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GREEN SYNTHESIS OF COPPER OXIDE NANOPARTICLES AND ITS APPLICATIONS

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ABSTRACT

The synthesis of metal oxide nanoparticles through green method approach is cost effective and environment friendly. Hence we propose a cost effective, eco- friendly green synthesis approach for the synthesis of copper oxide nanoparticles using environmentally benign plant leaf extract of Aloe vera and Camelia sinensis. The synthesised Copper nanoparticles was characterised using Solid UV, Infra-red Spectroscopy(IR), Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) studies. The antibacterial and photocatalytic studies of the as-synthesised nanoparticles were studied.

***Keywords*: Aloe Vera, CuA, CuGT, CuO NP, Fehling's solution**

I. INTRODUCTION

Metal oxide nanoparticles are of significant interest because of their unique tuneable optical, catalytic electronic and magnetic properties[1]. Copper (ll)oxide nanoparticles belongs to monoclinic structure system [2]. Cupric oxide is a *p*-type semiconductor [3,4] and has a optical band gap of 2.43 eV which is much larger than that of bulk CuO (1.85 eV)[5]. Applications of CuO NPs include antioxidant, antibacterial, anti fouling, anti-biotic, anti-fungal agent, catalysis and so on [6-10]. Though physical and chemical methods are widely used for the synthesis of CuO NPs, they show drawbacks like expensive reagent, hazardous reaction condition, longer time, tedious process to isolate nanoparticles [11], use of toxic chemicals and formation of dangerous by-products [12] Hence green synthesis is a better choice due to the eco-friendly approach of the synthesis.

In our study, we have highlighted the use of environmentally benign leaf extracts of aloevera and green tea for the synthesis of copper oxide nanoparticles. The morphology, topography, optical ,antibacterial, and photocatalytic studies of the as-synthesised nanoparticles were evaluated.

II. MATERIALS AND METHODS

The plant extracts used for the synthesis of nanoparticles were prepared using the plants such as Aloe vera [Aloe barbadensis Miller] collected from the herbal garden at Stella Maris College,Chennai and dried Green Tea leaves [Camellia sinensis], Tetley brand procured from Nilgiris Super Market. Copper (II) sulphate pentahydrate (Central Drug House (P) Ltd.,), Potassium sodium tartrate tetrahydrate A.R (Nice Chemicals (P) Ltd.,), Sodium Hydroxide Pellets (Avra Synthesis Pvt. Ltd.,) and distilled water along with the leaf extracts were used for synthesis of nanoparticles. Bacterial strains of *Staphylococcus aureus, Bacillus cereus, Escherichia coli* and *Pseudomonas aeruginosa* for antibacterial studies were obtained from microbial culture, Department of Botany,

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Stella Maris College, Chennai. The photocatalytic studies of as-synthesised CuNP were studied on Congo red (Loba Chemie Pvt. Ltd).

2.1 Preparation of Fehling's solution

Fehling's solution is a combination of equal parts of Fehling's A and Fehling's B Fehling's A was prepared by dissolving Copper(II) sulphate pentahydrate (14g) in distilled water (200 mL). Fehling's B was prepared by dissolving potassium sodium tartrate tetrahydrate(70g) and sodium hydroxide (30g) in distilled water (200 mL).

2.2 Preparation of plant extracts

120 g portion of thoroughly washed plant leaves were boiled in 240 mL of distilled water to a moderate boiling and cooled. The resulting extract is used as the Aloe vera extract.

2.3 Preparation of CuO nanoparticles using plant extracts

10 mL of the plant leaf extract was added to 10 mL of Fehling's solution (5 mL of Fehling's A and 5ml of Fehling's B). After 10 minutes, the colour of the solution changed from blue to brick red, indicating the formation of Cuprous Oxide nanoparticles, which was then washed thoroughly with distilled water and then calcined at 52-60 °C. It is then heated at 500 °C for 3 hours in a muffle furnace. The colour of the product thus obtained is black in colour indicating the formation of copper oxide nanoparticles.

2.4 Anti- Bacterial Studies

The antibacterial activity was studied using the disc- diffusion method (Bauer et al., 1996). *S. aureus, B.cereus, E. coli* and *P.aeruginosa* were grown overnight on the Nutrient media. A sterile cotton swab was dipped into the inoculum suspension and the swab was rotated several times with firm pressure on the inside wall of the tube. Different concentrations (50 and 100 µl) of the solvent extracts of CuO nanoparticles prepared using plant extracts were added on to separate sterile disc of 5 mm diameter and allowed to dry. The plates were incubated at 37^{o} C for 24 h. Clear zone of inhibition were measured and calculated.

