



IJEAST

INTERNATIONAL JOURNAL
OF ENGINEERING APPLIED SCIENCE
AND TECHNOLOGY



VOLUME : 4 ISSUE : 08 Print / Issue Publication Date: 11-Feb-2020



ISSN : 2455-2143



DOI : 10.33564/IJEAST.2019.v04i08.062

Indexed In



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COMPARATIVE STUDY OF PHOTOCATALYTIC DEGRADATION OF METHYLENE BLUE AND METHYL ORANGE IN PRESENCE OF SOLAR LIGHT USING GREEN SYNTHESIZED CuO NANOCATALYST

S. Nazima Banu

Assistant Professor, Department of chemistry and Physics,
Nadar Saraswathi College of Arts and Science, Theni, Tamilnadu, India

ABSTRACT: The use of colored semiconductor oxide like copper (II) oxide for photocatalytic bleaching of Methylene blue and Methyl Orange was investigated in detail. In order to harness the solar energy, the effective wavelength of the photocatalyst is to be expanded into the visible region and that increases the rate of photocatalytic bleaching of the dye. In progress of the reaction was observed spectrophotometrically. Metal oxide Nanoparticles are synthesized by green way because its low cost and doesn't affect the environment. The resultant nanoparticle was characterized using UV-vis, IR, SEM and XRD respectively. The comparative studies of photocatalytic activity of copper (II) oxide (CuO) as made using photocatalytic bleaching of Methylene blue as Methyl Orange. The rate of photocatalytic bleaching of the dye was observed and also determined the percentage of removal of dye. On the basis of rate of the reaction (rate constant) the order of photocatalytic activities of the semiconductor oxides was found to be $\text{CuO} > \text{PbO}$. A tentative mechanism for the photocatalytic bleaching of Methylene blue has also been proposed. The results showed that CuO photocatalyst shows a high activity for (Methyl Orange /Methylene Blue) degradation under UV irradiation.

Key Words: Photocatalytic degradation, CuO and PbO NPS, UV-Visible, SEM, IR, XRD, Photocatalyst.

I. INTRODUCTION

Now a days research is focused on reactive and other anionic dyes because a large fraction of these dyes are remain in waste water due to low removal efficiency of the conventional wastewater treatment plants Using various methods but it affects the environmental contamination caused by dyes, the purification of water and air is needed repoted by Batool et al.[1].

This Paper reported as the most effective and useful photocatalyst due to its wide application in the field of waste water treatment. Heterogeneous photocatalytic process is an authentic technique, which can be successfully used to oxidize the organic pollutants present in the aqueous system. They have various Process to removal of dye such as filtration, degradation, oxidation, precipitation, filtration, aerobic and anaerobic microbial degradation, coagulation, membrane separation, electrochemical treatment, flotation, hydrogen peroxide catalysis, and reverse osmosis, ozonation and biological techniques can be employed to remove various pollutant form the textile industry wastewater was reported by Aminia et al.[2]. This photocatalytic method was based on the reactive properties of photogenerated electron- hole pairs. They were generated in the semiconductor copper oxide nano particles under irradiation at suitable wavelengths ($\lambda \leq 400 \text{ nm}$). These electrons and holes could also recombine, it could decompose contaminants degraded on the CuO surface. Copper oxide particles show effective catalytic removal of organic dyes such as malachite green, when particles were added into it. The use of green method increased so much because of its easy preparation and low manufacturing cost have investigated by Wahyuningsih et al.[3]. Moreover, less to toxic starting materials and ease of handling make it more favorable Metal oxides have attracted increasing technological and industrial interest and tremendous application in various fields such as electronics, solar energy conversion, water treatment, catalysis, photonics and biosensors. They are also used as catalyst in the photo degradation of dyes has been reported Ghane et al. [4]. It is used as a semiconductors, solar energy transformation and high tech superconductors. Amount of adsorbed Methyl Orange increases with dye concentration and for concentrations higher than $1 \times 10^{-3} \text{ M}$ it increases only slightly. It means that there is a direct relation between amount adsorbed and degradation rate and thus Photodegradation of dyes using CuO can be used for

treatment of colored industrial effluents containing dyes. In place where we have plenty of sunlight solar radiation can be used for degradation has been investigated by Ashok V et al.[5].

