a UV-visible (UV–vis) spectrophotometer (PG Instruments, model T80, UK) using quartz cells of 1 cm pathlength, and in the wavelength range from 200 to 800 nm. Bidistilled water was used as the blank to adjust the baseline. The compounds present in CTJLE were qualitatively screened by GC/MS analysis using a Trace GC1310-ISQ mass spectrometer (Thermo Scientific, Austin, TX, USA) with a direct capillary column TG-5MS (30 m × 0.25 mm × 0.25 μm film thickness). The GC oven program was: 50 °C, 12 min isothermal/5 °C min⁻¹/230 °C, 2 min isothermal/30 °C min⁻¹/290 °C, 2 min isothermal. The solvent delay was set to 3 minutes, and diluted samples of 1 μl were automatically injected using an autosampler AS1300 and a split mode GC. In full scan mode, EI mass spectra were acquired spanning the range m/z 40–1,000 at 70 eV ionization voltages. The temperature of the ion source was set to 200 °C. The phytochemicals were identified by comparing the retention times and mass spectra of them to those of the WILEY 09 and NIST 11 mass spectral databases.

2.3. Preparation of CTJ leaves extract

For aqueous extract preparation, 150 g of dried powdered leaves of buckthorn were mixed with 1.5 liters of bidistilled water (10% w/v) in a 2,000-mL round-bottomed flask. The mixture was in a water bath at 100 °C for 3 hours, then soaked overnight, and then decanted and filtered twice through a cotton plug. The obtained extract was centrifuged at 5,000 rpm for 5 minutes at room temperature to remove leaf microparticles and insoluble fractions, then the pale brown clear solution, which

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indicated the release of the phytochemicals from the leaves, was collected and stored in the refrigerator at 4 °C (not more than 3–4 days to avoid possible decomposition of phytochemicals) for further use.

2.4. Biogenic synthesis of zinc oxide NPs
In total, 50 mL of 0.1 M zinc acetate dihydrate were mixed with 100 ml of the extract under vigorous stirring for 1 hour at room temperature (25 °C). After the completion of the reaction, the formed dirty yellowish-brown precipitate was left to settle for 24 hours (Figure 1). The precipitate was separated from the reaction solution by centrifugation at 6,000 rpm for 15 min, washed with deionized water repeatedly to remove the impurities, and dried in an oven at 80 °C. The as-synthesized sample was then calcined in a muffle furnace at 500 °C for 3 hours. Beginning with 2.4 g of zinc acetate, 1.9 g ZnO NPs were obtained with 89% yield.

2.5. Study of point of zero charge (PZC)
Five bottles, each containing 50 ml of an aqueous solution of NaCl (0.01 M) and a fixed sorbent loading of 2.0 g L⁻¹, were prepared using the methodologies described by Mahmood et al. (2011) with some modifications. The starting pH of the solution (pHᵢ) in each bottle was adjusted by using NaOH (0.1 M) or HCl (0.1 M) solutions at pH range 2–12. The final pH of the solutions (pHᶠ) was measured after 48 hours of agitation with the sorbent (a long enough time was allowed for diffusive mixing). The ΔpH (ΔpH = pHᵢ - pHᶠ) was calculated and plotted versus pHᵢ. The PZC will be the point which reaches the null value variation (ΔpH = 0). The pH meter was calibrated at pH values of 4, 7, and 10 prior to each run.

2.6. Photocatalytic activity study
The photocatalytic activities of biosynthesized ZnO NPs were assessed by measuring the photodegradation of MG in aqueous solution under UV light. The oxidation of MG took place due to the catalytic activity of the as-prepared ZnO NPs. As a general procedure, a selected amount of ZnO NPs was suspended in 50.0 mL of 20 mg L⁻¹ MG solution in a 100-mL beaker. After magnetically stirring in the dark for 30 min (UV measurements showed no change in MG concentration after that time) to attain the adsorption–desorption equilibrium of the working solution, this solution was magnetically stirred at room temperature under the exposure of a UV light source (Philips; TUV TL Mini; 8 W, main emission peak at 365–370 nm and light intensity of 0.72 mW/cm²), which was positioned at 15 cm above the

Figure 1 | Schematic representation of the biosynthesis of ZnO NPs.
suspension surface, for 1 hour. A certain amount of the supernatant solution was collected by centrifugation for the UV–vis spectroscopic measurement.

2.7. Optimization of photocatalysis conditions
To achieve the optimum photocatalytic conditions for MG degradation by ZnO NPs, various operational parameters were studied one by one. These parameters include light conditions (dark, solar, UV, and UV without catalyst), the solution pH

