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**ORIGINAL RESEARCH PAPER**

# Fabrication of Cu doped ZnO nanocrystals hybridised with Graphene oxide nanosheets as an efficient solar light driven photocatalyst for the degradation of Quinalphos pesticide in aqueous medium

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**ABSTRACT**
This present study involves the sonochemical and microwave synthesis of an efficient light harvesting nanocomposite, copper doped zinc oxide nanocrystals hybridised with graphene oxide nanosheets (ZnO/Cu/GO). The synthesised nanocomposite was characterised through various spectroscopic methods like XRD, SEM, EDX, FT-IR, UV-DRS and fluorescence analysis. This nanocomposite was employed to degrade; an organophosphorous pesticide, Quinalphos and its percentage efficiency of degradation was studied. The results have revealed that, 99 % of 40 ppm of Quinalphos pesticide could be degraded using ZnO/Cu/GO nanocomposite (3 mg/L) under visible light radiation within20 minutes at neutral pH. The presence of an intrinsic defects and the fluorescence property of the prepared nanocomposite were also detected. Finally, mineralisation of 98% was confirmed by COD and TOC analysis. The reaction rate followed pseudo - first order kinetics with a rate constant of 4.24 x $10^{-3}$ $min^{-1}$. Furthermore, the composite has demonstrated a reusable feature and was utilised for eight cycles without any change in its activity. These findings have illustrated an enhanced Photocatalytic activity of ZnO/Cu/GO nanocomposite due to decrease in the rate of electron hole recombination reaction. Moreover, the nanocomposites eco-friendly, more stable, and well organised, which could be preferred for the treatment of industrial and agricultural waste water containing organic contaminants relatively in shorter period under irradiation using sunlight. Henceforth, ZnO/Cu/GO nanocomposite was developed as a significant tool for the treatment of effluents in many environmental applications.

**Keywords:** Pesticide contaminants, Quinalphos, Hybridised nanocomposites, photocatalytic mineralisation, visible light.

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## INTRODUCTION

Rapid proliferation in the application of pesticides, dyes, pharmaceuticals, surfactants etc, in cultivation and large scale manufactories has resulted in the contamination of organic residues in the aqueous environment. These organic contaminants bring about an inauspicious consequence on the environment and they are a substantial provenance for water pollution, eutrophication and constitute interruption to aquatic creatures, as a consequence of their toxicity and endurance [1]. Among various water pollutants, the pesticide contaminants have constituted a vital role in the contamination of water resources. The insignificant and unlimited application of pesticides has created an acute intimidation for the environment and the health of humans. Rainfall, the activity of microbes, rate of application, temperature of soil etc., are certain constituents that are responsible for the migration

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of pesticide residues into aqueous streams and water bodies. Organophosphate pesticides are extensively utilised in agriculture to intensify the yield of the fodder and to protect the crops from pests. Qunalphos is an organophosphate pesticide applied in Indian cultivation fields for controlling caterpillar and scale insects on fruit trees, cotton, vegetables, sugarcane, nuts, coffee and rice [2]. Quinalphos affects the respiratory system and furthermore, it creates irritation to the skin and eyes. As Quinalphos is more stable, the residues of the specified pesticide get easily dispatched from the soli to the underground water streams, thereby contaminating them. Hence, the eradication of Quinalphos pesticide from aquifers is a matter of great concern. In the company of various preferred techniques, the photocatalytic degradation process furnishes a possible and fascinating rate for detoxicating virulent and precarious pollutants present in water.

Semiconductor materials were applied in this technique to originate more active species such as hydroxyl radicals, holes, and superoxide ions for the rapid oxidation of organic contaminants [3]. Among the several semiconducting materials, zinc oxide is an efficient photocatalyst because of its admirable peculiarities like chemical stability, easier fabrication, low cost, and other advantages [4, 5]. The out comings of zinc oxide associated studies have manifested that the photocatalytic potential of zinc oxide is adequately high to degrade certain organic pollutants present in the ecosystem. Aouissi et al have proposed 99 % degradation of methylene blue dye using zinc oxide nanoparticles in 45 minutes under natural sunlight [6]. Anyhow, the usage of zinc oxide in photocatalytic application has various drawbacks such as wide band gap, low quantum efficiency, etc [7]. In view of proliferating the photocatalytic capacity of zinc oxide, the semiconductor should be altered by doping procedure, noble metal deposition, or by preparing a multiple composite material [8].

Recombination of photogenerated electron hole pairs is one of the major factors for a dynamic photocatalytic reaction. To increase the lifetime of electron hole pairs, the photocatalyst can be prepared by using a carbon-based material [9]. However, zinc oxide has been associated with standard carbon-based substantials. Graphene and its derivatives are the most favourable option for this intention [10]. These materials display extra ordinary surface properties along with excellent electrical, thermal, chemical, and adsorption characteristics. Graphene oxide is the best choice for zinc oxide-based consolidated photocatalyst because of its capacity for charge separation [11]. Mirikaram et al synthesized ZnO/GO composite has showed an enhanced activity towards the degradation of vanillic acid [12]. Wang et al studies have revealed that ZnO/GO nanocomposite is also effective in the degradation of rhodamine B and methyl orange dye, under direct sunlight [13].