Green synthesis has been concerned in synthesis of highly stabilized nanoparticles. Synthesis of nanoparticles taking assistance of ecofriendly methods has achieved huge attention in the modern era has been reported by Awwad et al. [6]. The particles produced by green synthesis differ from those using physio-chemical approaches. Green synthesis, a bottom up approach, is similar to chemical reduction where an expensive chemical reducing agent is replaced by extract of a natural product such as leaves of trees/crops or fruits for the synthesis of metal or metal oxide NPs has been synthesized by Karami et al. [7].

Methylene blue, Methyl orange used in textile and printing. Of the recent technologies, heterogenous photo catalysis using CuO nanoparticles are three inexpensive, clean and promising method for the degradation of organic pollutants in water [8]. However, the photochemical process of CuO can only be initiated by UV light owing to its wide band gap which confines its application under visible light has been investigated by Abdulmalik et al. [9],[10]. Furthermore, the photocatalytic activity of CuO are hindered by the recombination of the photo generated electron hole pairs. The study also compares the catalytic activity of Methylene blue as well as Methyl Orange.

II. MATERIALS AND METHODS

Copper sulphate , Mentha longifolia, Spirit , De-ionized water

These are purchased from Scientific companies such as Modern Scientific and Universal Scientific.

A. Preparation of Mentha longifolia leaf extract

Mentha longifolia leaves were collected from home and was thoroughly washed with distilled water in order to remove the dust particle. All glass wares were washed with de-ionized water. 5gms of mentha longifolia weighed and boiled for 30 minutes, and filtered. The filtrate used as reducing agent.

B. Preparation of stock solutions

A stock solution of 0.1N copper sulphate was prepared by dissolving 3.79g/100ml using Double distilled water.

C. Green Synthesis of Copper Oxide Nanoparticles

The green synthesis of copper nanoparticles has been carried out using aqueous solution of copper sulphate and extract of Solanum nigrum. The solution was stirred for 30 minutes. The colour change from light green to dark green colour has been observed which confirms the presence of copper nanoparticles.



Fig 1. Green synthesis of CuO Nanoparticles

D. Preparation of dye solution

10^{-3} dye solution was prepared by weighing about 3.73 g and 3.27 g of methylene blue and methyl orange made upto 100 ml using double distilled water respectively. From this 10 ml of methylene blue and methyl orange were taken in a test tube and add 0.1 g of CuO and PbO nano catalysts then kept in sunlight respectively. The dye has been degraded by changing the colour detected with different time interval.

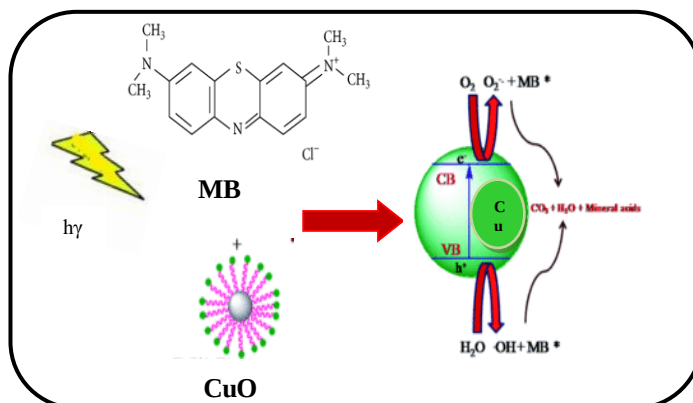


Fig 2: Schematic Diagram of Photodegradation of Methylene Blue dye using green Synthesized CuO NPs