Table 1 | Phytochemicals in CTJLE identified by GC/EI-MS analysis (RT: retention time, MW: molecular weight)

| No. | RT (min) | Compound name                                      | Molecular formula | MW | Peak area (%) |
|-----|---------|----------------------------------------------------|-------------------|----|--------------|
| 1  | 4.43    | Propylene glycol                                   | C₅H₁₀O₂           | 76 | 1.26         |
| 2  | 5.75    | Propanoic acid, 2-oxo-, methyl ester               | C₅H₁₀O₂           | 102| 0.33         |
| 3  | 6.58    | 2-Furaldehyde                                      | C₅H₆O₂            | 96 | 0.9          |
| 4  | 15.30   | 2,3-Dihydro-3,5-dihydroxy-6-methyle-4H-pyran-4-one| C₆H₁₀O₄           | 144| 0.7          |
| 5  | 19.71   | 5-Hydroxymethylfurfural                            | C₆H₁₀O₃           | 126| 8.69         |
| 6  | 25.26   | 4-(2-Hydroxy ethyl)phenol                           | C₆H₁₀O₂           | 138| 1.1          |
| 7  | 39.98   | 4,2′-Dihydroxychalcone                             | C₁₅H₁₂O₃          | 240| 78.98        |
| 8  | 40.92   | 3,7-Dimethyl-3,7-dihydro-1H-purine-2,6-dione       | C₁₂H₁₄N₂O₂        | 180| 0.67         |
| 9  | 48.83   | Bis(2-ethylhexyl)phthalate                          | C₂₄H₂₈O₄          | 390| 0.54         |
| 10 | 49.40   | (1-Phenyl-1-butenyl)benzene                        | C₁₆H₁₆             | 208| 0.97         |
| 11 | 52.03   | 1,1-Dicyano-2-methyl-4-(p-cyanophenyl)propene      | C₁₃H₁₄N₃          | 207| 5.53         |
| 12 | 52.42   | [(1-Methyl-2,2-diphenylcyclopropyl)sulfanyl] benzene| C₂₂H₂₀S           | 316| 1.43         |
(2, 4, 6, 7, 9, and 11), exposure time (up to 120 min), ZnO NPs dose (10, 25, 50, 75, and 100 mg), initial MG concentration (5, 10, 15, 20, 20, and 30 mg L\(^{-1}\)), and dissolved electrolytes (NaCl, Na\(_2\)CO\(_3\), NaHCO\(_3\), NaNO\(_3\), and Na\(_2\)SO\(_4\)). In each test, 50 mL of MG solution with a specified concentration were stirred with the selected mass of ZnO NPs under UV irradiation for the required time at 25 °C. After that, the solution was centrifuged to remove suspended ZnO NPs and the residual MG concentration was measured using UV–vis spectroscopy. The pH of the solution was adjusted using 0.1 M solution each of NaOH and HCl.

2.8. Chemical oxygen demand (COD) measurements

The COD was examined using the dichromate reflux method (Closed Reflux, Titrimetric Method) (American Public Health Association 2017). In brief, for 2 hours, the sample was refluxed with HgSO\(_4\), a known volume of standard K\(_2\)Cr\(_2\)O\(_7\), and H\(_2\)SO\(_4\), then titrated with ferrous ammonium sulfate (FAS), using ferroin as an indicator. Instead of a dye sample, bidistilled water was used in a blank titration. COD as mg O\(_2\)/L was calculated using Equation (1):

\[
\text{COD} = (A - B) \times M \times 8000 / \text{mL sample}
\]  
(1)

where A=mL of FAS used for the blank, B=mL of FAS used for the sample, M=molarity of FAS, and 8,000=milliequivalent weight of oxygen (8) x 1,000 mL/L.

![Figure 3](https://example.com/figure3.png)

**Figure 3** | (a) UV–vis spectra showing the formation of ZnO NPs by the bioreduction activity of CTJLE, (b) inset the color changes from light to brownish yellow, indicating ZnO NPs formation, (c) the optical band gap energy determination of ZnO NPs using Tauc’s model for \(n=1/2\), (d) TGA curve of the biogenic synthesized ZnO NPs, and (e) FTIR spectrum of CTJLE and the biogenic synthesized ZnO NPs. Please refer to the online version of this paper to see this figure in color: [http://dx.doi.10.2166/wst.2021.638](http://dx.doi.10.2166/wst.2021.638).
2.9. Reusability study
The reusability of the catalyst to be used in photocatalytic removal is one of the most important characteristics in realistic and large-scale applications. The ZnO NPs were applied for five runs using a 75 mg catalyst dose, a 20 mg L\(^{-1}\) pollutant concentration, and a 50 mL solution volume for 1 hour. Prior to reuse, the spent ZnO NPs were collected by centrifugation, washed three times with water and ethanol, and dried at 110 °C in an oven for 2 hours before being reused for a new batch of MG dye solution.

2.10. Mechanism of photocatalytic degradation
The reaction mechanism was accomplished by using three reagents of different affinities for different oxidizing species during the photocatalytic removal of MG. The used reagents are isopropanol (IP), disodium salt of ethylenediaminetetraacetic acid (EDTA-2Na), and 1,4-benzoquinone (BQ) to capture hydroxyl radicals, electron–hole pairs, and superoxide radicals, respectively. The typical procedures involved the incorporation of 1 mmol of the capturing reagents with about 50 mL of 20 mg L\(^{-1}\) of MG. This was conducted for 1 hour under UV light in the presence of 75 mg of biosynthesized ZnO at pH 10.