2.5 Photodegradation Studies

The dye used for photocatalytic studies was Congo Red. The experiment was carried out by introducing 100 mg of CuA /CuGT to 100 ml of a 25 ppm (12.5 mg in 500 mL distilled water) in solution of the Congo red dye and exposing it to UV light for a period of 3hours in a Haber Multi Lamp Photoreactor. The UV absorption profile of the dye was studied for every 30 min after the addition of the synthesized CuA and CuGT nanoparticles.

III. RESULTS AND DISCUSSION

3.1 UV Diffused Reflectance Spectroscopy

The band gap energy of CuGT and CuA were found to be 2.87eV and 2.65 eV by UV diffused reflectance studies Fig 3.1 (a) and Fig 3.1 (b) which confirmed copper oxide nanoparticles can be used as a semiconductor.

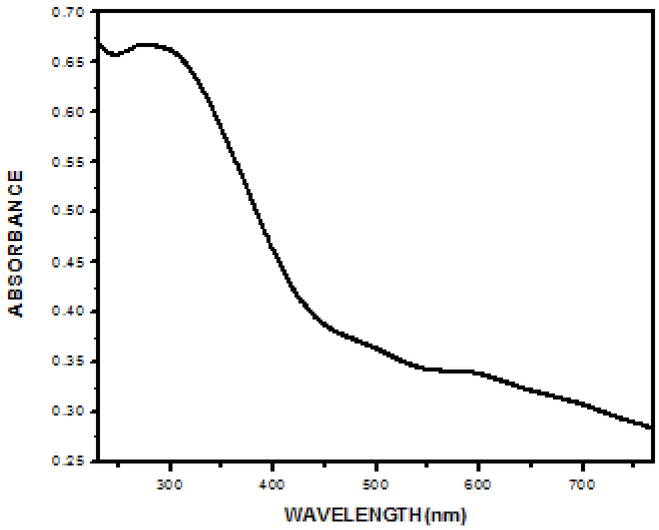

Fig 3.1 UV Absorption spectra of CuA and CuGT nanoparticles

3.2 Infrared Studies

The FT-IR spectra of CuA and CuGT respectively are shown in Fig.2. The spectra shows medium absorption in the region of 3679, 3487, 2934, 2373, 1655, 1448, 533 cm^{-1} for CuA and 3787, 3416, 2914, 2397, 1594, 541 cm^{1} for CuGT. Absorption at 533 cm^{-1} in the case of CuA and 541 cm^{-1} in the case of CuGT identified the presence of CuO nanoparticles.

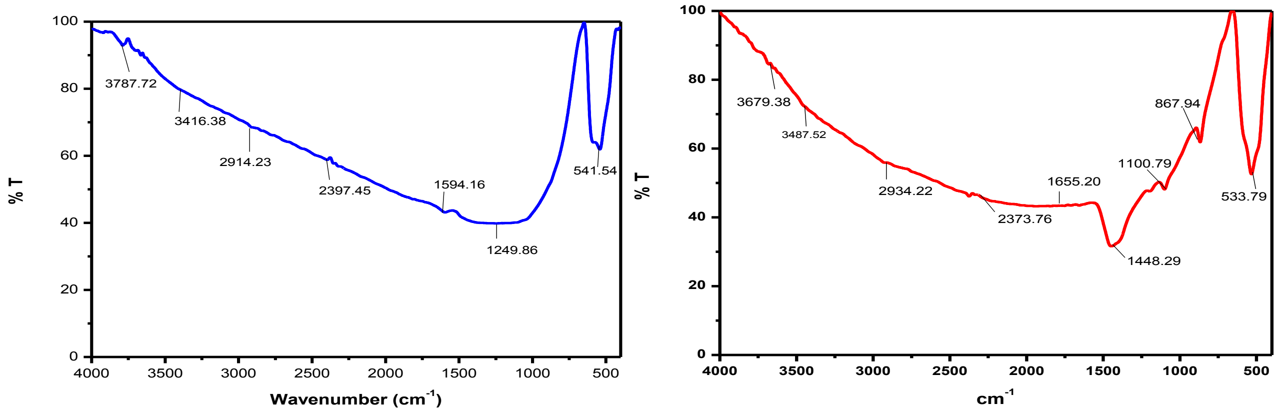

Fig 3.2 FT-IR spectrum of CuA and CuGT nanoparticles

3.3 X-ray Diffraction Analysis

The XRD spectra of as synthesized nanoparticles was carried out using XRD (Bruker AXS D8 Advance) for 2θ values ranging from 10 to 80° using CuKα radiation at λ = 1.5406Å. The 2θ values at 32.13, 35.17, 38.37, 48.47, 53.15, 61.26, 66.31 for CuA and in CuGT, the 2θ values at 32.28, 35.30, 38.47, 48.59, 53.25, 57.95, 61.36, 66.46 were observed. The average crystallite size of CuA and CuGT was found to be 21.10 nm and 20.11 nm.