Even now, very limited studies are accessible on the photocatalytic degradation of Quinalphos pesticide using various metal oxide nanocomposites. Pandey et al have articulated 98% of degradation of Quinalphos (20 ppm) in 180 minutes using an S doped $TiO_2$ photocatalyst. [14]. Lingaraj et al have examined the degradation of Qinalphos (20 ppm) in 90 minutes using a mercury vapour lamp together with Ce/ $TiO_2$/RGO nanocomposite as photocatalyst [15]. Nidhi et al. (2019) has reported 87.5% of Quinalphos degradation within 240 minutes using Mn-N-co-doped $TiO_2$ under visible light [16]. Kaur and Sud (2012) have studied the degradation of Quinalphos in 180 minutes using $TiO_2$ at pH 6 in the presence of UV light irradiation [17]. After a deliberated review of a literature survey, it was proposed that the degradation of Quinalphos is preferably a very long operation with less degradation efficiency and consumes more time. Specifically, the pH of the prepared test solution is not environmental friendly.

The main objective of the present work is to introduce a fast, energetic, effective, and commercial nanocomposite for the complete mineralisation of Quinalphos pesticide that exists in water streams within a short period. Garg et al has synthesised GO-ZnO nanoflowers for the degradation of Quinalphos at pH 6 in 45 minutes under UV irradiation [18]. As a mean to enhance the activity of ZnO/GO nanocomposite for the degradation of Quinalphos pesticide, the particular composite was consolidated distinctively using a metal dopant. Among various metals, copper posses extra ordinary advantages such as non-toxicity, low cost, and miscellaneous function. The distinctive character and feasible inner sphere catalytic behaviour authorise a copper- based catalyst as a fascinating contestant for fabricating an innovative and virtual photocatalyst [19]. Moreover, the light absorption proficiency of the composite can also be upgraded by doping copper cooperatively [20]. The Photocatalytic degradation process based on this

type of hybridised nanocomposites is gradually providing an unconventional technology for the treatment of aqueous contaminants. Furthermore, the dosage of photocatalyst used in the present study is small when compared to other studies available in the literature.

In this work, we have described the fabrication of ZnO/Cu/GO nanocomposite photocatalyst in a simple route which has been explored to degrade Quinalphos pesticide in short duration under direct sunlight at neutral pH. ZnO/Cu/GO nanocomposite was prepared by using zinc acetate, graphite powder, and copper sulphate as precursor. The quality and durability of the prepared composite was assured by recycling the catalyst for eight cycles. The structural, morphological, compositional, band gap energy, and fluorescent properties of the prepared nanocomposite were examined by SEM, EDX, FT-IR, XRD, UV-DRS and fluorescence analysis. Furthermore, the mineralisation of Quinalphos pesticide was confirmed by COD, TOC and UV- Vis spectral analysis.

## MATERIALS AND METHODS

All the chemicals used were of analytical grade. The chemicals were utilised as received without further purification. Zinc acetate, potassium permanganate, and ammonium hydroxide were purchased from Iso-Chem laboratories Kochi (India) respectively. Graphite powder, sulphuric acid, and ammonium nitrate were purchased from Merk specialities pvt. Ltd. Mumbai (India). Hydrochloric acid, hydrogen peroxide, copper sulphate and hydrazine hydrate were purchased from Global chemie Pvt. Ltd, Mumbai (India) and doubly distilled water was used throughout the experiment.

*Preparation of ZnO nanoparticles (ZnO NPs):*

To synthesize zinc oxide nanoparticles a required amount of zinc acetate dihydrate [Zn $(CH_3CO_2)_2.2H_2O$] is dissolved in 100 ml of double distilled water. To the dissolved suspension, calculated amount of ammonium hydroxide ($NH_4OH$) solution was added drop wise and the solution was stirred for 4 hrs. The mixture was placed in a water bath at 60°C for 1 hour and a white precipitate is obtained. The precipitate was filtered and dried in an air oven at 80 °C for 1 hour and was further calcined in a muffle furnace at 400 °C for 2hrs. Finally, ZnO nanoparticles were formed.

*Preparation of copper doped ZnO nanoparticles (ZnO/Cu) NPs:*

The synthesised ZnO nanoparticles (4 g) were added to 100 mL of doubly distilled water and sonicated for 10 minutes. Then a calculated quantity of copper sulphate ($CuSO_4$) solution was added gradually to the above mixture with vigorous stirring and the mixture was reduced by a reducing agent hydrazine hydrate ($N_2H_4$). The above solution was irradiated in a microwave for 3 minutes. The blue colour solid so formed was dried in an air oven at 80 °C for 1 hour and further calcined at 450 °C for 2 hrs.

*Preparation of Graphene oxide (GO):*

In a typical experiment, a required quantity of graphite powder and ammonium nitrate ($NH_4NO_3$) were taken in a beaker and was dissolved in 100 mL 98% sulphuric acid ($H_2SO_4$). The mixture was kept in an ice bath and stirred for 1 hour. Then a calculated amount of potassium permanganate ($KMnO_4$) was added slowly to the mixture in the ice bath and mixed thoroughly until a thick dark green colour paste is formed. The paste was diluted using 150 mL of double distilled water followed by the drop wise addition of 30% hydrogen peroxide ($H_2O_2$) solution. The colour of the suspension was turned from dark green to brown. The obtained solid was filtered, washed with 10% hydrochloric acid (HCl) solution in order to eliminate the metal ions and washed further with doubly distilled water for several times until pH 6 is attained. The resulting brown paste was dried at 50 °C for 5hrs to obtain black graphene oxide solid [21].

