

Photocatalytic Degradation of Brilliant Green Using ZnO Nanoparticles Synthesized via Green and Chemical Methods

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ORIGINAL STUDY

Photocatalytic Degradation of Brilliant Green Using ZnO Nanoparticles Synthesized via Green and Chemical Methods

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Abstract

The increasing contamination of environment by synthetic dyes poses a significant environmental challenge due to their toxicity and persistent. Photocatalytic degradation using semiconductor materials like zinc oxide (ZnO) has emerged as an effective approach for dye removal. This study explores the synthesis of ZnO nanoparticles through four different approaches: thermal decomposition of zinc(II) complex of salicylaldehyde thiosemicarbazone (ZnO-SB), hydrothermal (ZnO-HT) and cold-temperature (ZnO-CT) method using zinc nitrate hexahydrate as precursor and green synthesis method (ZnO-G) using the leaf extract of *Annona Muricata* (Soursop). The evaluation of their efficiency in degrading dye pollutants under UV light irradiation was also carried out. Salicylaldehyde thiosemicarbazone (L) was synthesized using both conventional reflux heating and microwave methods, while its zinc(II) complex (ZnL₂) was synthesized by reflux heating. SEM analysis showed that ZnO NPs exhibit irregular spherical morphology, with ZnO-G displaying a densely packed structure whereas ZnO-HT, ZnO-CT and ZnO-SB exhibited a more porous morphology. XRD analysis revealed that ZnO-G, ZnO-HT, ZnO-CT and ZnO-SB crystallize in the hexagonal wurtzite phase with the average crystallite sizes of 18.00 nm, 43.09 nm, 29.22 nm and 19.27 nm, respectively, and optical studies showed that the bandgap energies of these materials are 3.25, 3.26, 3.38 and 3.45 eV, respectively. The photocatalytic performance was evaluated by examining the degradation of brilliant green (BG) dye under UV irradiation. Among all samples, ZnO-CT exhibited the highest photocatalytic activity, achieving 98% degradation of BG at 210 min, following first-order kinetics. The effects of various parameters on the photocatalytic degradation of BG were also investigated. This study highlights the potential of ZnO-CT as an effective material for the degradation of harmful and persistent BG dye in environmental applications.

Keywords: Zinc oxide nanoparticles, Schiff base, Hydrothermal, Soursop leaf extract, Photocatalytic degradation, Brilliant green

1. Introduction

Nanotechnology, which involves manipulating matter at the nanoscale, has attracted significant interest due to its potential in sustainable applications [1]. ZnO NPs stands out for their multifunctionality, large surface area, and high catalytic activity [2]. ZnO is a II-VI semiconductor with a 3.37 eV direct bandgap, existing primarily in hexagonal wurtzite, zinc-blende

and rock salt structures. These properties make ZnO an excellent candidate for the degradation of organic pollutants, effective UV light absorption and high electron mobility, enhancing photocatalytic efficiency [3]. It is also cost-effective, environmentally friendly, and relatively simple to synthesize [4]. Nanoparticles are synthesized two main approaches: the bottom-up method, which involves using assembling particles from atoms or molecules; and the top-down method,

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which involves breaking bulk materials into nanoscale particles using techniques. This versatility enables tailoring NPs properties to suit specific applications.

This study compares four distinct bottom-up methods for synthesizing ZnO NPs and evaluates their efficiency in the photocatalytic degradation of carcinogenic and mutagenic BG dye [5]. The first method involves thermal decomposition of Zn(II) Schiff base complexes (**ZnO-SB**) as shown in Fig. 1a which offers precise control of composition and morphology [6]. Schiff bases are a class of compound named after Hugo Schiff. They contain an azomethine ($-\text{HC}=\text{N}-$) or imine functional group ($>\text{C}=\text{N}-$), with thiosemicarbazone being a key subgroup. These bases, featuring oxygen, nitrogen and sulfur donor atoms, form stable metal complexes by coordinating with zinc ions [7], which upon calcination yield ZnO NPs. The second method is hydrothermal synthesis (**ZnO-HT**) that utilizes elevated temperatures and pressures in a water-based solvent (Fig. 1b) which offers the ability to produce ZnO NPs with highly crystalline NPs with controlled size and morphology [8]. The third method involves a novel cold-temperature synthesis (**ZnO-CT**) which is similar to co-precipitation method but performed at lower temperature within ice-liquid phase reactions (Fig. 1c), which minimizes NPs aggregation and promote uniform size distribution. The final method employs green synthesis using *Annona Muricata* (*A. muricata*) leaf extract (**ZnO-G**), where plant phytochemicals act as both a reducing and a stabilizing agent (Fig. 1d). This eco-friendly, and cost-effective method facilitates rapid synthesis and enhanced NPs stability [3]. *A. muricata* commonly known as graviola or soursop, is native to tropical regions of Central and South America, Western Africa and South East Asia. [9], and its bark, seeds and leaves contains potent phytochemicals widely used in traditional medicine [10]. These phytochemicals play a key role in reducing metal ions.

This study evaluates ZnO NPs synthesized by these four routes (**ZnO-G**, **ZnO-HT**, **ZnO-CT** and **ZnO-SB**), focusing on their unique structural and functional characteristics such as particle size, surface area,

crystallinity and stability that can influencing photocatalytic performance in the degradation of BG. BG dye is one of the cationic industrial dyes that exhibit both carcinogenic and mutagenic properties [5], posing various health risks and its resistance to biodegradation [11], hence making it a good test for evaluating the efficiency of the synthesised ZnO. The green synthesis method using *A. Muricata* leaf extract provides a natural capping agent from phytochemicals on the ZnO NPs [12], whereas chemical hydrothermal and cold-temperature methods offer precise control over pH and reaction conditions to optimize nanoparticles characteristics [8]. Additionally, thermal decomposition method derived from Zn(II) complex from salicylaldehyde thiosemicarbazone (**ZnL₂**) to produce ZnO NPs (**ZnO-SB**) has not been widely studied, therefore, the morphology and photocatalytic performance of its NPs would be interesting to explore. To date, there are no reports of the use of ZnO NPs derived from Zn(II) complex as photocatalyst. Therefore, the objectives of this work are to assess and compare the photocatalytic activities of ZnO NPs prepared through these four methods, with the goal of identifying the most effective synthesis approach for ZnO NPs for their application in the photocatalytic degradation of BG.

2. Methods

2.1. Materials and instrumentation

All chemicals used were obtained from Sigma Aldrich or Merck were analytical-grade and used without purification. Microwave-assisted synthesis of Schiff bases was performed with a Panasonic NN-SM33 oven (50 Hz, 800 W) in 30- and 100-ml microwave vessel. All of the dried products were tested by Whatman Partisil K6 60 TLC plates to identify the completion of the reaction using benzine and ethyl acetate as eluent. *A. Muricata* leaves were collected from Kg Penanjong, Tutong district, Brunei Darussalam. The photocatalytic dye degradation experiments used a Boekel Scientific's UV Crosslinker AH (1200 kW).