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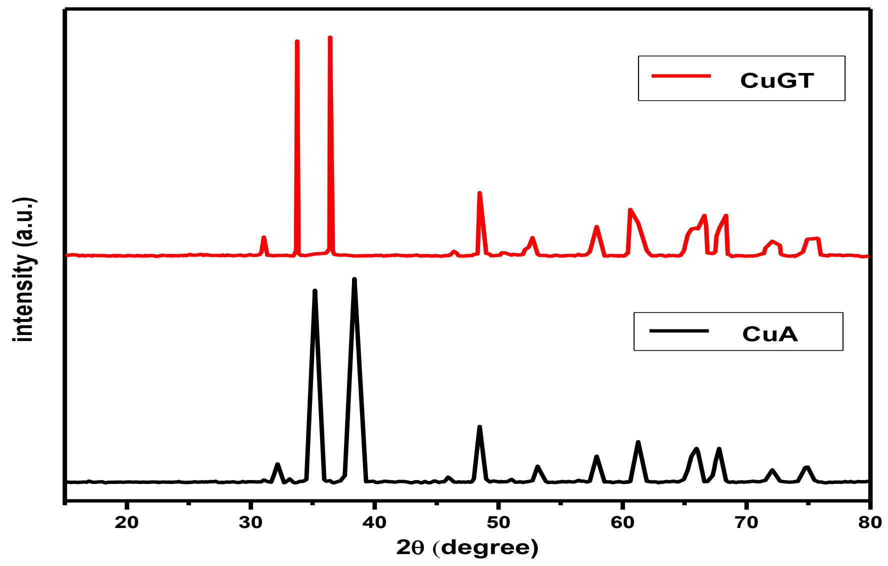
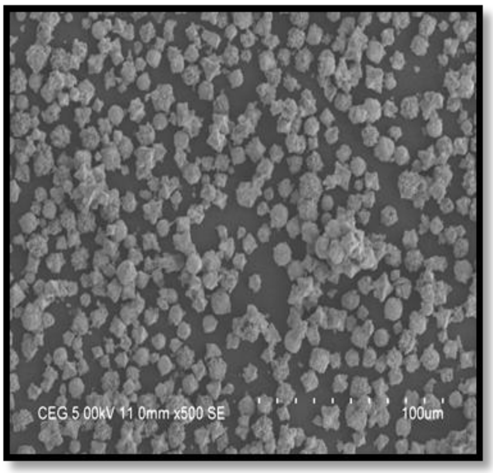


Fig 3.3 XRD pattern of CuA and CuGT

3.4 SEM Analysis

SEM images of synthesised CuA and CuGT nanoparticles are shown in Fig. 3.4. The SEM images of CuA and CuGT indicate a small amount of agglomeration of the nanoparticles. The morphology of CuA nanoparticles exhibits a mixture of truncated stars, spheres and cubes.SEM images shows the particle size ranging from 99.2-113 nm for CuA whereas for CuGT, it is 119 nm- 166 nm.



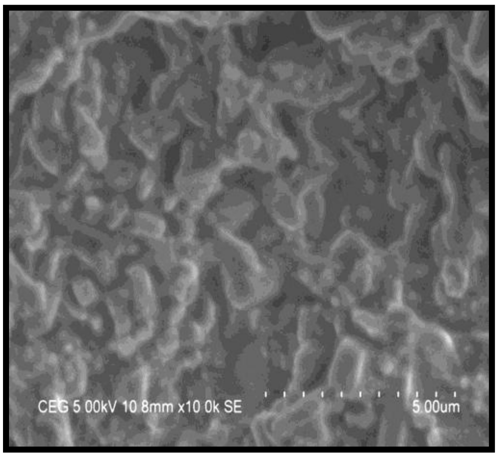


Fig.3.4 SEM images of CuA and CuGT nanoparticles

3.5 Antibacterial Studies

The presence of antibacterial activity on the synthesized CuO NPs (Fig.5) was detected by the Disc Diffusion Method. The antibacterial studies of CuA and CuGT showed reduced activity towards Gram positive and Gram negative bacteria. Temperature affects the antibacterial activity of Copper oxide nanoparticles. At high temperatures, the antibacterial activity of both gram positive and gram negative bacteria as well as the zone of inhibition of the bacteria was found to be reduced.