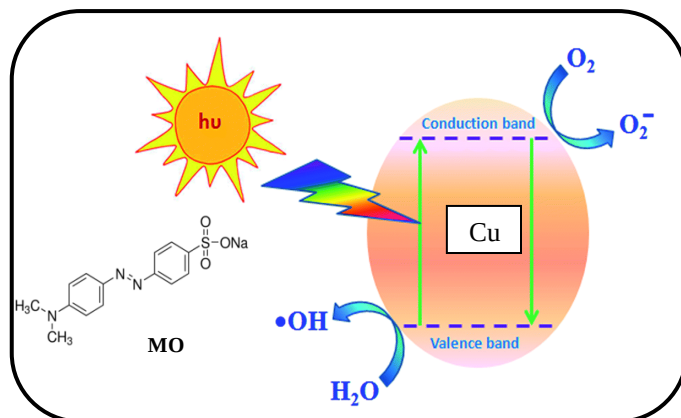


Fig 3: Schematic Diagram of Photodegradation of Methyl Orange dye using green Synthesized CuO NPs

III. RESULT AND DISCUSSION

A. Characterization of CuO NPs by UV-Visible Spectroscopy

The presence of copper oxide nanoparticles is confirmed at the range of 200-1100nm. The eco-friendly method for the synthesis of copper oxide nanoparticles using *mentha longifolia* leaves extract proved feasible, cost free and successful method. UV-Vis spectra analysis has apparently shown the formation of copper oxide nanoparticles. Nanoparticles synthesized have variety of application in the different field. In these spectra λ_{max} for CuO are observed at maximum absorption peak is between 265-285nm. The peak at about 280nm was achieved (Figure 4). This indicates the absorption shift towards the shorter wavelength, because of the particle size reduction.

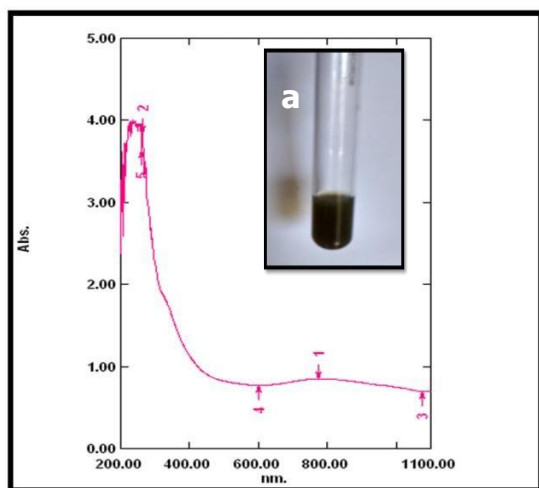


Fig 4. UV-Visible Spectrum of CuO NPs. Insert: Photographs of corresponding UV-Vis spectra of CuO NPs

From these spectra, it is evident that resultant nanoparticles were embedded in silica matrix and exhibited the significant blue shift. This is an indication of strong quantum confinement. The bulk value for CuO are at 200-380nm.

B. Characterization of CuO NPs by SEM, XRD and IR

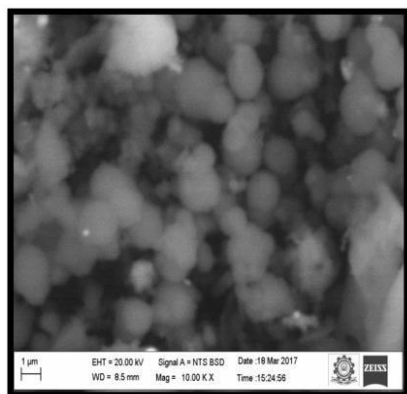


Fig.5 SEM Image of CuO Nanoparticle

The average particle size of copper nanoparticle was analyzed by SEM model (JEOL-6390). The range of grain of copper oxide nanoparticle was calculated about 50.5-130nm by SEM micrograph. It was observed that particles were smooth with a spherel shape (Figure 5). The CuO Nano particles have been distributed well within the range of 100nm which is the favorable for some other purpose [11]. We can conclude that the samples of CuO synthesized are having particle size in the Nano scale.

Copper oxide nanoparticles were examined by X-ray diffractometer. Copper oxide powder was put in cubes of XRD for calculation of intensity. The resultant pattern of synthesized nanoparticles was analyzed. The peaks at 2θ correspond to intensity as the peaks at 28, 29.8, 32.1, 35.8, 36, 43.3, 47.5, 51.1, and have 112, 200, 103, 202, 004, 111, 301 and 200, pattern which is compare to JCPDS card no (049-1832). The pattern of Cu nanoparticles compared to JCPDS card no (01-085-1326), the peaks at 2θ . XRD pattern confirmed that CuO nanoparticles are highly crystalline with cubic crystal structure. The average size of the particle calculated by Scherrer equation was 60-100nm (Figure 6). Fig. 6 shows the XRD pattern of CuO. The observed " 2θ " values come in good agreement with standard " 2θ " values. This confirms that powder prepared was CuO. The size of the CuO nanoparticles thus estimated was found to be 6.64 nm.