3. RESULTS AND DISCUSSION

3.1. Phytochemical screening of organic compounds in CTJLE by GC/MS
A GC/MS analysis was performed to identify the phytochemical constituents present in the aqueous CTJLE. The chromatogram shows several peaks of bioactive compounds at different retention times, as shown in Figure 2(a). Twelve main compounds were tentatively identified by GC/MS and the detailed information about these phytochemicals is listed in Table 1 and their structures are shown in Figure 2(b). Majorly, five compounds have the highest peak areas: 4,2’-dihydroxychalcone (78.98%), 5-hydroxymethylfurfural (8.69%), 1,1-dicyano-2-methyl-4-(p-cyanophenyl)propene (3.53%), propylene glycol (1.26%), and 4-(2-hydroxy ethyl)phenol (1.1%). Further GC/MS revealed the presence of bioactive phytochemical constituents such as sugars, amides, alcohols, aldehydes, ethers, ketones, carboxylic acids, amino acids, fatty acids, alkaloids, phenolic compounds, flavonoids, tannins, and terpenoids in CTJLE (Shahat et al. 2001; Kadioglu et al. 2016). These bioactive phytochemical constituents can act as a key factor for the bioreduction of metal ions to ZnO NPs and their stabilization. Based on the GC/MS results and published researches, the most probable mechanism for ZnO NPs formation is shown in Figure 2(c). A complex is formed by bonding between Zn\(^{2+}\) ions and chalcone molecules in aqueous medium. This may be followed by the formation of Zn(OH)\(_2\). Then, heating of either the complex or the hydroxide led to the formation of ZnO NPs via oxidation by air oxygen. Formed ZnO is surrounded by organic moieties (capped), preventing further growth of the nanoparticles (El-Belely et al. 2021; Huang et al. 2021).

3.2. Characterization of the biosynthesized ZnO NPs
3.2.1. Optical characterization
The formation of ZnO NPs was observed by the gradual color change of the solution from yellow to yellowish-brown, which was attributed to the surface plasmon resonance (SPR) of the synthesized NPs as shown in the inset of Figure 3(b). The bioreduction of Zn\(^{2+}\) to ZnO NPs was mainly due to the phytochemicals present in buckthorn leaf extract (Sharmila et al. 2019). Figure 3(a) represents the UV–vis spectra of zinc acetate, CTJLE, and the synthesized ZnO NPs. The aqueous solution of zinc acetate showed a broad peak at 222 nm. The leaf extract showed a specific peak at 220 nm, which corresponds to polyphenolic compounds present in the extract. The absence of a peak at 220 nm in the ZnO NPs spectrum indicated that polyphenolic compounds react with zinc acetate to form ZnO NPs. The maximum absorbance peak was obtained at 305 nm. The bandgap energy of ZnO NPs was calculated using Tauc’s formula:

\[
(\alpha h\nu)^{1/n} = B (h\nu - E_g)
\]

where \(\alpha\) is the absorption coefficient, \(h\) is Planck’s constant, and \(\nu\) is the frequency (\(\nu = c/\lambda, \lambda\) is the wavelength, \(c\) is the light speed) (Kannan et al. 2020). For the allowed direct bandgap, the value of \(n\) was equal to 1/2. Exponent \(n\) values of 1/2, 2, 3/2, and 3 corresponded to the allowed direct, allowed indirect, forbidden direct, and forbidden indirect transitions, respectively (Sayilk et al. 2007). B is a constant and is generally called the band tailing parameter. Thus, the band gap energies were
obtained graphically by plotting \((\alpha h)^2\) vs. \(h\) for direct transition, extrapolating the linear part on the abscissa (Figure 3(c)). The band gap energy of ZnO NPs was 3.01 eV. Therefore, it was confirmed that ZnO NPs are the most efficient photocatalysts in the UV region for the photodegradation of MG dye. It can be noted that the \(E_g\) value of ZnO (3.01 eV) was much smaller than the bulk value of ZnO (3.37 eV); this bandgap narrowing is usually associated with a quantum confinement effect when the particle size is reduced to the nanoscale.

### 3.2.2. TGA

Figure 3(d) shows the TGA curve of the biosynthesized ZnO NPs, which demonstrated significant weight losses with increasing temperature from 50 °C to 400 °C. Firstly, a 10% weight loss was observed in the range 50 °C–150 °C, which may be assigned to the vaporization of adsorbed water molecules on the ZnO NPs surface. The steep weight loss at 150 °C– 400 °C (27.5%) may be due to the thermo-oxidative decomposition of ZnO NPs (Pai et al. 2019). There was no significant weight loss above 400 °C, and the total weight loss after 600 °C exposure was approximately 37.5%, indicating that the ZnO NPs were thermally stable.

### 3.2.3. FTIR

FTIR spectroscopic analyses were carried out to determine the vibration characteristics of chemical functional groups located on the surface of the as-synthesized ZnO NPs. Here, comparative FTIR spectra illustrate absorption peaks in a wavenumber range from 400 to 4,000 cm\(^{-1}\) (Figure 3(e)). The FTIR spectrum of CTJLE showed major peaks in the region of 3,415 and

![Figure 4](http://iwaponline.com/wst/article-pdf/85/2/664/998272/wst085020664.pdf)

**Figure 4** | (a) X-ray diffraction (XRD) pattern, (b) FESEM images at different magnifications, and (c) EDAX spectra of the biosynthesized ZnO NPs.
1,637 cm\(^{-1}\). These peaks were attributed to O–H stretching and possible stretching of the N–H group of amides. The peaks at 2,924 and 1,059 cm\(^{-1}\) indicate the existence of unsaturated (C–N) groups and C–H bending vibration, respectively.