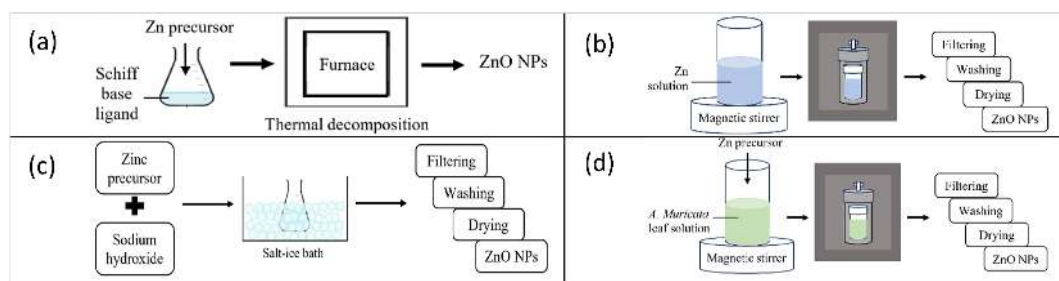


Fig. 1. General steps to produce ZnO NPs: (a) thermal decomposition, (b) hydrothermal, (c) co-precipitation (cold-temperature) and (d) green synthesis methods.

Several techniques characterized the synthesized compounds. Fourier-transform infrared (FTIR) spectra were recorded using a Shimadzu ATR IR Spirit spectrophotometer ($400\text{--}4000\text{ cm}^{-1}$). The UV–Visible absorbance (UV–Vis) spectra of ligand, metal complex, and photocatalytic dye degradation was measured on a Shimadzu 1900 UV–Vis spectrometer ($200\text{--}800\text{ nm}$), with BG dye's λ_{max} at 620 nm . The bandgap energies of NPs were measured from the UV–Vis reflectance (UV–DRS) spectra using Shimadzu UV-2600i ($300\text{--}800\text{ nm}$), at ambient temperature with BaSO_4 as the reference standard. Scanning electron micrograph-energy dispersive X-ray (SEM-EDX) using FESEM (JSM-7610 JEOL JAPAN) provided high-resolution images and elemental composition. The crystallinity and phase purity were determined using X-ray diffraction (XRD) analysis, Shimadzu XRD-700 (Cu $K\alpha$ radiation, 2θ ($20^\circ\text{--}80^\circ$)). Data were processed using OriginPro, Microsoft Excel 365, and ImageJ software. All experiments and measurements were performed at the Faculty of Science (FOS), UBD, otherwise stated.

2.2. Synthesis of ZnO NPs

The four methods used to produce ZnO NPs are shown in Fig. 2. The first method involves the synthesis of salicylaldehyde thiosemicarbazone (**L**) via conventional and microwave-assisted methods, and complexation with zinc(II) ion forming zinc(II) salicylaldehyde thiosemicarbazone (**ZnL₂**) via conventional method, followed by thermal decomposition to form ZnO (**ZnO-SB**), the second method is preparing ZnO via hydrothermal and calcination (**ZnO-HT**), the third

method is synthesizing ZnO at cold conditions at -2°C (**ZnO-CT**), and the fourth method is the green synthesis of ZnO using the leaf extract of *A. Muricata* leaves (**ZnO-G**).

2.3. Preparation of ZnO-SB

2.3.1. Synthesis of salicylaldehyde thiosemicarbazone (**L**)

Two methods were used to synthesize **L**: conventional method *i.e.*, heating under reflux, and green synthesis method *i.e.* the microwave-assisted synthesis method.

2.3.1.1. Heating under reflux method. Salicylaldehyde (0.2 mL , 1.92 mmol) and thiosemicarbazide (0.1746 g , 1.92 mmol) were added into ethanol and acetonitrile at 1:1 molar ratio (17 mL each) or water (20 mL). 2 drops of hydrochloric acid were added as catalyst. The reaction mixture was heated on a steam bath for 21 mins (solvent mixture) or 5 mins (water). After cooling, the resulting mixture was monitored by TLC in benzene and ethyl acetate of 2:1 molar ratio. A yellow solid product was immediately formed which was collected using gravity filtration, washed with cold ethanol, and left to dry. For product prepared from solvent mixture, crude yield: 0.1795 g (48%); m.p.: $218\text{--}220^\circ\text{C}$. The crude product was recrystallized in methanol to get pure product. Yield: 0.1052 g (28%); m.p.: 220°C . IR data (ν_{max} , cm^{-1}): $1615\text{ }\nu(\text{C}=\text{N})$, $1242\text{ }\nu(\text{C}-\text{O})$, $787\text{ }\nu(\text{C}=\text{S})$, $1092\text{ }\nu(\text{N}-\text{N})$, $3414\text{ }\nu(\text{O}-\text{H})$ and $3144, 3299\text{ }\nu(\text{N}-\text{H})$. For product prepared from water, crude yield: 0.1979 g (53%); m.p.: $218\text{--}220^\circ\text{C}$. The

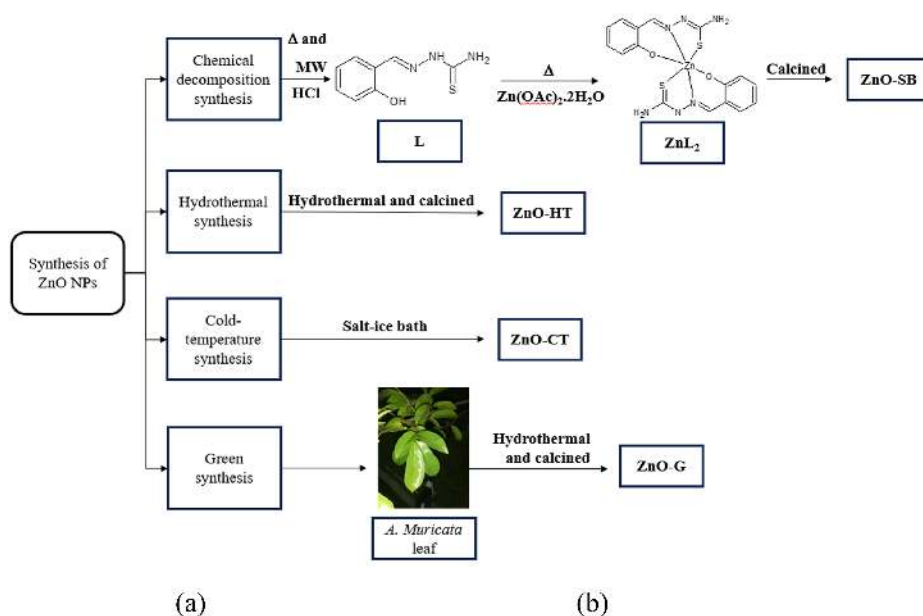


Fig. 2. The four methods used to synthesize ZnO NPs in this work.

crude product was recrystallized from methanol. Yield: 0.0774 g (18 %); m.p.: 220 °C. IR data ($\nu_{\max}$, cm^{-1}): 1615 $\nu(\text{C}=\text{N})$, 1242 $\nu(\text{C}-\text{O})$, 787 $\nu(\text{C}=\text{S})$, 1092 $\nu(\text{N}-\text{N})$, 3426 $\nu(\text{O}-\text{H})$ and 3144, 3305 $\nu(\text{N}-\text{H})$. Analysis calculated for $\text{C}_8\text{H}_9\text{N}_3\text{OS}$ (195.24 g mol^{-1}) (%): C, 49.22, H, 4.65, N, 21.52. Found: C, 48.96, H, 4.55, N, 21.34.