*Preparation of ZnO/Cu/GO nanocomposite:*

A known quantity of the above synthesised copper doped ZnO nanoparticles and graphene oxide was dispersed in 100 mL of ethanol by sonication for 30 minutes. The above suspension was centrifuged at 5000 rpm. The product so formed was further washed with double distilled water, filtered, and dried in an air oven at 50 °C for 2hrs.The obtained precipitate was finally calcined at 450 °C for 2hrs.

## CHARACTERISATION OF NANOCOMPOSITE

The structural and crystalline phases of the sample were recognised using a Bruker D8 advance X-ray diffractometer (XRD) with Cu-Kα radiation 40 mA with a scanning rate of 2°

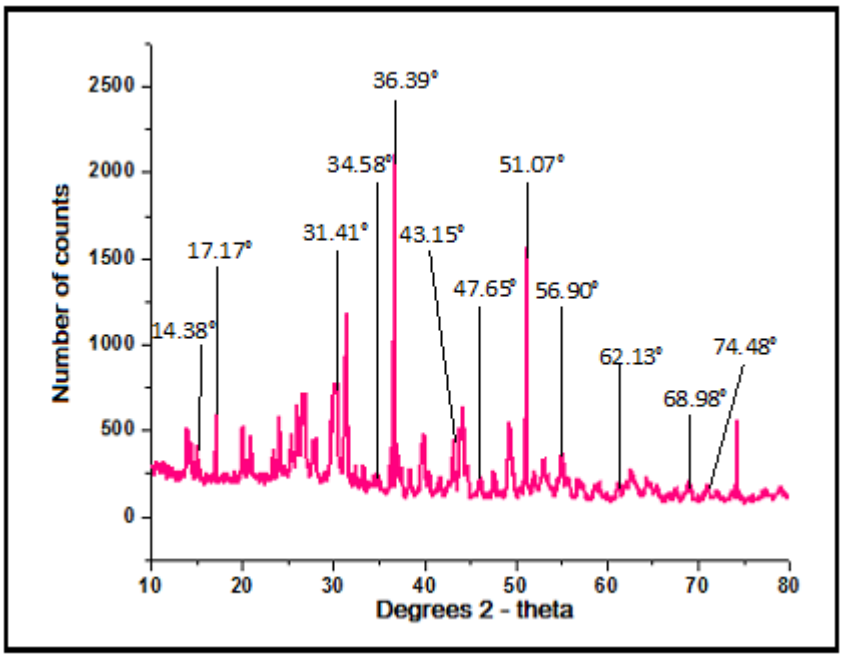


Fig. 1: XRD pattern of synthesized ZnO/Cu/GO nanocomposite

$min^{-1}$. The morphology and structural analysis of ZnO/Cu/GO nanocomposite was examined using a scanning electron microscope (model Jeol 5800LV). Elemental composition was analysed by using energy dispersive X-ray spectrometry (EDS) analysis (model JSM-7100F). The FT-IR analysis of the nanocomposite was studied by using a Bruker Invenio spectrometer in the range of 400 - 4000 $cm^{-1}$, and the diffuse reflectance absorption spectra (DRS) were recorded on JASCO equipment in the range of 200-2500 nm. The fluorescence property of this nanocomposite was examined by using a Spectrofluorimeter (model RF-5301).

## RESULTS AND DISCUSSION:

*Structural Analysis:*

The crystal structure of the prepared nanocomposite was investigated by manipulating an XRD spectrometer. XRD is more convenient for the determination of crystal size, phase identification and purity of the sample. Fig. 1 has depicted the X-ray diffractogram of pure ZnO/ Cu/GO nanocomposite. The existence of seven distinct peaks for zinc oxide situated at2θ values of 31.41°, 34.58°, 36.39°, 47.65°, 56.90°, 62.13° and 68.98° constitute to (100), (002), (102), (110), (103) and (112) lattice planes. This arrangement has authenticated the typical hexagonal wurtzite phase structure of zinc oxide (JPCDS card no: 361451) [22, 23]. The diffraction peaks located at 2θ values of 14.38° and 17.17° affirmed the presence of graphene oxide [24]. Moreover, three characteristic peaks at 2θ values of 43.15°, 51.07°, 74.48° angles corresponds to (111), (200) and (220) planes indexed to face structure of cubic lattice of copper nanoparticles (JCPDS card no: 004-0836) [25, 26]. Further, the characteristic peaks at 2θ values of 43.15° and 51.07° have delegated the doping of copper on the structure of ZnO-GO nanocomposite respectively. The good crystalline nature of the synthesized ZnO/Cu/GO nanocomposite is stipulated by the appearance of sharp diffraction peaks in the XRD spectrum. The average size of the synthesised nanocomposite was evaluated by using the Debye- Scherer equation as 21 nm which was calculated from the most intense peak obtained from the XRD pattern of the prepared ZnO/Cu/GO nanocomposite.