The FTIR spectrum of ZnO NPs (Figure 3(e)) displayed a peak at 1,416 cm\(^{-1}\), indicating bending vibration of the CH\(_3\) group. In addition, another weak peak at 3,446 cm\(^{-1}\) was attributed to the adsorbed water molecules, and the characteristic Zn–O peak was observed at 470 cm\(^{-1}\) (Pai et al. 2019). The small shifting of the peaks probably implied that polyphenols, organic acids, and aliphatic amines were stabilizing agents in the synthesis.

### 3.2.4. X-ray diffraction (XRD)

Utilizing XRD analysis, the phase structure and its crystallite size were calculated. The formation of ZnO NPs with a wurtzite structure was revealed by the XRD pattern shown in Figure 4(a). The strong intensity of the diffraction peaks exhibits the crystallinity of the as-synthesized ZnO NPs. These peaks at 2\(\theta\) of 31.77\(^{\circ}\), 34.43\(^{\circ}\), 36.3\(^{\circ}\), 47.5\(^{\circ}\), 56.6\(^{\circ}\), 62.9\(^{\circ}\), 67.9\(^{\circ}\), 72.6\(^{\circ}\), and 76.9\(^{\circ}\) were indexed as (1 0 0), (0 0 2), (1 0 1), (1 0 2), (0 1 0), (1 0 2), (2 1 2), (0 0 4) and (2 0 2) planes, respectively, of ZnO, in good agreement with the standard data of the COD Card number: 9004180 and the corresponding lattice parameters (\(a = b = 3.25\) and \(c = 5.2\)). Other than the ZnO phase, no other peaks were observed, ensuring the high phase purity of the synthesized ZnO NPs. The Debye–Scherrer's formula was utilized to determine the average crystallite size of the prepared ZnO NPs, which was 11 nm.

### 3.2.5. FESEM and EDAX

The morphology of the biosynthesized ZnO sample was also identified by using FESEM. Figure 4(b) shows images of ZnO at different magnifications. These images show aggregations of ZnO NPs with closely packed, nearly spherical,

![Image](attachment:ZnO_NPs.png)

**Figure 5** | HRTM images (a, and b), SAED pattern (c), and particle size distribution (d) of ZnO NPs.
and randomly oriented particles with a narrow space between them. The narrow space between particles and their aggregation may have occurred because the synthesis was carried out in an aqueous medium and the high surface energy of ZnO NPs (Madhumitha et al. 2019). The elemental structure of ZnO nanoparticles was 89% zinc and 11% oxygen, as shown in the EDAX spectrum in Figure 4(c). No additional peaks were observed, which confirmed the purity of the sample.

3.2.6. HRTEM

The shape and size of ZnO NPs were analyzed as dark spots of irregular shape with a size of 8–11 nm as observed in HRTEM images (Figure 5(a) and 5(b)). SAED displays well defined and sharp spotted diffractions, confirming the consistent crystalline nature of ZnO NPs (Figure 5(c)). This matched the XRD pattern peaks, which confirmed the creation of ZnO NPs crystals by the reduction of Zn$^{2+}$ ions using CTJ. Figure 5(d) shows the particle size distribution curve of ZnO NPs and illustrates that the average particle size was about 10 nm.

3.2.7. Brunauer–Emmett–Teller (BET) analysis

The catalytic efficiency of a material is substantially affected by its surface area where the reactions take place. The higher surface area normally corresponds to higher catalytic activity. The BET surface area and non-local density functional theory/grand canonical Monte Carlo (NLDFT/GCMC) pore size of ZnO were investigated using N$_2$ adsorption and desorption measurements at 77 K. The sorption isotherm of ZnO NPs is shown in Figure 6(a). The isotherm can be classified as Type IV, whose final plateau was reduced to a single point according to IUPAC. In addition, its hysteresis loop is Type H3, which refers to mesoporous solid (Thommes et al. 2015; Moghaddas et al. 2020). The specific surface area of ZnO was found to be 5.2 m$^2$/g as calculated by the BET equation in its regular range of applicability and adopting a value of 16.2 Å for the cross-section area of the N$_2$ molecule. However, the total pore volume at saturation pressure and stated as liquid volume was found to be 0.02 cm$^3$/g for ZnO. Also, the pore radius calculated by the NLDFT/GCMC distribution curve was found to be 6.7 nm, as seen in the inset in Figure 6(b).
3.2.8. PZC

The PZC value is an intensive property that depends on the surface chemical and physical structure and the preparation procedure. Results indicated that the PZC of ZnO NPs was about 7 (Figure 6(c)). This means that the surface of ZnO NPs is positively charged at pH < 7 and negatively charged at pH > 7. In the latter situation, the surface of tested ZnO NPs becomes suitable for the adsorption of cationic dyes such as MG.