2.3.1.2. Microwave-assisted method. Salicylaldehyde (0.2 mL, 1.92 mmol) and thiosemicarbazide (0.1746 g, 1.92 mmol) were added into ethanolic and acetonitrile with 1:1 molar ratio (9 mL each) or water (20 mL), 2 mL of methanol and 2 drops of hydrochloric acid were added as catalyst into a microwave vessel. After cooling, the resulting mixture was monitored by TLC in benzene and ethyl acetate of 2:1 molar ratio. A yellow solid product was formed and further rotatory evaporated to get all the solid. For the product prepared from EtOH/MeCN, IR data ($\nu_{\max}$, cm^{-1}): 1615 $\nu(\text{C}=\text{N})$, 1247 $\nu(\text{C}-\text{O})$, 782 $\nu(\text{C}=\text{S})$, 1092 $\nu(\text{N}-\text{N})$, 3426 $\nu(\text{O}-\text{H})$ and 3150, 3310 $\nu(\text{N}-\text{H})$. For the product prepared from water, IR data ($\nu_{\max}$, cm^{-1}): 1615 $\nu(\text{C}=\text{N})$, 1247 $\nu(\text{C}-\text{O})$, 787 $\nu(\text{C}=\text{S})$, 1109 $\nu(\text{N}-\text{N})$, 3432 $\nu(\text{O}-\text{H})$ and 3155, 3310 $\nu(\text{N}-\text{H})$.

2.3.2. Synthesis of zinc(ii) salicylaldehyde thiosemicarbazone (ZnL_2)

$\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.0281 g, 0.13 mmol) and salicylaldehyde thiosemicarbazone (0.05 g, 0.26 mmol) were dissolved in methanol with molar ratio of 1:2 (metal: ligand molar ratio) and heated on a steam bath for 7 mins. After cooling, the resulting mixture was monitored by TLC in benzene and ethyl acetate of 2:1 molar ratio, forming a yellow solid, which was filtered, washed with cold methanol, and dried. Yield: 0.0256 g (33%); m.p.: 335 °C (decomposed). IR data ($\nu_{\max}$, cm^{-1}): 1593 $\nu(\text{C}=\text{N})$, 1274 $\nu(\text{C}-\text{O})$, 763 $\nu(\text{C}-\text{S})$, 1148 $\nu(\text{N}-\text{N})$, 3453 $\nu(\text{O}-\text{H})$ and 3167, 3313 $\nu(\text{N}-\text{H})$. Analysis calculated for $(\text{C}_8\text{H}_8\text{N}_3\text{OS})_2\text{Zn}$ (453.87 g mol^{-1}) (%): C, 42.34; H, 3.55; N, 18.52. Found: C, 38.309; H, 2.987; N, 16.025.

2.3.3. Synthesis of ZnO NPs (ZnO-SB)

Zinc(II) salicylaldehyde thiosemicarbazone (1 g) was transferred into a crucible and calcined at 600 °C for 2 h. The powdered **ZnO-SB** NPs (0.2372 g, 24%) were collected, ground and stored for further use.

2.4. Preparation of ZnO-HT

$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.7849 g, 6 mmol, 0.2 M) was added to distilled water (30 mL) in a beaker and the pH of the solution recorded was 4. NaOH (0.9599 g, 24 mmol, 0.8 M) was added dropwise to reach pH 11. The mixture was stirred for 15 mins before transferred to Teflon autoclave stainless steel and heated at 180 °C in

an oven for 2 h. The solution mixture containing ZnO NPs was decanted into a ceramic cubicle cup and calcined at 600 °C for 2 h. **ZnO-HT** powder (0.448 g, 25%) was collected, ground and stored for further use.

2.5. Preparation of ZnO-CT

$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (3.5699 g, 12 mmol, 0.2 M) was added into a beaker containing distilled water (60 mL). NaOH (1.9199 g, 48 mmol, 0.8 M) was added into the solution until the pH reached 11. The solution was then stirred for 15 min at room temperature, followed by an ice-salt bath for 6 h at -2 °C. The reaction mixture was later vacuum filtered. Powder **ZnO-CT** NPs (0.3581 g, 10%) collected were ground and stored for later use.

2.6. Preparation of ZnO-G

2.6.1. Extraction of *A. Muricata* leaves

A. Muricata leaves were collected from local trees at Kampung Penanjong, Tutong district in Brunei Darussalam. They were washed with tap water and rinsed with distilled water to remove any excess dust and debris. The leaves were air-dried at room temperature for an hour. They were cut into smaller pieces, and ground to fine powder. The extract powder (5.0 g) was added to distilled water (50 mL) in a beaker, and the mixture was stirred at 80 °C for 1 h. This process allows the extraction of natural substances from the powder. The solution was vacuum filtered and the leaf extract was used to prepare **ZnO-G**.

2.6.2. Synthesis of ZnO-G

$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.7849 g, 6 mmol, 0.2 M) was added into the leaf extract (30 mL) and stirred for 15 min. The pH of the solution recorded was 4. The reaction mixture was then transferred into a Teflon autoclave stainless steel and heated in an oven for 2 h at 180 °C. After cooling, the reaction mixture was transferred into a crucible and heated for 30 mins to reduce the volume of the solution. The brown paste obtained was annealed at 600 °C in a furnace for 2 h. The powdered **ZnO-G** NPs (0.4604 g, 26%) were collected, ground and stored for further use.

2.7. Photodegradation of ZnO NPs

Three different experiments were conducted to examine the photocatalytic degradation of BG dye using all synthesized ZnO NPs. These experiments aim to (i) identify the most effective photocatalyst amongst **ZnO-G**, **ZnO-HT**, **ZnO-CT** and **ZnO-SB** which give the highest BG degradation under UV light; (ii) assess the photocatalytic performance of the best-performing

ZnO NPs with and without UV light; and (iii) optimize parameters for the best-performing ZnO NPs, focusing on varying the pH of the solution (pH 7, 9 and 11) using NaOH, initial concentration of BG dye (5, 10 and 15 ppm), amount of catalyst (1, 5 and 10 mg) and the addition of 30% hydrogen peroxide (μl) as oxidant. H_2O_2

100 ppm of BG stock solution was prepared by dissolving 10 mg of BG with 100 mL of water in a volumetric flask, sonicated for 3 mins so that the dye is well distributed. ZnO NPs were added into 10 ppm BG solution from the stock solution in a basin, stirred using magnetic stirrer bar in the dark for 10 mins to establish adsorption–desorption equilibrium. The degradation was performed in a Pyrex basin under the UV illumination using Boekel Scientific's UV Cross-linker equipped with three 254 nm UV lamps. The distance of the light source from the upper level of dye solution is 7.5 cm for maximum utilization of light which remained consistent throughout the experiment conducted. The zero-time reading was taken and the solution was the irradiated with visible light. Aliquots of 5 ml reaction mixtures were taken out of the basin, the ZnO catalyst was separated by centrifugation (3500 rpm for 3 min at room temperature) and the absorption of remaining solution is measured at 620 nm (λ_{max}) employing a UV–Vis spectrophotometer at 0, 15, 30, 60 min at every 30 min interval. Each photodegradation of BG dye experiment using each photocatalyst (**ZnO-G**, **ZnO-HT**, **ZnO-CT** and **ZnO-SB**) was repeated three times. Standard solutions of BG dye were prepared to construct a calibration curve. Beer Lambert's law (Eq. (1)) was applied to determine the photocatalytic degradation efficiency of BG. The degradation percentage of BG was calculated using the formula (Eq. (2)); and the kinetics were determined using the first order Langmuir-Hinshelwood (L-H) model as shown in (Eq. (3)).

$$A = \epsilon cl \quad (1)$$

where A is the absorbance, ϵ is the molar absorption coefficient, c is the concentration of BG and l is the path length of 1 cm.

$$\text{Degradation rate (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

$$\ln \frac{C_0}{C_t} = -kt \quad (3)$$

where C_0 is the initial concentration of BG and C_t is the final concentration of BG dye after UV and Visible light irradiation, k is the first-order rate constant and t is the reaction time. A graph of $\ln \frac{C_0}{C_t}$ was plotted against t and the rate of reaction was determined.