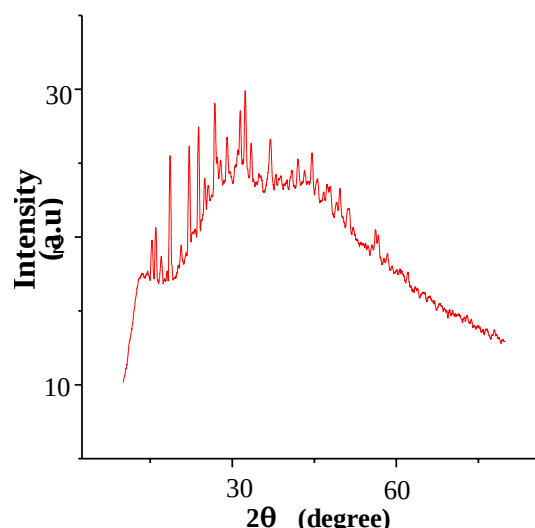
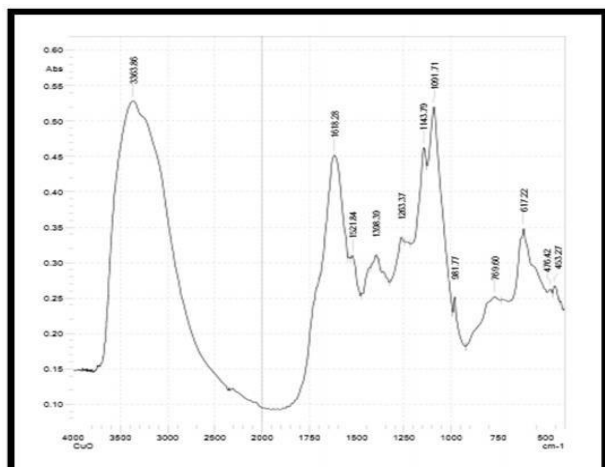


Fig.6 XRD spectrum of CuO Nanoparticle

In this analysis, FTIR spectrum was analyzed. The analyzation confirms the presence of copper nanoparticles. Different peaks were observed at 1100cm⁻¹ confirm

formation of Copper oxide nano particle speaks was observe in range of 400-4000cm⁻¹. The FTIR spectrum of Copper oxide nanoparticle exhibits that the broad absorption band at



32cm⁻¹ corresponds to the hydroxyl (OH) functional group in alcohols and phenolic compounds (Figure 7). The peak at 1601.2cm⁻¹ is due C=C aromatic bending.

Fig.7 FT-IR Spectrum of CuO

Groups	Stretching and Bonding	Peaks
OH-stretch	Stretching	3250.8
C-H	Stretching	2860.1
C=C	aromatic bending	1650.7
C=O	Stretching	2250.1
CuO stretch	Stretching	1100
C-Cl	Stretching	550-850

Table 1: Absorption peak at 1038.0cm⁻¹ stretching vibration of C–O group of primary and secondary alcohols (C–O), while smaller peaks at 900–700 cm⁻¹ were also assigned to the aromatic bending vibration of C–H group

Absorption peak at 1038.0cm⁻¹ stretching vibration of C–O group of primary and secondary alcohols (C–O), while smaller peaks at 900–700 cm⁻¹ were also assigned to the aromatic bending vibration of C–H group.