3.3. Evaluation of the performance of ZnO NPs for MG photocatalytic degradation

The catalytic performance of the as-synthesized ZnO NPs was examined using MG as a target pollutant under different conditions. At original pH 9.5, 20 mg L⁻¹ MG solution was used to conduct photodegradation experiments at RT for 1 hour. Experiments were carried out under the conditions of UV light without ZnO NPs photocatalyst, and with 50 mg of ZnO NPs in the dark, under sunlight, and under UV light irradiation. The degradation percentage was calculated according to Equation (3):

\[
\text{Degradation \%} = \left( \frac{C_0 - C_t}{C_0} \right) \times 100
\]

where \(C_0\) is the initial MG concentration and \(C_t\) is the concentration after time t of treatment.

During the photodegradation process, a decrease in the MG absorbance at 617 nm was observed, indicating the decomposition of MG (Figure 7(a)). The highest MG degradation of 82.9 ± 0.15% was obtained with ZnO NPs under UV light, followed by 65.2 ± 0.16% with ZnO NPs under sunlight. MG concentration was decreased by 20 ± 0.25% with ZnO NPs in the dark, which could be attributed to the adsorption process. No degradation was observed in the absence of ZnO NPs under UV light. This demonstrated the excellent photocatalytic activity of ZnO NPs for MG decomposition under UV light.

3.3.1. Effect of pH

pH is a critical operational parameter for assessing the effectiveness of the photocatalytic degeneracy of various contaminants in wastewater. The effect of pH was studied in the range from 2 to 11 using a 20 mg L⁻¹ MG solution, over a ZnO photocatalyst (50 mg) under UV irradiation. The degradation efficiency was at a minimum (7.5 ± 0.1%) at pH 2. It increased with increasing pH, reaching its maximum value (97.4 ± 0.21%) at pH 11, as seen in Figure 7(b). This was due to the dependency of MG adsorption on the surface charge of ZnO NPs, which is consecutively dependent on pH. As ZnO has a PZC of 7, the ZnO surface is positively charged (at acidic pH), which decreased the active sites available for adsorption of a cationic dye like MG. At pH > PZC, the ZnO surface is negatively charged (at pH 11). Therefore, at alkaline pH, the adsorption of MG will be improved as a result of the increase in the number of surface deprotonated hydroxyl groups at the ZnO surface. Therefore, the degradation will be enhanced. Rabie et al. (2020) discovered that at higher pH values (pH 11), some dye molecules may change to the colorless leuco form, which may contribute to photodegradation efficiency. Thus, pH 10 was chosen as the optimum pH value for the degradation process.

3.3.2. Effect of ZnO catalyst dose

The increase in the proper dosage of the ZnO will enhance the rate of generation of electron/hole pairs and hence the formation of OH⁻ radicals, which leads to an increase in photodegradation efficiency. The decolorization activity of MG increased as the photocatalyst amount increased (to the optimum value of 75 mg) and then decreased, as represented by Figure 7(c). An increase in the amount of the photocatalyst resulted in increasing the active sites on the catalyst surface, which led to the development of the hydroxyl radical’s formation (Abukhadra et al. 2019). Nevertheless, a more negative effect was shown by a further increase in the amount of the catalyst that was assigned to the masking effect that may inhibit the photons reaching the inner surface of the catalyst. This effect results from the piling up of particles of the catalyst (Devi et al. 2020). Also, the penetration of light decreased as the dosage of the catalyst increased due to the capping effect of the hanged particles, and subsequently the photodegradation rate decreased (Kuzhalosai et al. 2013).

3.3.3. Effect of irradiation time

Experiments were carried out to study the kinetics of MG photodegradation on ZnO NPs. The operating conditions were as follows: an initial MG concentration of 20 mg L⁻¹, a ZnO NPs dosage of 1.5 g L⁻¹, and a pH of 10 at room
temperature. Extending the exposure time results in better removal of MG from the aqueous solution. This increase in the degradation efficiency may be associated with the increase in the generated number of hydroxyl and superoxide radicals at longer exposure times. Obviously, at the beginning, the degradation of MG was rapid, followed by a more gradual process as illustrated in Figure 7(d). The fast removal at the beginning may be due to the rapid adsorption of the dye molecules on the ZnO surface, and the intraparticle diffusion is probably responsible for the following slower removal. With an initial dye concentration of 20 mg L\(^{-1}\), 96.5 ± 0.24% of MG removal was achieved within 1 hour.
3.3.4. Effect of initial MG concentration

Figure 7(e) depicts the effect of the initial MG concentration on the degradation process by varying its concentration from 5 to 30 mg L\(^{-1}\) while fixing the catalyst dose of ZnO at 75 mg. It was observed that the degradation efficiency initially increased for dye concentrations up to 20 mg L\(^{-1}\), and a further increase in concentration led to a gradual decrease in MG degradation. Therefore, the MG removal efficiency could be enhanced by lowering the dye initial concentration. The degradation efficiency was strongly influenced by the possibility of OH\(^-\) radical formation on the catalyst surface and the reaction with MG molecules (Mohamed et al. 2018). As the initial concentration of MG molecules increased, the probability of reaction between oxidizing species and MG will also increase, which results in raising the degradation efficiency (Anju et al. 2019). Conversely, MG degradation efficiency decreased as the concentration further increases. This was attributed to the decrease in OH\(^-\) radical generation on the catalyst surface as the active sites were wrapped by dye molecules. Additionally, by preventing photons from reaching the photocatalyst surface, the number of photons absorbed by the photocatalyst is reduced (Devi et al. 2020; Rabie et al. 2020).