3. Results and discussion

3.1. Synthesis of L, ZnL_2 and ZnO NPs

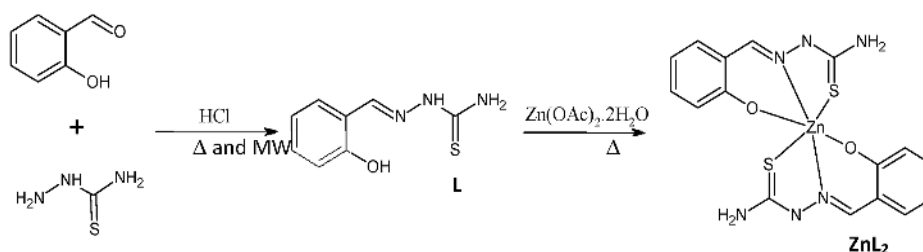
The synthesis of **L** is depicted in Fig. 3. The microwave-assisted method produced better yield than heating under reflux method, and at a shorter reaction time as shown in Table 1. Microwave-assisted method with solvent mixture took 1 min, producing 38% yield whereas the reflux method took 21 min (28% yield). Meanwhile, with water as the solvent in the synthesis of **L**, microwave-assisted method took 2 mins at 21% whereas the reflux method took 5 mins (18% yield). Verma et al. [13] reported a similar observation whereby they have prepared four thiosemicarbazone ligands with a higher yield in a shorter period using a domestic microwave when compared to the heating method which is then used for antibacterial activity. According to Ruan et al., [14] closed microwave-assisted synthesis systems depend on the solvent used, feed ratio, and vessel size. For the latter, it was reported that smaller vessels with an equivalent solvent-to-feed ratio as bigger vessels tend to generate more internal pressure. The extraction yield can be boosted by extending solvent extraction time; however, prolonged extraction periods may degrade the target compounds. In this research work, a bigger vessel was used for the solvent mixture, along with solvent-to-feed ratio three times higher than that used with smaller vessel. The results indicate that the optimal conditions for the bigger vessel involve a 2 mins extraction time, achieving a better yield of 49% of **L** compared to a 6 mins extraction time at 34% yield.

The synthesized **L** was complexed with zinc(II) acetate dihydrate in a 1:2 (metal: ligand) molar ratio to form ZnL_2 . All ZnO NPs have been successfully synthesized using four different methods. The solids appear creamy to white coloured powder with percentage yield of 26%, 25%, 10% and 24% for **ZnO-G**, **ZnO-HT**, **ZnO-CT** and **ZnO-SB**, respectively.

3.2. Characterization

3.2.1. Fourier-transform infrared analysis

FTIR analysis confirmed the functional groups present in all ZnO NPs. The FTIR spectra of *A. Muricata* leaf extracts and **ZnO-G** spectra (Fig. 4a), show functional groups at 3314 cm^{-1} (hydroxyl), 1726 cm^{-1} (ester), 1602 cm^{-1} (alkene), 1369 cm^{-1} (alkane), 1154 cm^{-1} (anhydrides), and 1012 cm^{-1} (amine), which are commonly associated with flavonoids, saponins and tannin, the key components in the extract responsible for the reduction of the metal salt. Sierra et al. [12] reported similar observation peaks and confirmed the presence of functional groups through

Fig. 3. Synthesis of **L** and **ZnL₂**.Table 1. Results of **L** using reflux and microwave-assisted method.

Solvent	Reflux method		Microwave-assisted method	
	Time (mins)	Yield (%)	Time (mins)	Yield (%)
EtOH/MeCN	21	28	1	38
Water	5	18	2	21

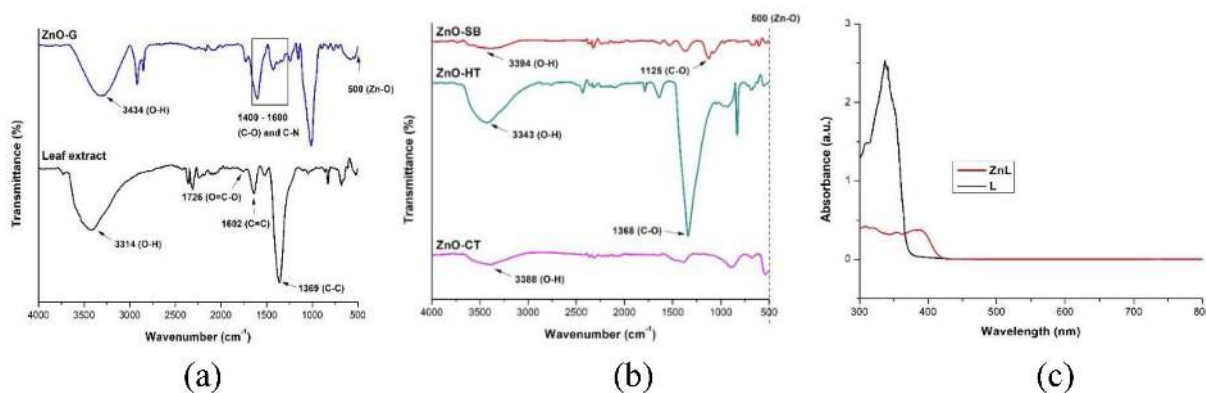
colorimetric tests. Sharp broad peaks observed at 1638 cm^{-1} and broad absorption between 1400 and 1600 cm^{-1} are due to the presence of C-O and C-N stretches from the flavonoids and alkaloids originating from the leaf, respectively. The observed peak shifts correspond to secondary metabolites, indicating that polyphenols, alkaloids, and flavonoids chelate with zinc ions, facilitating to the formation of ZnO NPs [10]. Alternatively, another plausible mechanism involves the bioreduction of Zn^{2+} ions by phytochemicals into metallic zinc, which subsequently reacts with dissolved oxygen in the precursor solution to generate ZnO nuclei.

For all the synthesized ZnO NPs as shown in Fig. 4a and b, the presence of $\nu(\text{O-H})$ at 3394 cm^{-1} , 3434 cm^{-1} , 3433 cm^{-1} and 3388 cm^{-1} are assigned for **ZnO-SB**, **ZnO-G**, **ZnO-HT** and **ZnO-CT**, respectively. For **ZnO-G**, the peak is due to the O-H bond of the polyphenols which was confirmed by Selvanathan et al. [10] For **ZnO-SB**, the peak is attributed to hydroxyl groups bearing a negative charge, which attach

to surface defects with a positive charge, such as oxygen vacancies present in the metal oxides which is reported by Gharagozlou et al. [16] For **ZnO-HT** and **ZnO-CT**, the peak could be due to the adsorption of water. Furthermore, **ZnO-SB** exhibits a peak at 1125 cm^{-1} , attributed to $\nu(\text{C-O})$ which is due to residuals from **ZnL₂**. For **ZnO-HT**, $\nu(\text{C-O})$ are present at 1368 cm^{-1} which is associated with elongation of the C-O bond from the atmospheric CO_2 molecule [17]. In addition, at 500 cm^{-1} , formation of Zn-O in the synthesized ZnO NPs were detected, and this confirm the successful synthesis of ZnO as the band is within the literature range of $400\text{--}700\text{ cm}^{-1}$ [8].