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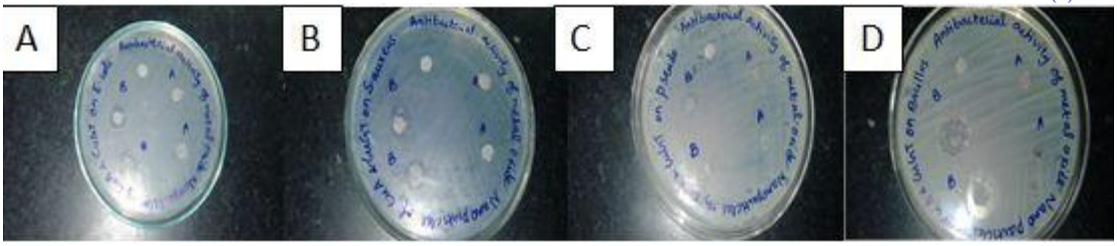


Fig.3.5 Antibacterial activity of CuGT on (A) E.coli (B) S.aureus and CuGT on (C) E.coli (D) S.aureus (control:Plant leaf extract)

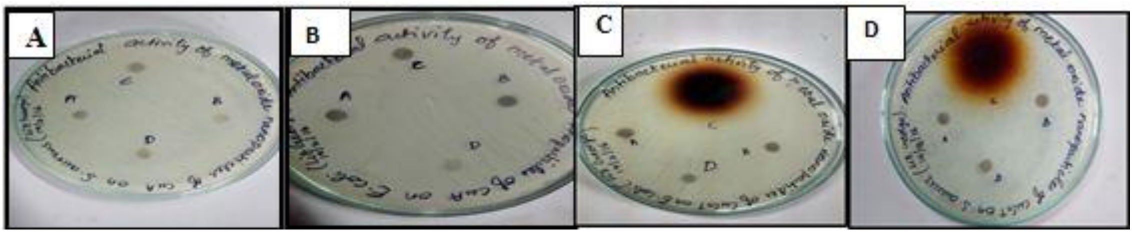
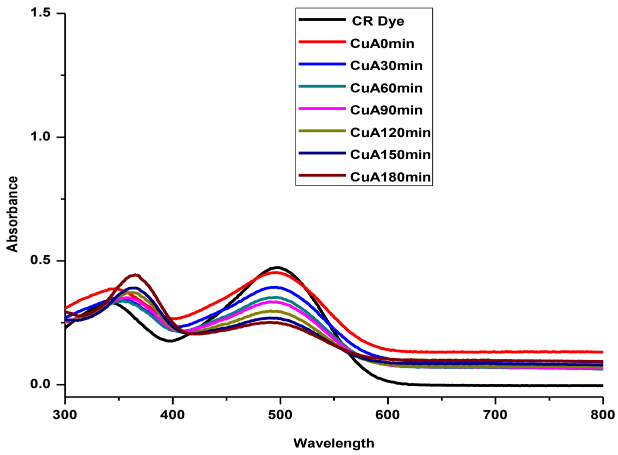


Fig.3.6 Antibacterial activity of CuA on(A) E.coli (B) S.aureus and CuGT on (C) E.coli (D) S.aureus (control:Plant leaf extract)

3.6 Photocatalytic Studies

The UV–Vis absorption curves of CuA and CuGT nanoparticles showing photocatalytic studies are represented in Fig 3.7 and Fig 3.8 respectively. The photocatalytic activity of the synthesized Copper oxide nanoparticles, CuA and CuGT were studied by degrading Congo red(CR) dye. To 100 mL of 25 ppm concentrated dye, 100 mg of the catalysts (CuA and CuGT) were added and the degradation was carried out as mentioned above and the results were recorded.. Initially UV absorption of the CR dye is measured followed which the absorption is measured periodically at an interval of 30 min for 3 hrs with the addition of the catalyst. The Figure shows reduction in the absorption maximum between 350 nm and 500 nm which is a clear indication of the photocatalytic activity of CuA and CuGT nanoparticles.