3.3.5. Effect of different inorganic anions

The wastewater of dye industry contains a considerable number of inorganic anions such as carbonates, bicarbonates, chlorides, nitrates, and sulfates. These salts cause colloidal instability, increase mass transfer, and reduce surface contact between the target dye molecule and the photocatalyst (Chong et al. 2010). The investigation of the impact of these dissolved electrolytes such as NaCl, Na\(_2\)CO\(_3\), NaHCO\(_3\), NaNO\(_3\), and Na\(_2\)SO\(_4\) on the degradation of MG dye was carried out under UV...
irradiation over ZnO NPs, and the results are shown in Figure 7(f). The concentration of these anions varied from 0.5 to 5%, and all other experimental parameters were kept constant. In the presence of CO$_3^{2-}$/C0$_3$ and HCO$_3^{-}$/C0$_3$, MG degradation decreased from 96.5 ± 0.24% to 84.2 ± 0.68%. These ions have the potential to scavenge OH$^-$ radicals (Rauf & Ashraf 2009):

$$\text{CO}_3^{2-} + \text{OH}^- \rightarrow \text{CO}_3^{-} + \text{OH}^- \quad (4a)$$

$$\text{HCO}_3^{-} + \text{OH}^- \rightarrow \text{CO}_3^{-} + \text{H}_2\text{O} \quad (4b)$$

$$\text{CO}_3^{-} + \text{OH}^- \rightarrow \text{HCO}_3^{-} \quad (4c)$$

In the presence of chloride ion, the degradation efficiency decreased from 96.5 ± 0.24% to 90.7 ± 0.64% due to the hole scavenging properties of chloride ion:

$$\text{Cl}^- + h_{\text{VB}} \rightarrow \text{Cl}^- \quad (5)$$

The chloride radical anions formed can also block the active sites of the catalyst surface (Liao et al. 2001). Inversely, the presence of nitrate ions increased the degradation efficiency from 96.5 ± 0.24% to 98.4 ± 0.4% due to the direct or indirect hydroxyl radical formation as follows (Zhu et al. 2005; Wang et al. 2011a, 2011b):

$$\text{NO}_3^{-} + \text{hv} \rightarrow \text{NO}_2^{-} + \text{O} \quad (6a)$$

$$\text{NO}_3^{-} + \text{H}_2\text{O} + \text{hv} \rightarrow \text{NO}_2^{-} + 2\text{OH}^- \quad (6b)$$

$$\text{O} + \text{H}_2\text{O} \rightarrow 2\text{OH}^- \quad (6c)$$

Finally, the presence of SO$_4^{2-}$ ions enhanced the photocatalytic degradation (from 96.5 ± 0.24% to 98.4 ± 0.4%) by driving the dye molecule to bulk interface, increasing aqueous ionic strength, and forming SO$_4^{2-}$ via reaction of adsorbed SO$_4^{2-}$ with generated valence band holes. This reaction between SO$_4^{2-}$ and photogenerated $h_{\text{VB}}$ on the photocatalyst surface can prevent

| Table 2 | Comparison of the photocatalytic degradation of MG using as-prepared ZnO NPs and other reported ZnO-based photocatalysts |
| --- | --- |
| **Photocatalyst** | **Preparation method** | **Light source** | **MG conc. (mg/L)** | **Degradation (%)** | **Catalyst dose (g L$^{-1}$)** | **Time min** | **Ref.** |
| ZnO | Biosynthesis | Visible | – | 79.06 | 0.1 | 120 | Yulizar et al. (2020) |
| La$_2$CuO$_4$–ZnO | Biosynthesis | Visible | – | 91 | 0.1 | 120 | Yulizar et al. (2020) |
| Pt/ZnO | Photo-assisted deposition method | Visible | 100 | 100 | 0.8 | 30 | Mohamed et al. (2016) |
| Chitosan/ZnO | Microwave irradiation | Visible | 5 | 54 | 1 | 90 | Saad et al. (2020) |
| Chitosan/Ce–ZnO composites | Microwave irradiation | Visible | 5 | 87 | 1 | 90 | Saad et al. (2020) |
| Ir-doped ZnO | Sonochemical technique | Visible | 10 | 90 | 0.2 | 120 | Babajani & Jamshidi (2019) |
| ZnO/MWCNT nanocomposites | Ball milling–hydrothermal method | Visible | 30 | 79 | 0.1 | 60 | Arsalani et al. (2020) |
| ZnO-doped Dy$_2$O$_3$ | Precipitation method | Visible | 10 | 99 | 0.3 | 60 | Josephine et al. (2015) |
| Polydiphenyl acetylene–ZnO | Dispersion methodology | UV | 5 | 88 | 0.67 | 150 | Dimova et al. (2020) |
| ZnO NPs | Biosynthesis | UV | 20 | 96.5 ± 0.24 | 1.5 | 60 | This work |
the recombination of electrons and holes, and thus enhanced photodegradation rate (Wang et al. 2011b):

$$\text{SO}_2^{2-} + h^+_\text{(VB)} \rightarrow \text{SO}_4^{-}$$  \hspace{1cm} (7a)

$$\text{SO}_4^{-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + \text{OH}^{-} + \text{H}^+$$  \hspace{1cm} (7b)