3.2.2. UV–Visible spectroscopy

The electronic spectra of **L** and **ZnL₂** in DMSO are shown in Fig. 4c. There is an absorption peak at 310 nm in the **L** spectrum, attributed to the $n \rightarrow \pi^*$ transition involving the promotion of an electron of the free electron pair on the nitrogen to a π -anti-bonding orbital of the azomethine group of the thiosemicarbazone moiety. A second $n \rightarrow \pi^*$ transition at 337 nm originates from the thioamide group within the thiosemicarbazone moiety. Paul et al. [15] reported to have similar observation regarding the absorption behaviour of salicylaldehyde thiosemicarbazone. There is no $d \rightarrow d$ transitions of the diamagnetic Zn(II) complex which is consistent with its electronic configuration, and absorption peaks at 308 , 354 and 386 nm ,

Fig. 4. FTIR spectra of synthesized ZnO NPs using (a) green method (**ZnO-G**) and its leaf extract, (b) chemical method of different methods (**ZnO-CT**, **ZnO-HT** and **ZnO-SB**), and (c) electronic spectra of **L** and **ZnL₂** recorded in DMSO.

assigned to $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ and ligand to metal charge transfer transitions, respectively.

3.2.3. XRD analysis of ZnO NPs

The XRD spectra of all synthesized ZnO NPs are presented in Fig. 5a. The XRD peaks observed at 31.8° , 34.5° , 36.3° , 47.6° , 56.7° , 63.0° , 66.5° , 68.1° and 69.2° correspond to the (100), (002), (101), (102), (110), (103), (200), (112) and (201) planes, respectively, confirming the formation of hexagonal wurtzite zinc oxide phases as per the Joint Committee on Powder Diffraction Standards (JCPDS 01-079-9878). The XRD patterns for **ZnO-LT** and **ZnO-G** exhibit strong and narrow diffraction peaks, indicating that the NPs are pure and crystalline in nature. No additional diffraction peaks of other phases are detected, affirming the phase purity of ZnO NPs. On the other hand, **ZnO-HT** and **ZnO-SB** have an additional XRD peaks observed at 29.8° for **ZnO-HT** and at 28.9° for **ZnO-SB**, respectively, indicating the presence traces of $\text{Zn}(\text{OH})_2$ during synthesis or calcination process [18].

The average crystallite size of all the synthesized ZnO NPs was determined by employing the Debye-Scherrer equation (Eq. (4)) [8].

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (4)$$

where D is the value of the crystallite size, β is the full width at half maximum (FWHM) intensity in radian, θ is the Bragg's angle in radian [8], and λ is the wavelength of Cu $K\alpha$ radiation ($1.54178 \text{ \AA}$). Table 2 presented values of the average crystallite size and the lattice parameters a and c which computed based on the three prominent peaks. The corresponding unit cell volumes of the NPs are calculated using (Eq. (5)) and tabulated in Table 2.

$$V = \frac{\sqrt{3}}{2} a^2 c \quad (5)$$

The average crystallite size for **ZnO-G**, **ZnO-HT**, **ZnO-CT** and **ZnO-SB** were to be 18.00, 43.09, 29.22

and 19.27 nm, respectively. The small size of **ZnO-G** could be due to the phytochemicals present in the *A. Muricata* leaf extract reducing particle aggregation [4]. The study by Selvanathan et al. [10] reported crystallite size of ZnO NPs derived from *A. Muricata* leaves that was similar to the present study, with sizes ranging between 10 and 20 nm. **ZnO-HT** exhibited a larger crystallite size compared to ZnO NPs reported by Josun et al. [8] who synthesized them using a hydrothermal method at 180°C for 20 h with 0.5 M NaOH, resulting in a crystallite size of 26.44 nm. This suggests that a longer hydrothermal duration may lead to smaller crystallite size. Piri et al. [6] reported that ZnO NPs derived from Zn(II) complex had a larger crystallite size of 41.6 nm compared to the **ZnO-SB** produced in the present study.

3.2.4. Optical studies of ZnO NPs

The optical studies of all synthesized ZnO NPs were evaluated using UV-vis DRS. The diffuse reflectance spectra of all synthesized ZnO NPs are shown in Fig. 5b. The absorption/reflectance edge of **ZnO-G**, **ZnO-HT**, **ZnO-CT** and **ZnO-SB** occur at wavelengths 377, 377, 364 and 327 nm, respectively which are within the typical range of 300–400 nm of ZnO peaks [19]. The optical bandgap energy (E_g) were plotted using Tauc's model (Eq. (6)) [20].

$$(\alpha h\nu)^{1/n} = K (h\nu - E_g) \quad (6)$$

where K is a constant, $\alpha(\nu)$ is the absorption coefficient which can be defined by Beer Lambert's law, E_g is the optical bandgap and exponent n of the equation depends on the type of transition.

The E_g value of **ZnO-G**, **ZnO-HT**, **ZnO-CT** and **ZnO-SB** were 3.25, 3.26, 3.38 and 3.22 eV, respectively, as shown in Fig. 5c, obtained by extrapolating the linear portion of the graph [8]. Variations in bandgap are attributed to differences in preparation methods affecting crystal lattice structures, particle size and surface defects. **ZnO-CT** shows a blue-shift, indicating

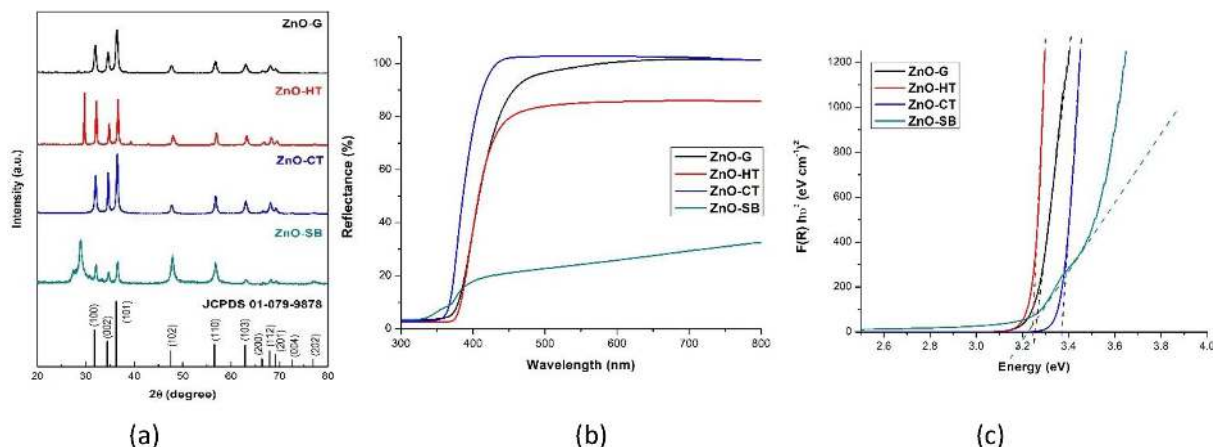


Fig. 5. (a) XRD pattern, (b) reflectance spectra and (c) Tauc's plot of **ZnO-G**, **ZnO-HT**, **ZnO-CT** and **ZnO-SB**.