C. PHOTO CATALYTIC DEGRADATION STUDIES

Effect of variation of initial concentration of Methylene blue and Methyl Orange dye

The catalytic activity of the CuO NPs analyzed by the degradation of Methylene blue and Methyl Orange dye. The catalytic activity of the CuO NPs analyzed by the degradation of Methylene blue and Methyl Orange dye. The mixture containing the dye solution and the nanoparticles is exposed to sunlight and its effect on rate of bleaching was studied. The extent of degradation of the dye in solution is

studied at definite intervals of time (30 minutes) using UV-visible spectrum. Fig.8 & 9. If more concentration of dye is taken, it imparts a darker colour to the solution and it may act as filter to the incident light reaching the semiconductor surface. As a consequence, the rate of Photo catalytic bleaching of Methylene blue and Methyl orange dyes decreases. When CuO irradiated with light, CuO is excited by photons led to the formation of electrons and holes in the conduction and valance band of CuO. The electrons react with surface adsorbed O₂ to produced O₂^{•-} and holes react with H₂O to create •OH.

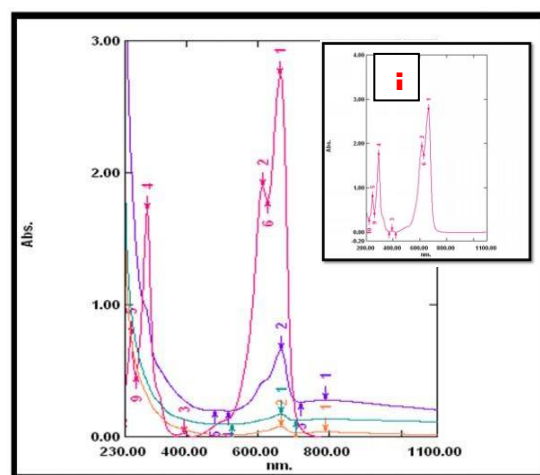


Fig.8 UV-Vis spectra of Photodegradation of Methylene blue (MB).Insert: (i) UV-Vis spectrum of MB alone.

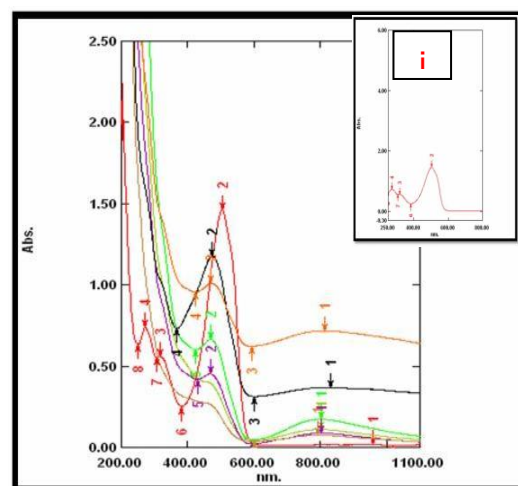


Fig.9 UV-Vis spectra of (a), (b) Photodegradation of Methyl Orange (MO). Insert: (i)UV-Vis spectrum of MO alone respectively.

D. DETERMINATION OF PERCENTAGE REMOVAL OF DYE

Stock solution of dyes (0.372M of methylene blue and 0.327 M of Methyl Orange) was suitably diluted to the required initial concentration of dye with double distilled water. 10 ml of the dye solution of known initial

concentration (C_0) was taken in test tube. Required amount of one of the photocatalysts (such as CuO) were exactly weighed and then transferred into the dye solution. The beakers were then exposed to sunlight, for a fixed period of contact time. The final Concentrations (C) were obtained from Beer graph.

The extent of removal of the dye in terms of the value of percentage removal of dye has been calculated using the following relationships.[12]

$$\text{Percentage removed} = 100(C_0 - C) / C_0$$

Where C_0 =Initial concentration of dye (ppm), C =Final concentration of dye (ppm)

Methylene Blue with CuO

Where $C_0 = 0.373 \text{ M}$; $C = 0.0170 \text{ M}$,
Percentage removed = 95.44

Methyl Orange with CuO

Where $C_0 = 0.327 \text{ M}$; $C = 0.0545 \text{ M}$, Percentage removed = 83.33%

E. Time Effect on Dye Removal:

Decolorization of dye Methylene blue and Methyl Orange at room temperature was analyzed. Initially 10ml dye solution was taken and 1mg of greenly synthesized copper nanoparticles using *mentha longifolia* leaves extract dissolved in it. 0.1mg of CuO was degraded as a MB and MO. The photo catalytic degradation of the dyes were carried out in the presence of solar light. The time interval was taken in consider gradually during reaction. The removal percentage of decolorization was calculated and draws graphically. The maximum time was 120 mints with 95.44 % and 83.33% color removal respectively.. This confirms the rapid reaction of copper oxide nanoparticles Photodegradation of Methylene blue and Methyl Orange dye solutions with CuO nanoparticle.