3.7 Photocatalytic degradation of Congo Red using CuA nanoparticles

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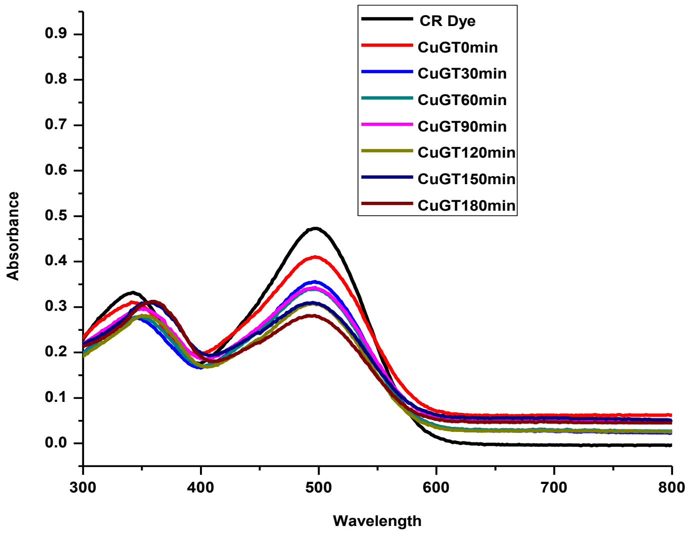
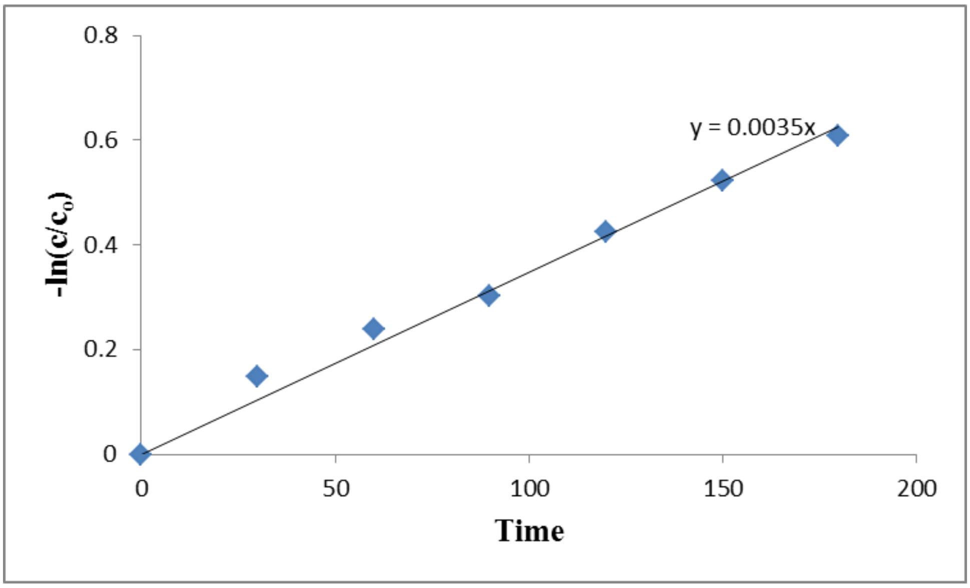


3.8 Photocatalytic degradation of Congo Red using CuGT nanoparticles

3.6.1. Effect of Amount of CuA and CuGT Catalyst on Decolourization of CR

After equilibration time of 20 minutes, photocatalytic experiments were carried out for 3 hours. Concentration of CR at different time intervals was determined spectrophotometrically and the results are shown as a plot of $\ln(C/C_O)$ Vs time in Fig. 3.9 and 3.10 respectively, where C is the concentration at various time intervals and C_O the initial concentration. A linear fit plot was obtained which indicated that the reaction followed the pseudo first order rate kinetics. Rate constants were calculated from each linear plot. Increase in the pseudo first order rate constant with increase of CuA catalyst indicated that the decolourization was truly photocatalytic.