Table 2. Structural lattice parameters a and c (Å), crystallite size (nm) and unit cell volumes ($\text{\AA}^3$) obtained from the prepared ZnO NPs.

Samples	Lattice parameters		Crystallite size (nm)	Unit cell volume $V(\text{\AA}^3)$
	a (Å)	c (Å)		
ZnO-G	3.24	5.19	18.00	47.16
ZnO-HT	3.22	5.16	43.09	46.20
ZnO-CT	3.23	5.18	29.22	46.91
ZnO-SB	3.23	5.17	19.27	46.68

quantum confinement effects which give rise to smaller particle size, and enhanced crystallinity, resulting in a higher bandgap due to the restrict charge carriers' movement and improved photocatalytic efficiency [19]. Red-shifts in **ZnO-G**, **ZnO-HT** and **ZnO-SB** were attributed to aggregation and large cluster formation of NPs as observed in their SEM images, that reduces the quantum confinement effect, leading to decrease in the bandgap energy [21]. The E_g value for **ZnO-G** is low which could be due to surface modification by the phytochemicals in the leaf extract [22]. This aligns with quantum confinement effect, as green synthesized NPs often show higher reactivity due to an increased electron population in lower energy bands. The presence of native defects such as zinc interstitial and oxygen vacancies in **ZnO-HT** attributed to the reduction in bandgap energy as more localized electronic states introduced within the energy gap [23]. The surface defects or agglomeration of NPs in **ZnO-SB** disrupt the electronic states that alter the optical properties of the NPs and resulting a shoulder in its Tauc's slope [24]. **ZnO-CT** has a bandgap energy close to that of typical ZnO, around 3.37 eV, indicating it possesses high exciton binding energy, rapid electron-hole recombination, and enhanced photocatalytic activity [25]. **ZnO-CT** performed the best in the photocatalytic degradation of BG in this work, hence, this indicates that there is an efficient electron-hole pairs generation, and minimized recombination under UV light, enhancing photocatalytic efficiency.

3.2.5. SEM-EDX of ZnO NPs

SEM analysis determined the particle size and surface morphology of ZnO NPs. Fig. 6a–d shows the SEM images of synthesized ZnO NPs at x50,000 magnification, revealing method-dependent variations in shape and morphology, with size distributions measured using ImageJ software. The average particle sizes of 37, 47, 33 and 83 nm for **ZnO-G**, **ZnO-HT**, **ZnO-CT** and **ZnO-SB**, respectively. The SEM images reveal the formation of ZnO NPs exhibiting agglomeration to irregular spherical shape. The surface morphology of **ZnO-G** is densely packed, while **ZnO-HT**, **ZnO-CT** and **ZnO-SB** appear more porous. The porous nature enhances the availability of active sites for reactions and improves the adsorption properties [26]. Selvanathan et al. [10] reported ZnO NPs derived from *A. Muricata* leaf with quasi-spherical compared to the present study. **ZnO-HT** has a larger size compared to the ZnO NPs reported by Josun et al. [8] who used hydrothermal method at 180 °C for 20 h resulting in a size of 16.67 nm and a flower-like shape nanorods. This further confirmed that longer hydrothermal treatment affects the size of ZnO NPs. Piri et al. [6] reported ZnO NPs derived from Zn(II) complex had a smaller size, ranging between 20 and 40 nm, with a spherical shape compared to **ZnO-SB** synthesized in the present study.

Energy dispersive X-ray (EDX) analysis was employed to determine the elemental composition of all synthesized ZnO NPs, with the results presented in Fig. 6a–d. The ZnO NPs contained Zn, O and a trace number of other elements, which suggest the successful synthesis of ZnO NPs.

3.3. Photocatalytic degradation of BG dye

Photocatalytic process starts when ZnO NPs absorb photons, exciting electrons from the valence band to the conduction band and creating electron–hole pairs. The photogenerated electrons reduce oxygen to form

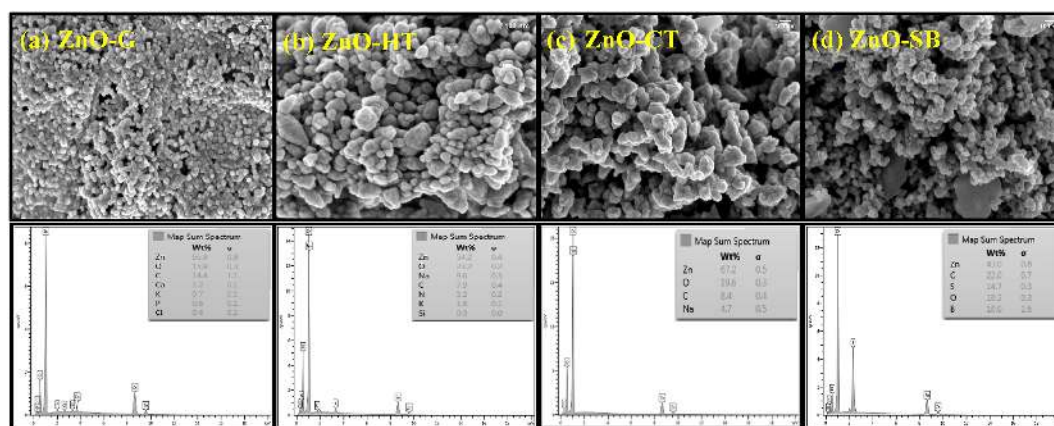


Fig. 6. SEM images and EDX spectra of (a) **ZnO-G**, (b) **ZnO-HT**, (c) **ZnO-CT** and (d) **ZnO-SB** at 50,000x magnification.

superoxide radicals ($\cdot\text{O}_2^-$), while holes oxidize water or hydroxide ions to produce hydroxyl radicals ($\cdot\text{OH}$). These reactive oxygen species attack BG dye molecules, breaking them down into smaller, non-toxic compounds such as CO_2 and H_2O . **ZnO-G** exhibits phytochemical capping that promotes dye adsorption [4], **ZnO-HT** yields highly crystalline ZnO with well-defined morphology [8], **ZnO-CT** produces ZnO NPs with unique surface properties favorable, and **ZnO-SB** features increased oxygen vacancies that enhance visible-range absorption and ROS formation, thereby improving charge separation and degradation efficiency [27]. The difference in surface chemistry, crystallinity and stability among these NPs govern their photocatalytic efficiency.

Photodegradation experiments with **ZnO-G**, **ZnO-HT**, **ZnO-CT**, and **ZnO-SB** under UV-light (620 nm) showed the decline of BG concentration by 97% with **ZnO-CT** at 180 min, turning the dye solution from blueish-green colour to colourless solution, confirming successful degradation as reported by Prerna et al. [28] This indicates dye mineralization into water and carbon dioxide. The photocatalytic degradation of BG by **ZnO-G**, **ZnO-HT** and **ZnO-SB** show similar UV–Vis spectra as Fig. 7a of **ZnO-CT**.

Fig. 7b displays BG degradation percentage by **ZnO-SB**, **ZnO-G**, **ZnO-HT** and **ZnO-CT** at 30-mins time interval up to 330 mins. At 210 mins, **ZnO-CT** achieved the highest degradation (98%), followed by **ZnO-G** (95%), **ZnO-HT** (94%) and **ZnO-CT** (72%). **ZnO-CT**'s superior performance is due to its smaller particle size and porous morphology, providing more active sites for photocatalytic reactions [26].