*SEM Analysis:*

The surface morphology of the synthesised ZnO/Cu/GO nanocomposite was examined by SEM analysis. The SEM image has manifested the non-homogeneity of the particles in terms of their shape and size. Fig. 2a clearly illustrated that a massive volume of zinc oxide and copper nanoparticles are positioned together with the nano sheets of graphene oxide without any

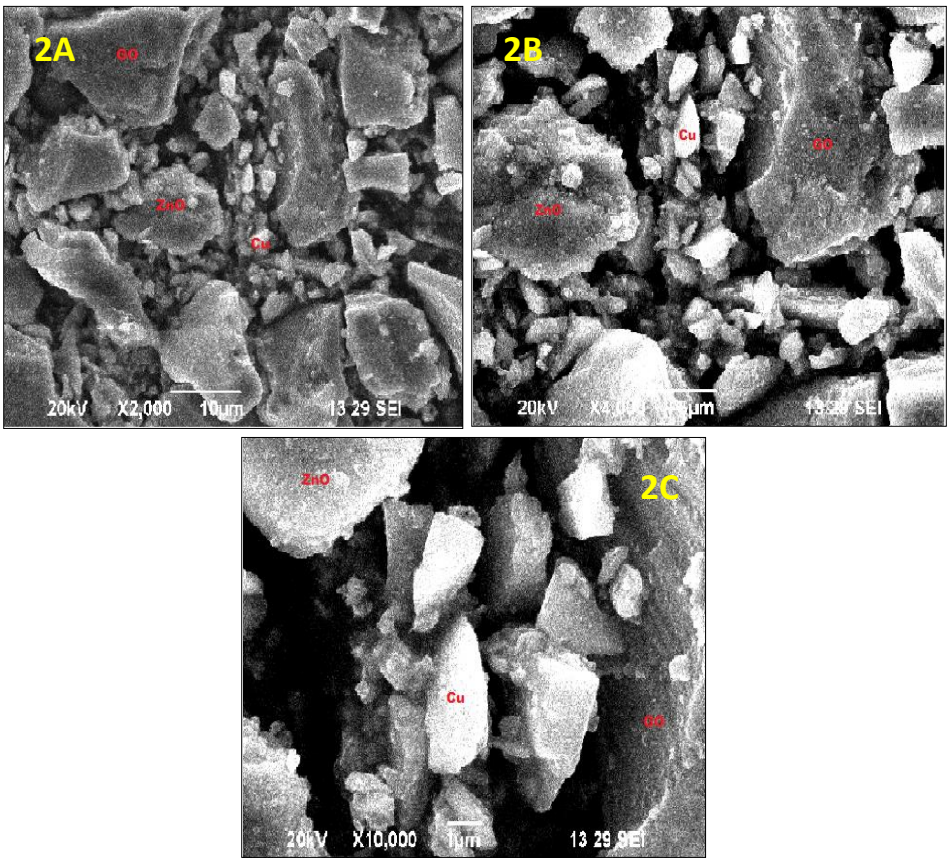


Fig. 2: SEM image of ZnO/Cu/GO nanocomposite at different magnification

agglomeration. The light harvesting ability of ZnO/Cu/GO photocatalyst was promoted due to the flat and smooth surface of graphene oxide nano sheets [27, 28]. The zinc oxide nanoparticles have grown larger in size with spongy nature and possessed a crystalline structure as displayed in Fig. 2b [29]. Furthermore, in Fig. 2c the nanoparticles of copper have exhibited cubic and sharp-edged structures [30, 31] which is in good agreement with the out comings obtained from the XRD analysis.

*EDX Analysis:*

To substantiate the successful preparation and elemental purity of ZnO/Cu/GO nanocomposite, EDX analysis was evaluated. Fig. 3 displays the presence of zinc, copper, oxygen, and carbon in the prepared ZnO/Cu/GO composite. Since graphite is an allotrope of carbon, the existence of a carbon peak in the spectrum has revealed the presence of graphite in the synthesised nanocomposite. These out comings are in good agreement with the XRD pattern of the synthesised ZnO/Cu/GO nanocomposite. The absence of any additional peaks authenticated the elemental purity of the prepared ZnO/Cu/GO nanocomposite [32]. The weight percentage of zinc, carbon, copper, and oxygen is 28.39 %, 26.61 %, 17.01% and 27.99 %respectively.

*Diffuse reflectance spectroscopic (DRS) Analysis:*

DRS is a versatile methodology that helps to ascertain the impact of copper and graphene oxide on the optical properties of zinc oxide. The obtained data is further processed to estimate the band gap value of the prepared nanocomposite. The UV-Visible diffuse reflectance spectrum of pure ZnO/Cu/GO is shown in Fig. 4A. The broad absorbance in a range of 250-300nm has denoted the presence of graphene oxide in the synthesised nanocomposite [33]. A broad absorption peak at 250 nm denoted the existence of $cu^{+}$ ions and the characteristic band between the absorption region320-370nm corresponded to the charge transfer bands in ZnO/Cu/GO [34]. Moreover, an additional band at 357nm has confirmed the presence of zinc oxide in nanocomposite [35].