### 3.3.6. Determination of COD

As the decolorization study can be correlated only with the modification of the chromogenic group and not with the real mineralization of MG, the determination of the COD is essential. The COD of MG dye was estimated before and after the photodegradation reaction. The COD is a measure of the oxygen equivalent of the organic content in a sample that can be oxidized to CO$_2$ and H$_2$O by a strong oxidant (American Public Health Association 2017). The initial dye concentration and catalyst loading taken for COD measurement were 20 mg L$^{-1}$ and 75 mg, respectively. Figure 8(a) shows the reduction of COD from 32.8 ± 0.16 to 1 ± 0.15 mg O$_2$ L$^{-1}$ after degradation and is in good agreement with the previously determined data by the UV method.

### 3.3.7. Stability and reusability of the catalyst

To make the process cost-effective and greener, the stability and reusability of ZnO NPs towards photocatalytic degradation of MG were evaluated (Figure 8(b)). Thus, the ZnO photocatalyst was recovered from the reaction mixture through centrifugation, rinsed thoroughly with distilled water and ethanol, dried at 110 °C, and subsequently reused for five cycles. After the fifth run, the efficiency decreased slightly from 96.5 ± 0.24% to 92.9 ± 0.2%, probably due to the loss of some catalyst during centrifugation. The ZnO photocatalyst was characterized by XRD before and after recycling to elucidate its structural stability.
(Figure 8(c)). No difference was observed between the two XRD spectra indicating the good structural stability of the catalyst even after five recycling runs. To evaluate MG degradation by the synthesized ZnO NPs photocatalyst, the obtained results from this study were compared with previously reported ZnO-based photocatalysts in the literature (Table 2). Many of the published work used a composite of ZnO with other materials whose synthesis can be costly and environment threatening. Conversely, bare green synthesized ZnO NPs in this work yielded a better photodegradation than most of these reported ones. One limitation was the use of UV irradiation compared with solar irradiation. It can be concluded that ZnO is a stable, robust, effective, easily recyclable, and separable photocatalyst for dye removal. Thus, it is a promising material for environmental remediation.

3.3.8. Degradation kinetics

The degradation rate of MG dye on 1.5 g L\(^{-1}\) of ZnO NPs photocatalysts was estimated under UV irradiation. The kinetics of dye degradation using ZnO NPs is shown in Figure 9(a) and 9(b). In addition, the kinetic rate constant (k) value was determined for the degradation of MG onto the photocatalysts by applying the frequently used Langmuir–Hinshelwood, pseudo-first-order model (\(R^2 = 0.922\)) and the newly applied network model (\(R^2 = 0.824\)) (Tekin et al. 2019) as shown in Equations (8) and (9), respectively:

\[
\ln\left(\frac{C_t}{C_0}\right) = -kt \quad (8)
\]

\[
t/(C_0 - C_t) = \left(\frac{k_\text{a}}{k_\text{b}}\right) + \left(\frac{1}{k_\text{a}}\right)[\ln\left(\frac{C_0}{C_t}\right)(C_0 - C_t)] \quad (9)
\]

where \(C_0\) and \(C_t\) are MG initial concentration and at time t, respectively, \(k\) is 1st order rate constant and \(k_\text{a}\) and \(k_\text{b}\) are network model constants.

Data fitted well the pseudo-first-order kinetics (Pruna et al. 2018; Tekin et al. 2019) with the apparent rate constant (k) of \(5.4 \times 10^{-2} \text{ min}^{-1}\), which was larger than that of other photocatalysts utilized in the recently published works (Kundu & Mondal 2019; Antony & Yadav 2020; Dimova et al. 2020; Liu et al. 2020; Solís-Casados et al. 2020; Sreedharan & Ong 2020; Tao et al. 2020). In addition, the pseudo-first-order rate constant was plotted against different initial MG concentrations as shown in Figure 9(c). The rate constant increased with increasing initial MG concentration up to the maximum value of \(5.4 \times 10^{-2} \text{ min}^{-1}\) at 20 mg L\(^{-1}\) due to the increase in MG molecules that reached to ZnO active sites and were then photodegraded by active species. Further increase in concentration resulted in a decrease in the rate constant due to the occupation of most ZnO active sites by MG molecules and the more intense color which prevented penetration of light.
(Sreedharan & Ong 2020). Thus, it may be concluded that the rate of photocatalytic degradation is dependent on MG concentration at optimum conditions. It was observed that the values of degradation efficiency for different initial MG concentrations are consistent with the kinetic data.