The Langmuir-Hinshelwood (L-H) kinetic model showed that photocatalytic degradation of BG follows first-order kinetics for all ZnO NPs. The linear relationship between $\ln(C_0/C_t)$ and time, as depicted in Fig. 7c. The rate constant k in min^{-1} was determined by the linear fitting of the slope of $\ln(C_0/C_t)$ versus time yields. The photocatalytic activity was evaluated

by comparing the k values and the linear regression coefficients for the BG degradation data using different synthesized ZnO NPs methods, summarized in Table 3. **ZnO-CT** has the highest k value, confirming it as the best photocatalyst for BG degradation. Makropoulou et al. [29] has the same results where higher k value enhanced photocatalytic performances.

3.3.1. Absorption reactions in the presence and absence of UV irradiation

Three experiments were carried out to study the adsorption process of **ZnO-CT**. The first experiment involved degradation of BG dye with the presence of both UV light and photocatalyst; the second experiment was with UV-light but no photocatalyst; and the third experiment was with photocatalyst but without UV-light. Fig. 8a shows that after 210 min of irradiation, 98% of degradation occurred using both **ZnO-CT** and UV light, 82% with UV light only, and 48% with **ZnO-CT** in the dark, indicating adsorption on the catalyst's surface. Similar observations were reported by Prerna et al. [28] where the degradation BG dye efficiency reached 98.1% under UV light and ZnO, and negligible with UV only and ZnO catalyst in the dark. This indicates that the presence of both ZnO and UV light is crucial for effective degradation.

The Langmuir-Hinshelwood kinetic model was also applied to analyze the photocatalytic degradation rate of BG dye using **ZnO-CT** in the dark with photocatalyst with the rate constants and correlation coefficient (R^2) values of 0.00310 min^{-1} and 0.999, respectively, and the plots are displayed in Fig. 8b. As evidenced by the

Table 3. Kinetic result of photocatalytic degradation of BG dye.

Samples	Rate constant (k) min^{-1}	Linear regression coefficient (R^2)
ZnO-G	0.0144	0.9895
ZnO-HT	0.0135	0.9978
ZnO-CT	0.0192	0.9762
ZnO-SB	0.008	0.9639

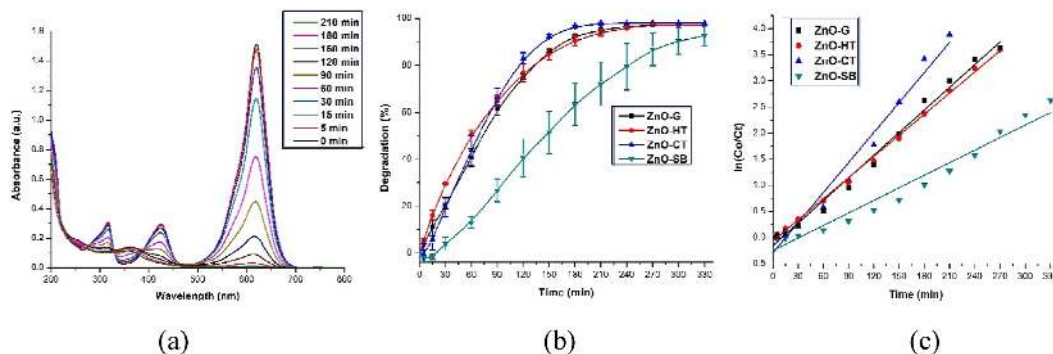


Fig. 7. (a) UV–Vis spectra of BG degradation using the **ZnO-CT** photocatalyst at different time intervals, (b) % degradation of BG over time for all synthesized ZnO NPs, and (c) the linear plots of $\ln(C_0/C_t)$ against UV exposure time for all synthesized ZnO NPs.

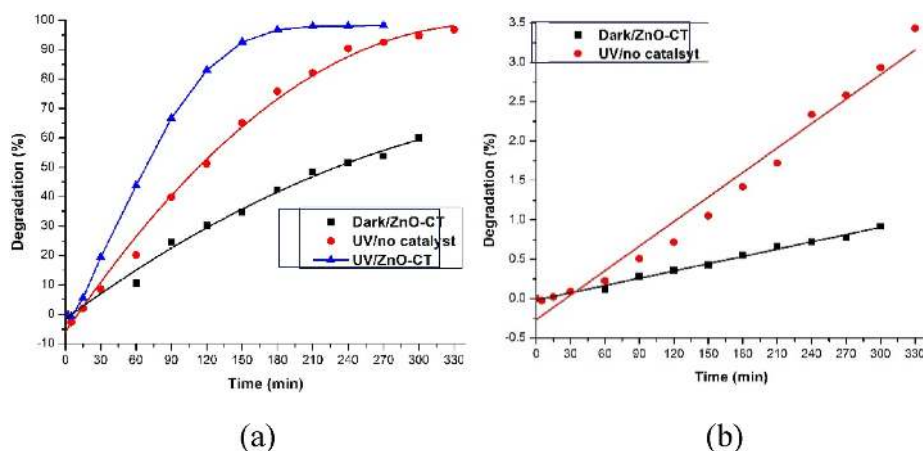


Fig. 8. (a) Photocatalytic degradation and (b) kinetic plot of BG dye using **ZnO-CT** under different experimental condition obtained from a single run.

linear relationship with R^2 values close to 1, this indicates that photocatalytic degradation follows the first-order kinetic of L-H model.

3.3.2. Effect of pH conditions

In photocatalytic studies, pH plays an essential role as it regulates the generation of hydroxyl radicals. Effect of pH on BG dye removal was studied between pH 4 to 11 by adding drops of 1 M of sodium hydroxide. All other experimental conditions viz., catalyst dose 10 mg and BG concentration 10 ppm were kept constant. From Fig. 9a, **ZnO-CT** NPs have degraded the BG dye solution at pH 4, 7, 9 and 11.

The effect of ZnO NPs were investigated acidic, neutral, pzc and alkaline solutions. The degradation efficiency reached 98% for 210 mins at pH 4, 98% for 240 mins at pH 7, 98% for 180 mins at pH 9 and 97% for 60 mins at pH 11. **ZnO-CT** degraded the dye faster in alkaline solutions. Below the point of zero charge (pzc) of ZnO (pH 9), the surface is positively charged, while above it, the surface becomes negatively charged, promoting electrostatic attraction with the

dye as BG dye is a cationic dye that carries a positive charge. The increased degradation rate at elevated pH is attributed to higher hydroxyl ion concentration, which reacts with photogenerated holes to produce $\text{OH}^\cdot$ radicals that accelerates the breakdown of BG dye [30]. Furthermore, the positive charge of surface BG dye facilitates electron transfer from the surface of ZnO NPs to the molecular structure of BG which leads to decomposition of BG. In acidic or neutral conditions, the degradation rate declines as hydroxyl ions are insufficient for $\text{OH}^\cdot$ formation [31]. Kazeminezhad et al. [30] similarly reported an increased photocatalytic degradation at pH 11, followed by pH 4 and pH 8, highlighting the role of pH in modulating ZnO NPs photocatalytic performance.