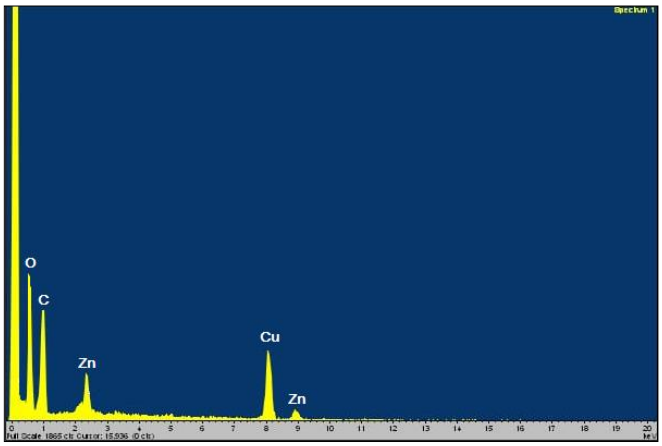


Fig. 3: EDXpattern of ZnO/Cu/GO nanocomposite

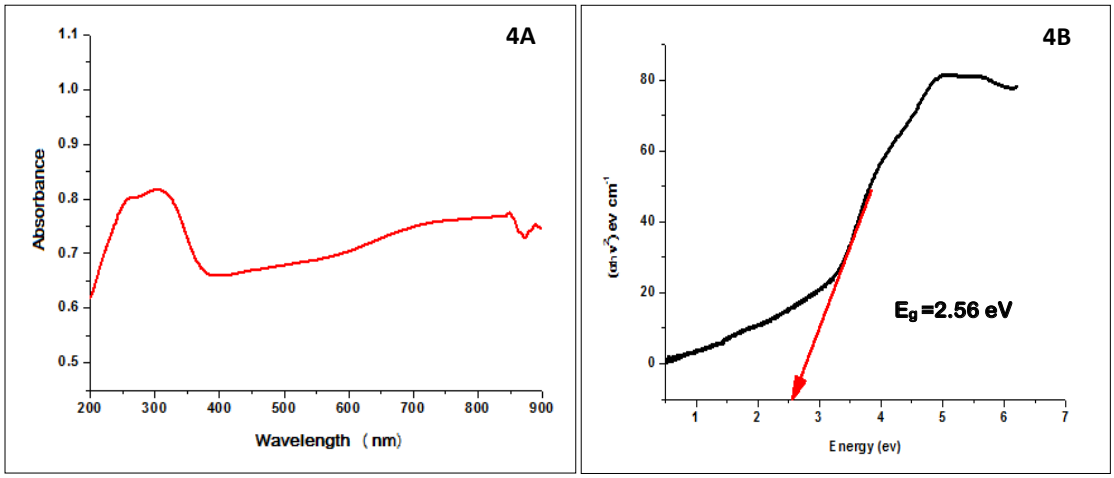


Fig. 4: (A) - UV-Vis DRS spectrum and (B) Taut plots for the corresponding ZnO/Cu/GO nanocomposite

The band gap value can be calculated using Tauc's graph based on Fig. 4B. The band gap energy of zinc oxide nanoparticles is 3.37 eV whereas the value of pure ZnO/Cu/GO nanocomposite is approximately calculated as 2.56 eV. This tremendous decrease in band gap energy has improved significantly the light harvesting ability of synthesised ZnO/Cu/GO nanocomposite and makes it more efficient for the photodegradation of environmental pollutants in the presence of visible light.

*FT-IR Analysis:*

Fig. 5 illustrated the FT-IR spectrum of pure ZnO/Cu/GO nanocomposite. The nature of functional groups present in the synthesised ZnO/Cu/GO nanocomposite is ascertained by FT-IR analysis within the range of 400-4000 $cm^{-1}$.The characteristic bands at 452 and 582 $cm^{-1}$correspond to the stretching vibration between zinc and oxygen present in the heraldic wurtzite phase of zinc oxide [36]. The peak at 502 $cm^{-1}$ denotes the presence of zinc oxide in the nanocomposite. A sharp band at 1362 $cm^{-1}$is a characteristic feature of the symmetric and asymmetric stretching vibration of Zn - O - Zn framework [37]. The characteristic band at 1614 $cm^{-1}$ has mentioned the existence of an $sp^2$ hybrid bond in graphene oxide and a prominent peak at1146 $cm^{-1}$signified the stretching vibration of alloy and epoxy C – O bond. The existence of a functional group holding an oxygen atom has declared the oxidation of graphene into graphene oxide [38]. Moreover, a significant band at 629 $cm^{-1}$ has assured the existence of copper in the synthesised ZnO/Cu/GO nanocomposite [39]. The specific peaks at 1510, 2360, 2974 and 3722 $cm^{-1}$ are identified as a result of the C=C aromatic