### 3.3.9. Degradation mechanism

Many factors can contribute to improving the photocatalytic properties of ZnO such as bandgap energy, crystal structure, surface area, and recombination of electron-hole pairs (Topkaya et al. 2014). Generally, there are two steps involved in the photocatalytic degradation process: first the adsorption of the contaminants on the surface of photocatalysts, and then the degradation of the contaminants. In the case of MG, molecules can be adsorbed onto the imprinted layer of the catalyst to form a moderately stable complex. When the ZnO NPs photocatalyst was illuminated under the excitation of UV light, it could absorb light and generate electron–hole pairs leading to the formation of the reactive species; \(e^{-}, h^{+}, \text{OH}^{-}, \text{and O}_2^{-}\). Thus, the photocatalytic degradation mechanism of MG over ZnO NPs was proposed using active radicals trapping experiments. The photodegradation was studied using EDTA-2Na (electron–hole pairs scavenger) (Li et al. 2015), 1,4-benzoquinone (BQ) (superoxide radicals' scavenger) (Tang et al. 2013), and isopropanol (IP) (hydroxyl species scavenger) (Van Doorslaer et al. 2012) in the reaction solution (Figure 10(a)) (Huang et al. 2015). Adding BQ slightly decreased the photocatalytic degradation of MG dye from 96.5 ± 0.25% to 90.7 ± 0.25%. However, the degradation rates were considerably reduced to 53.8 ± 0.53% and 38.4 ± 0.1% with the addition of a scavenger for electron–hole pairs (EDTA-2Na) and OH\(^{-}\) (IP), respectively. As can be seen, the removal rate decreased in the presence of scavengers, which presents at the following trend: IP > EDTA-2Na > BQ. Hence, the main reactive species during the photocatalytic degradation of MG were the hydroxyl radicals and electron–holes pairs.

When the photons (\(h\nu\)) irradiate on the photocatalyst (ZnO) with energy equal to or more than its bandgap energy (3.01 eV), the electrons (\(e^{-}\)) in the valence band (VB) are excited and jump to the conduction band (CB) leaving behind equivalent holes (\(h^{+}\)) in the VB:

\[
\text{ZnO} + h\nu = \text{ZnO} (h^{+}_{\text{VB}}) + \text{ZnO} (e^{-}_{\text{CB}})
\]  

where \(h\nu\) is the essential energy required to transfer the electron from the VB to the CB. These photoexcited electrons can reduce dissolved oxygen to generate superoxide radical anions (\(\text{O}_2^{-}\)), while the photoexcited holes in VB can oxidize \(\text{H}_2\text{O}\) and \(\text{OH}^{-}\) to generate hydroxyl radicals (OH\(^{-}\)). These generated radicals are highly active and have the ability to destroy MG molecules to \(\text{CO}_2\) and \(\text{H}_2\text{O}\) (Houas 2001):

\[
\begin{align*}
\text{e}^{-}_{\text{CB}} + \text{O}_2 & = \text{O}_2^{-} \\
\text{O}_2^{-} + \text{H}_2\text{O} & = \text{HO}^{-} + \text{OH}^{-}
\end{align*}
\]

Simultaneously, the photoinduced holes could be intercepted by surface hydroxyl groups (or \(\text{H}_2\text{O}\)) on the surface of the photocatalyst to produce hydroxyl radicals (OH\(^{-}\)) (Saikia et al. 2015):

\[
\begin{align*}
\text{OH}^{-} + h^{+}_{\text{VB}} & = \text{OH}^{•} \\
\text{H}_2\text{O} & \rightarrow (\text{H}^{+} + \text{OH}^{-}) + h^{+}_{\text{VB}} \rightarrow \text{OH}^{•} + \text{H}^{+}
\end{align*}
\]

Finally, these highly active radicals achieved degradation of MG molecules to yield carbon dioxide and water as follows (Figure 10(b)):

\[
\text{OH} + \text{MG} + \text{O}_2^{-} \rightarrow \text{products (CO}_2 \text{ and H}_2\text{O)}
\]

### 4. CONCLUSION

According to GC/MS analysis, mesoporous ZnO NPs were green synthesized, most likely via complexation of Zn\(^{2+}\) with chalcone from buckthorn leaves, followed by oxidation in air during heating. The synthesized ZnO NPs had near-spherical crystals with a mean size of 11 nm, surface area of 5.2 \(\text{m}^2 \text{g}^{-1}\) and a total pore volume of 0.02 \(\text{cm}^3 \text{g}^{-1}\). They showed excellent
photocatalytic degradation of MG (96.5 ± 0.24% within 1 hour using 1.5 g L⁻¹ ZnO at pH 10 and 298 K) and stability (92.9 ± 0.2% after five cycles). The pseudo-first-order kinetic model fitted the experimental data well. Furthermore, scavenging experiments revealed that hydroxyl radicals had the greatest impact on the photocatalytic process. Thus, the biosynthesized ZnO is an ecofriendly nanophotocatalyst for the efficient removal of MG from aqueous solutions.

DATA AVAILABILITY STATEMENT
All relevant data are included in the paper or its Supplementary Information.

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