3.3.3. Effect of initial concentration of BG dye

The effect of BG dye concentration on its removal was studied between 5 and 15 ppm. All other experimental conditions, such as pH 4 and a catalyst dose of 10 mg were kept constant. Fig. 9b shows the degradation of BG dye solution at 5, 10 and 15 ppm by **ZnO-**

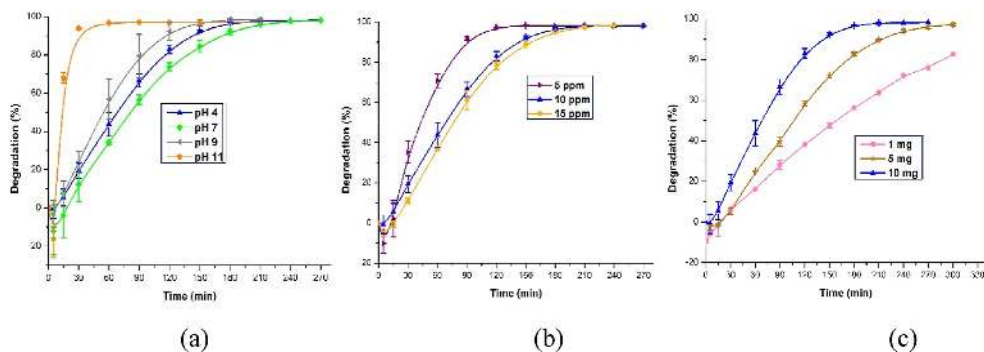


Fig. 9. Photocatalytic degradation of BG dye at (a) varying pH (pH 4, 7, 9 and 11), (b) different concentration of BG dye (5, 10 and 15 ppm), and (c) different amounts of catalyst of **ZnO-CT** (1, 5 and 10 mg).

CT. At 120 min, 5 ppm initial concentration of BG gave the highest degradation at 97%, whereas 10 ppm and 15 ppm gave 83% and 79% respectively. Lower dye concentrations lead to higher degradation, as fewer active sites are occupied and more light reaches the catalyst, enhancing free radical generation. Also, increased dye concentration obstructs incident UV light [5], and competes for active sites [11], hence, reducing degradation efficiency. Kataria et al. [11] reported to have similar observation in their photo-degradation experiments with BG dye where increased dye concentration, the degradation decreases from 98.7% to 54%.

3.3.4. Effect of catalyst dose

The effect of catalyst amount on BG dye removal was studied using 1–10 mg of **ZnO-CT** at pH 4 and 10 ppm of BG. Fig. 9c shows the degradation of BG with 1, 5 and 10 mg of **ZnO-CT** NPs. The highest degradation, 98% occurred with 10 mg of catalyst at 210 min, compared to 56% with 1 mg. Higher amount of catalyst used enhances photocatalytic activity by providing more active sites and improving UV light penetration scattering, which accelerates dye degradation. Similar observation has been conducted by Kataria et al. [11] with the degradation of BG dye using ZnO NPs over a range of 20–80 mg.

3.3.5. Effect of oxidants

The effect of adding oxidants (H_2O_2) on BG dye degradation with **ZnO-CT** was studied at pH 4 and 11 by adding drops of 1 M of sodium hydroxide under UV irradiation, while keeping all other experimental conditions constant. Fig. 10a and b shows that **ZnO-CT** effectively degraded BG dye solution with addition of 1 μl of H_2O_2 at pH 4 and pH 11. The addition of 1 μl of

H_2O_2 significantly enhanced degradation, reducing the time for 98% degradation from 210 min to 60 min at pH 4. At pH 11, the degradation increased from 68% to 95% in 15 min H_2O_2 accelerates the process by trapping photogenerated electrons under UV light, which reduces electron-hole recombination [32]. The extra $\text{OH}\cdot$ from sodium hydroxide might contribute to the faster degradation rate. However, at pH 11, the degradation rate decreases slightly from 97% to 95% due to H_2O_2 acting as a radical scavenger for $\text{OH}\cdot$. Inderyas et al. [33] reported similar observation with addition of H_2O_2 in alkaline condition degradation rate decreases is due to H_2O_2 instability, and $\text{OH}\cdot$ radical scavenging caused by carbonate and bicarbonate ions from carbon dioxide.

4. Conclusion

Four methods for synthesizing ZnO NPs were successfully employed. The chemical methods included thermal decomposition of Zn(II) complex of salicylaldehyde thiosemicarbazone (**ZnO-SB**), hydrothermal (**ZnO-HT**) and cold-temperature (**ZnO-CT**) methods whereas the green (**ZnO-G**) method involves the use of *A. Muricata* leaf extract. FTIR spectrum confirmed the characteristics of Zn-O bonds at 500 cm^{-1} across all samples, while the XRD results showed a hexagonal wurtzite structure of with an average crystallite size of 18.00 nm, 43.09 nm, 29.22 nm and 19.27 nm for **ZnO-G**, **ZnO-HT**, **ZnO-CT**, and **ZnO-SB**, respectively. SEM analysis revealed average particle sizes of 37, 47, 33 and 83 nm and the estimated bandgap energies were 3.25, 3.26, 3.38 and 3.22 eV of the respective samples. Among the synthesized ZnO NPs, **ZnO-CT** demonstrated the highest photocatalytic performance in the degradation of BG dye under UV irradiation, attributed

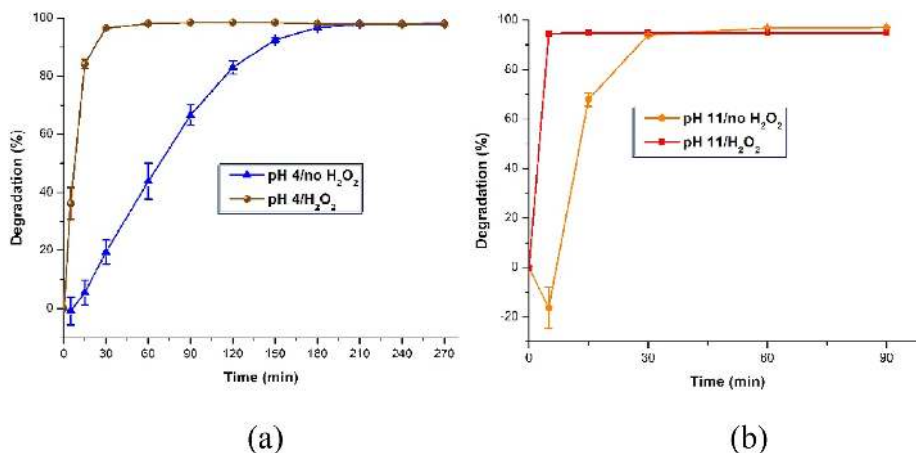


Fig. 10. Photocatalytic degradation of BG dye with addition of H_2O_2 in (a) pH 4 and (b) pH 11.

to its favorable properties including a bandgap energy of 3.38 eV, smaller particle size and high porosity. The optimal photocatalytic degradation conditions were determined to be an initial dye concentration of 5 mg, a photocatalyst dosage of 10 mg, and a solution pH of 11. Furthermore, the addition of 1 µl of oxidant at pH 4 resulted in the highest degradation rate. This study highlights the potential of cold-temperature synthesized **ZnO-CT** as a promising approach for environmental remediation, particularly in treating dye contaminated water, and could contribute to the advancement of sustainable nanotechnology for addressing water pollution.

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Conflicts of interest

The authors declare no competing financial or personal interests influencing this work.

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