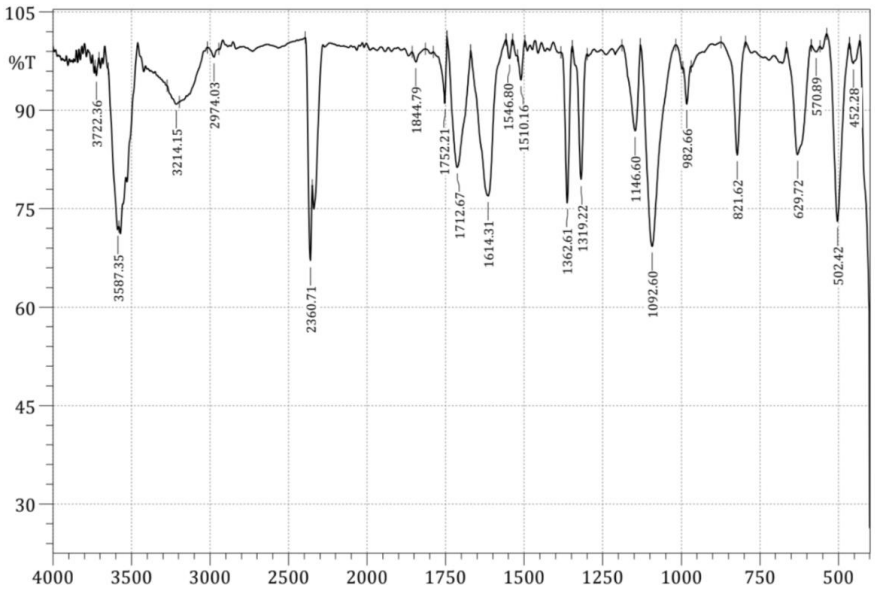


Fig. 5: FT-IR specta for pure ZnO/Cu/GO nanocomposite

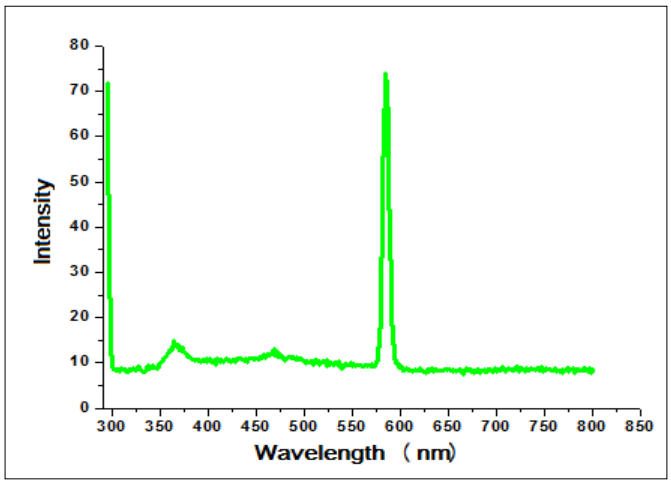


Fig. 6: Fluoresence spectra for synthesized ZnO/Cu/GO nanocomposite

ring, absorbed $CO_2$, and C-H stretching vibration respectively.

*Fluorescence Analysis:*

The prominent quality of the modified ZnO/Cu/GO nanocomposite depends on the fluorescent character of the specified sample. Fig. 6 represents the fluorescent spectrum of the synthesised ZnO/Cu/GO nanocomposite. A small broad peak at 369 nm designated the, near band edge emission of zinc oxide nanoparticles which is a pivotal requirement for an efficient photocatalytic reaction to take place [40]. The formation of a sharp peak at 585 nm is due to the intrinsic defects of zinc and oxygen, which has promoted the charge separation and has increased the life time of $e^-$-$h^+$ recombination reaction [41] and hence the photocatalytic activity of the synthesised nanocomposite has been upgraded. Furthermore, this sharp peak is also responsible for the blue green fluorescence emission which has also authorised the existence of copper atoms embedded in the synthesised nanocomposite [42, 43].The incorporation of copper atoms in the synthesized ZnO/Cu/GO nanocomposite has improved the vacancies by the formation of intrinsic point defects and thereby the


Fig. 7: Visual representation of photocatalytic degradation experiment under direct sunlight

photocatalytic performance of the nanocomposite has increased widely when compared to ZnO/GO nanocomposite.

*Photocatalytic experiment:*

The photocatalytic activity of ZnO/Cu/GO nanocomposite was assessed based on the photocatalytic degradation of Quinalphos. About 3 mg/L of the prepared ZnO/Cu/GO photocatalyst was dispersed in 100 ml of aqueous organic pesticide solution (40 ppm). The pH of the test solution was maintained neutral. The suspension was stirred in the dark for thirty minutes in order to attain adsorption-desorption equilibrium between the catalyst and the pesticide molecule [44, 45]. The blended suspension was then exposed to sunlight and stirred continuously until the solution became clear as displayed in Fig. 7. The concentration of the test solution was monitored continuously using a calorimeter, by departing 3ml of the Quinalphos suspension, followed by centrifugation to eliminate the catalyst from the test solution [46]. The degradation yield in percentage can be defined as follows,

$$\text{Efficiency of degradation (\%)} = \frac{C_o - C}{C_o} \times 100 \qquad (1)$$

*Analysis of the UV-Vis absorption spectrum of Quinalphos during degradation:*

The degradation of Quinalphos was accomplished in the presence of ZnO/Cu/GO nanocomposite under direct sunlight. The absorption spectrum displayed a decrease in the intensity of absorption peaks for Quinalphos at regular intervals of time. In the first instance, the maximum absorption peak at 240 nm for Quinalphos pesticide decreased progressively with an increase in radiation time which specified the effective photocatalytic degradation of Quinalphos in the presence of visible light. The termination of the complete degradation of the pesticide under study was recognised by the gradual decrease and disappearance of the spectral band at 240 nm within 20 minutes. Therefore, the synthesised ZnO/Cu/GO nanocomposite has performed a marvellous operation to degrade Quinalphos solution with a short duration under direct sunlight irradiation. The decrease in the intensity of the absorption peaks with irradiation time has been shown in Fig. 8.

*Chemical Oxygen Demand (COD) removal:*

The COD analysis was performed to evaluate the capacity of the ZnO/Cu/GO nanocomposite in eliminating the chemical oxygen demand present in the pesticide effluent [47]. COD is generally manipulated to estimate the organic strength of polluted water. In the photocatalytic process, COD analysis was analysed in both raw and treated pesticide solutions. The COD value for Quinalphos pesticide solution under study was about 11752 mg/L and it was decreased to a value of 178 mg/L for the above sample after irradiation. The reduction in COD values of the treated pesticide solution signified the mineralisation of the pesticide molecule, together with the removal of colour [48].