3.9 Plot of ln(C/Co) Vs Time for the degradation of CR on CuA nanoparticles

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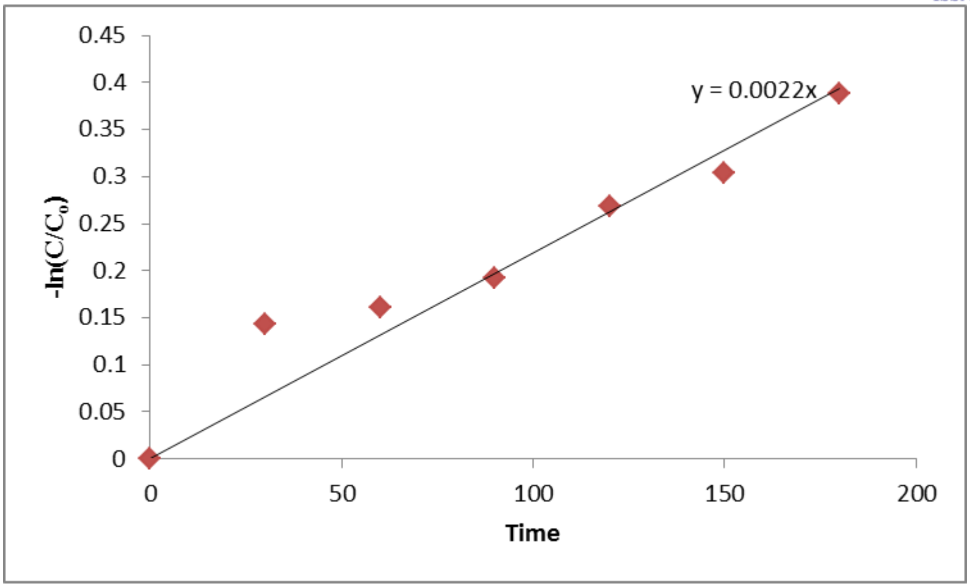
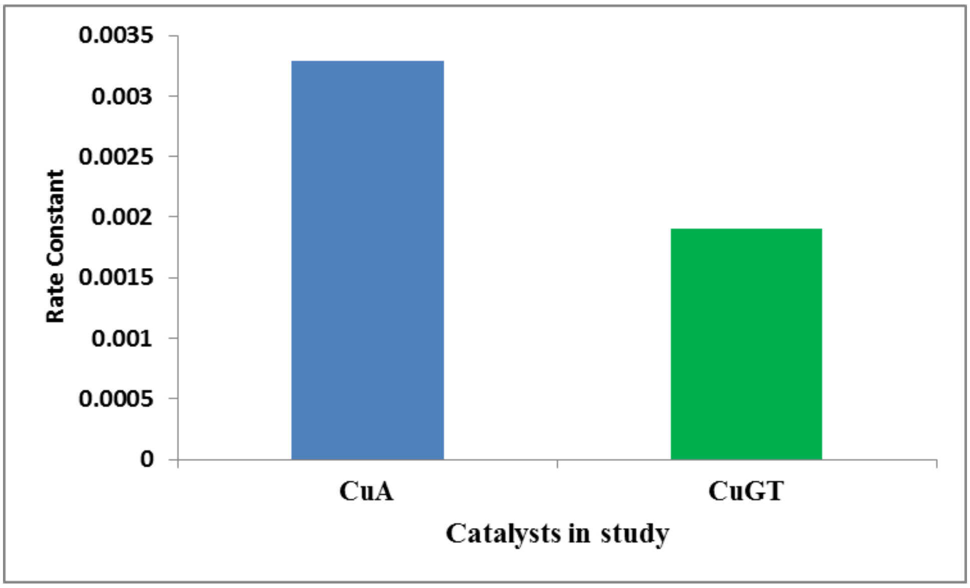


3.10 Plot of ln(C/Co) Vs Time for the degradation of CR on CuGT nanoparticles

3.6.2 Efficiency of the Photocatalytic behaviour of the as prepared Catalyst

A comparison of the efficiency of the photocatalytic behavior of CuA and CuGT were studied. It is observed from Fig (3.11) that CuA .has a higher photocatalytic activity when compared to CuGT. This may be due to the high antioxidant property of alovera which is used as a stabilizing /capping agent in the synthesis of the catalyst. CuA prevents the recombination of electrons from the conduction band to the valence band thereby enhancing its photocatalytic activity than CuGT nanoparticles.



3.11 Plot of Rate Constant against CuA and CuGT nanoparticles

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IV. CONCLUSION

A cost effective and an eco- friendly method was used to synthesize copper oxide nanoparticles with environmentally benign plant leaves extract of Aloe vera and Green tea. UV-DRS, IR, SEM and XRD studies confirmed the formation of copper oxide nanoparticles. The antibacterial studies of CuA and CuGT nanoparticles showed reduced antibacterial activity. Photocatalytic degradation of the as synthesised CuO NPs with congo red dye showed higher photocatalytic activity for CuA when compared to CuGT nanoparticles.

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