Beer Lambert's Law:

The absorption of light in the visible and near ultraviolet regions by a solution is governed by a photo physical law known as the Lambert- Beer Law. The time increases as the concentration of dye decreased.(Figure 10 & 11) and it described by pseudo order kinetics, confirmed by removal of dye from water.[12]

$$A = \epsilon b C$$

Where,

ϵ =Extinction coefficient or molar Absorption coefficient ($\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)

A =Absorbance, b =Path length (cm), C =Concentration (mol dm^{-3})

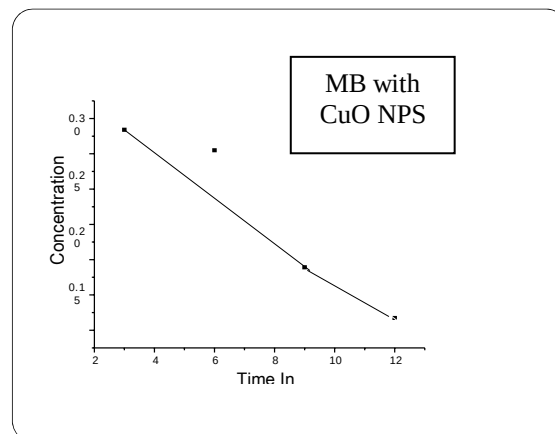


Fig 10. The Photo degradation of dye Methylene Blue with CuO can be described by pseudo First Order Kinetics

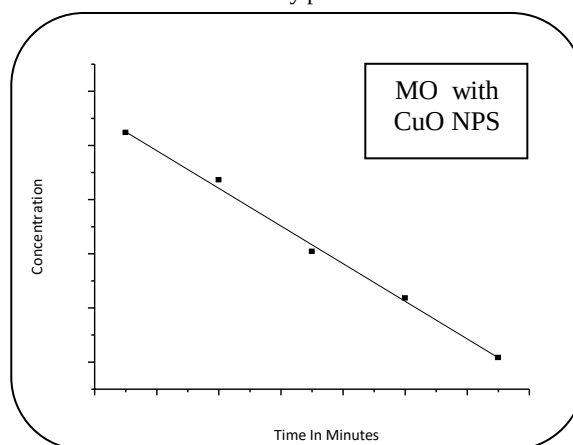


Fig 11. The Photo degradation of dye Methyl Orange with CuO can be described by pseudo First Order Kinetics

IV. CONCLUSION

Here in conclusion, we concluded a method of green synthesis of CuO nanoparticles by leaf extract of *mentha longifolia* plant. This eco-friendly way of synthesis of nanoparticles is more recommended over other methods as green synthesized CuO NPs are cost-effective, biogenic molecules with the capability to serve as dye absorbent. From vast of analyzation on nanotechnology for synthesis of nanoparticles it is declared that it is safer and best by using natural plants. Nanoparticles synthesized can be applicable in the different field of biochemistry, Pharma, agriculture and industry. Copper oxide nanoparticles have the ability to remove carcinogenic dyes. In the present study, Methylene Blue and Methyl Orange was removed by nanoparticles and its time then the contact time was observed. The maximum contact time was 120min was observed , nanoparticle amount 1mg which proved green synthesized copper nanoparticles, as best removal of carcinogenic dye like Methylene blue and Methyl orange. The photo catalytic degradation of the dyes were carried out in the presence of solar light and the photodegradation for methylene blue and Methyl Orange with CuO was found to be 95% and 83% respectively. The green synthesized nano



catalysts have good photocatalytic properties for the degradation of organic pollutants of dyes like basic methylene blue as well as acidic methylene orange.

Acknowledgement:

I would like to thank my colleagues and Management NSCAS, Theni.

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