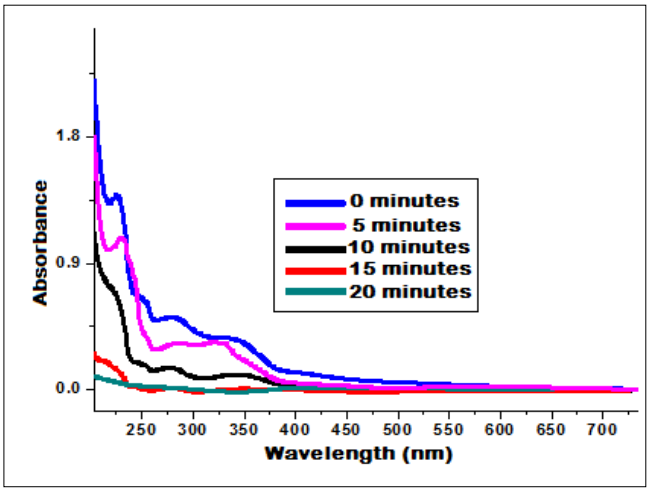


Fig. 8: UV-Visible absorption spectrum for degradation at various intervals of time at neutral pH

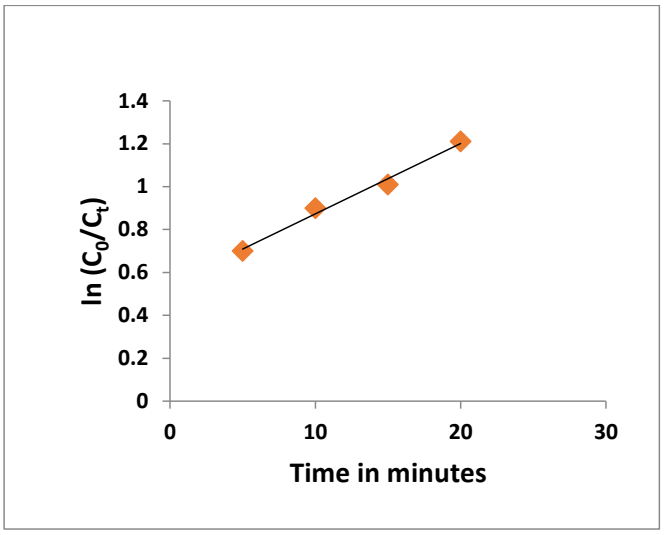


Fig. 9: Kinetics of photocatalytic degradation experiment

*Total Organic Carbon Analysis:*

The mineralisation of cationic and anionic pollutants and their intermediate products during the photocatalytic reaction was assessed by calculating the total organic carbon (TOC) of the aqueous pesticide solution under study [49]. The TOC measurements have revealed the disappearance of organic carbon in the Quinalphos test solution. The outcome displayed the complete degradation of Quinalphos pesticide solution with an efficiency of 95% after 20 minutes of irradiation under direct sunlight. From this evaluation, it was observed that the synthesised ZnO/Cu/GO nanocomposite is an efficient novel photocatalyst which has the ability to decompose toxic organic pollutants effectively in a very short period.

*Kinetics:*

The Langmuir-Hinshelwood kinetic model has been employed to designate the kinetics of photocatalytic reactions. The rate of the reaction has been demonstrated as,

$$r = \frac{dc}{dt} = k\,\frac{KC}{1} + KC \qquad (2)$$

Where, r is the rate of the reactant, c is the concentration of the reactant, t is the time taken, k is the rate constant of the reaction, K is the adsorption coefficient of the reactant.

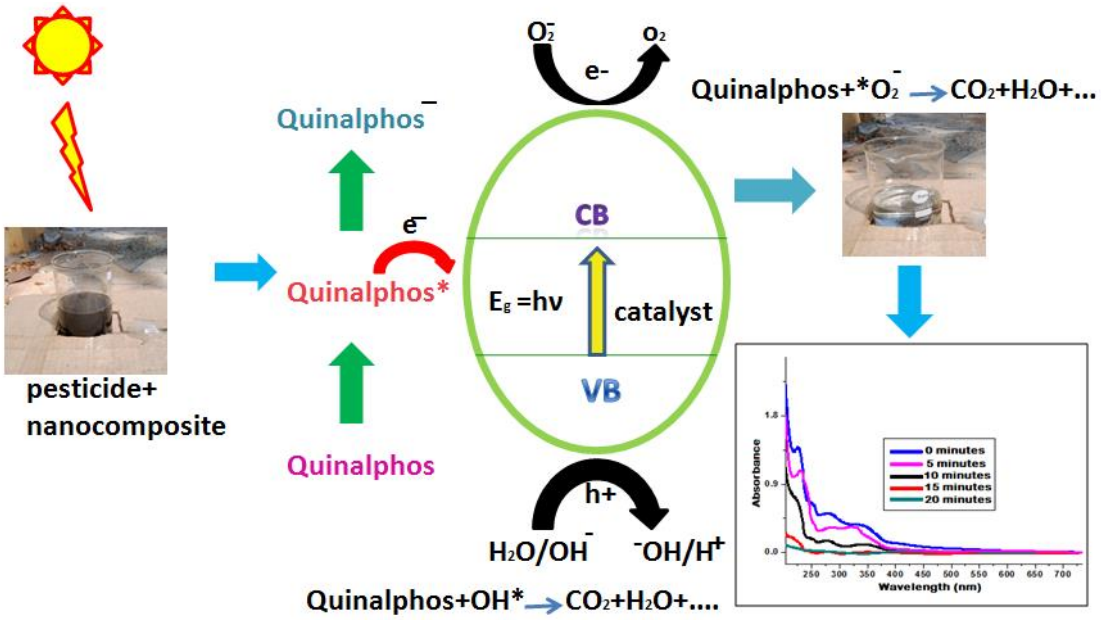


Fig. 10: Representation of charge transfer in the compound materials used in Quinalphos photocatalytic degradation

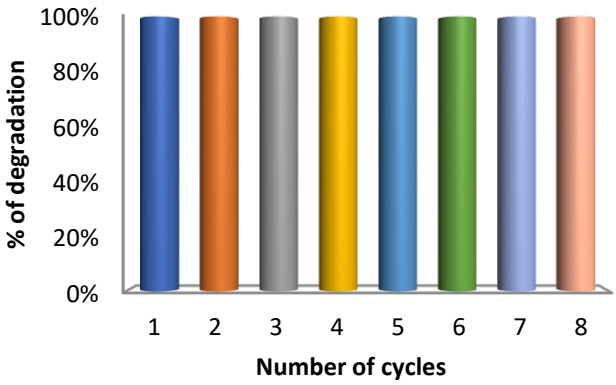


Fig. 11: Recycling ability of ZnO/Cu/GO nanocomposite

When the concentration of c is small, the above equation can be simplified to a credible first order

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

The annotation of linear plots represented in Fig. 9 denotes that the reaction followed pseudo-first order reaction kinetics. [50, 51, 52].

This degradation of Quinalphos pesticide performed using ZnO/Cu/GO nanocomposite followed pseudo-first order reaction kinetics with a reaction rate constant of 4.24 x $10^{-3}$$min^{-1}$and a regression value 0.988.

*Mechanism:*

The photocatalytic mechanism of the synthesised ZnO/Cu/GO nanocomposite for degrading Quinalphos pesticide was sugestted as follows, The phocatalytic activity of ZnO/Cu/GO nanocomposite was improved bt the large surface area of graphene oxide that can contribute to the effective adsorption of the pesticide molecules on the surface of the catalyst and increase the formation of π-π* interaction between the Quinalphos molecules. Further more the doping of copper could minimise the recombination of excited electrons in the conduction band (CB) with the holes in the valence band (VB), which would increase the generation of oxy radicals leading to the oxidative degradation of Quinalphos molecules. The possible mechanism of the photocatalytic degradation of Quinalphos pesticide is given in Fig. 10.

*Turn over frequency of the catalyst:*

Recycling ability of the catalyst was an indispensable property associated with the remediation of environmental pollutants, order to gain a feasible waste water treatment [53]. This quality of the photocatalyst considerably elevated the application cost and strength of the catalyst [54, 55, and 56]. Hence, it was required to substantiate whether the synthesised ZnO/Cu/GO nanocomposite could be recycled in the photodegradation of Quinalphos or not. The expended catalyst was utilised after conscientious washing with double distilled water and recovered by drying after each photocatalytic experimental cycle. It was observed that the synthesised nanocomposite has exhibited the same photocatalytic activity for eight cycles as displayed in the Fig. 11. The out comings has authenticated that the prepared ZnO/Cu/GO nanocomposite could be auspiciously implemented for the elimination of organic contaminants present in aqueous medium.

## CONCLUSION

In the present study, ZnO/Cu/GO nanocomposite was synthesized successfully and characterised by various spectroscopic techniques. The hexagonal wurtzite phase of ZnO and face centered cubic structure of metallic copper was approved by XRD analysis. The SEM analysis has revealed that the prepared ZnO/Cu/GO nanocomposite was an effective photocatalyst due to its increased surface area and excellent light harvesting potentiality. The presence of oxides of zinc and graphene was confirmed by FT-IR analysis. The small band gap of ZnO/Cu/GO nanocomposite has reduced the electron hole recombination reaction; and hence the synthesised nanocomposite has displayed a superior photocatalytic performance for degrading Quinalphos in a very short period. The fluorescence study has exposed the presence of an intrinsic defect which promoted the separation of charges and is responsible for the marvellous photocatalytic activity of the synthesised nanocomposite. A kinetic study was accomplished by using the Langmuir- Hinshelwood model and was found to follow pseudo-first order kinetics. The complete mineralisation (98%) of Quinalphos pesticide solution was further authorised by the reduction in COD and TOC measurements. The synthesised ZnO/Cu/GO nanocomposite was found to be stable and could be reusable without loss in its light-harvesting activity even after eight consecutive runs. Moreover, the photocatalytic degradation of Quinalphos pesticide was successively executed by using ZnO/Cu/GO nanocomposite under sunlight. Fascinatingly, ZnO/Cu/GO nanocomposite has displayed the highest degradation of 100 % at benign pH in a short duration in the presence of sunlight, which was considered as the main advantage of the catalyst. To the best of our knowledge, ZnO/Cu/GO nanocomposite was applied for the first time for photocatlytic degradation of Quinalphos pesticide under visible light irradiation. Therefore, the synthesised ZnO/Cu/GO nanocomposite is a promising, suitable, outstanding, and energetic photocatalyst for mineralisation of toxic organic contaminants present in natural streams and water bodies in a short duration of time with effective application of solar energy.

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## CONFLICT OF INTEREST

The authors declare no conflicts of interest.

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