INDO AMERICAN JOURNAL OF PHARMACEUTICAL RESEARCH

PHOTO KINETIC STUDIES OF METHYLENE BLUE DYE BY USING GREEN SYNTHESISZED COPPER NANOPARTICLES FROM *AREVA LANATA* LEAF EXTRACT

Seeram. Hari Prasad*, G.Susheela Bai, B.Kishore Babu, M S N A Prasad
Department of Engineering Chemistry, Andhra University, Visakhapatnam, India.

ARTICLE INFO

Article history
Received 25/08/2017
Available online
20/10/2017

Keywords
Copper Nanoparticles (CU-NP),
Areva Lanata,
Methylene Blue Dye,
Photo Degradation.

ABSTRACT

Green synthesized copper nanoparticles are applied to photo degradation of methylene blue organic dye and their photo-kinetics also studied. copper nanoparticles are prepared from green method by using *Areva lanata* leaf extract. The kinetic studies are carried out at different time intervals under sun radiation of exposure of time is 90 minutes. The degradation percentage is 72.60. the rate constant obtained from this studies is 3.4545×10^{-4} Sec^{-1}.

Corresponding author
Seeram Hariprasad
Department Of Engineering Chemistry,
Andhrauniversity,
Visakhapatnam-530003-India.
hari1986chem@gmail.com

*Please cite this article in press as **Seeram Hariprasad** et al. Photo Kinetic Studies of Methylene Blue Dye by Using Green Synthesiszed Copper Nanoparticles from Areva Lanata Leaf Extract. Indo American Journal of Pharmaceutical Research.2017:7(09).*

INTRODUCTION

Metallic nanoparticles plays major role in the field of nano medicine and Nanotechnology. because of their variety and large applications. nanoparticles used in almost all fields. Several methods have been used for the synthesis of nanoparticles. But green method is best suitable method. Due to non-toxic chemicals were used.

Dyes are belongs to organic compounds [8]. Dyes are mainly used as a coloring agent in textile and paper industries. They are non degradable and carcinogenic agents. Moreover, to unique in their products most of the industries uses colour dyes, without any treatment the coloring material are liquidated in water leads to contamination of resources [9]. The release of dye effluents in aquatic system is major environmental concern because coloration not only decreases sunlight penetration and toxic compounds during chemical or biological reaction pathway that effects aquatic flora and fauna. [10].

Many reports are suggested that Metal and Metal oxide nanoparticles are used to photo degradation process such as fish scale of *Labero rohita* [1], *Hypnea musciformis* [2], *Casuarina equisetifolia* leaf extract [3], *Zanthoxylum armatum* [4], *Carica papaya* [5], *centella asiatica* (L.) [6], *pyrus pyrifolia* [7].

In this present study, we discuss photo catalytic degradation of methylene blue orange dye by using green synthesized copper nanoparticles as a catalyst under sun light of various time intervals. Copper nanoparticles are acting as a good catalyst in photodegradation of methylene blue dye.

EXPERMENTAL WORK:

MATERLS AND METHODS:

Preparation and characterization of green synthesized copper nanoparticles from *Areva lanata* leaf extract was already done and reported [11].

Areva lanata extract is prepared by 10 gm of dried leaves are taken in clean and dry conical flask. To it add 100 ml of double distilled de ionized water. The colour of the extract is light brown. 10 ml of leaves extract is added to 90 ml of 1 mM copper sulphate solution. The colour of solution is changes from light brown to green, indicates the formation of copper nanoparticles. the reaction mixture incubated 24 hours at room temperature. The mixture is centrifuged 20 minutes at 10,000 RPM and washed double distilled de ionized water, dried at 60^0C.

CHARACTERIZATION:

UV-Visible absorption spectra are measured suing shimdzu uv-2203 doublem beam spectrophotometer. FTIR spectra are obtained with IR-prestige-21shimaduz, FTIR spectrophotometer, using Kbr pellet method. SEM studies of silver nanoparticles is done by using jsm-6610lv machine. The morphology of copper nanoparticles is done by TEM analysis, by using x-pert pro machine.

PHOTO DEGRADATION:

The photocatalytic activity of green synthesized CuNPs is tested against aqueous solution of methylene blue dye.

An aqueous solution of Methylene blue 30 ppm solution is prepared by in 500ml of double distilled water.250 ml of 30 ppm aqueous solution of the dye is taken out in 250 ml of clean, dry conical flask. to this 5 mg of green synthesized copper nanoparticles is added. the solution appeared as colloidal nature. the mixture of solution is exposed to sun light for about 150 minutes. Experiment is done between 11 am to 1 pm {temperatures 35-39^0c.}.

In every 15 minutes of time intervals, 5 ml of reaction mixture is taken out into centrifuging tubes and centrifuged, after that the filtrate is studied to monitor the absorption maximum values using UV-visible spectrophotometer. The readings are noted in Table. Before exposure to sun light the aqueous Methylene blue solution gives UV-Visible absorption maximum value at 664 nm. The blue colour of the solution is found to slowly decolorizes within an exposure time of 90 minutes.

RESULTS AND DISCUSSIONS:

The VU-VISIBLE, SEM, FT-IR, TEM, spectral studies of green synthesized copper nanoparticles from *Areva lanata* leaf extract was reported [11].

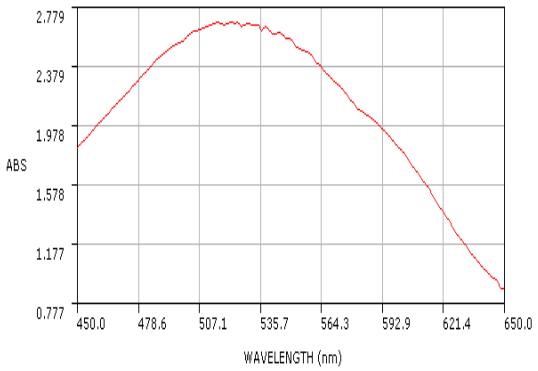


Fig.1: UV-Visible spectrum [11].

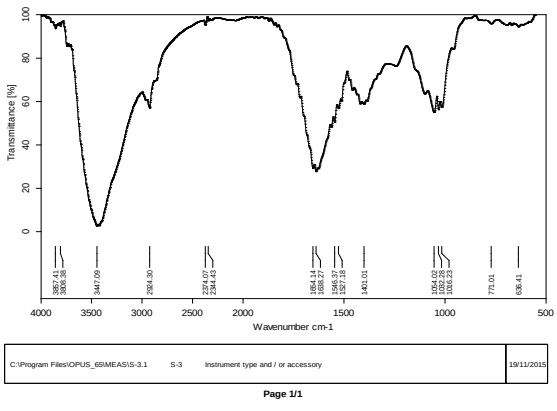
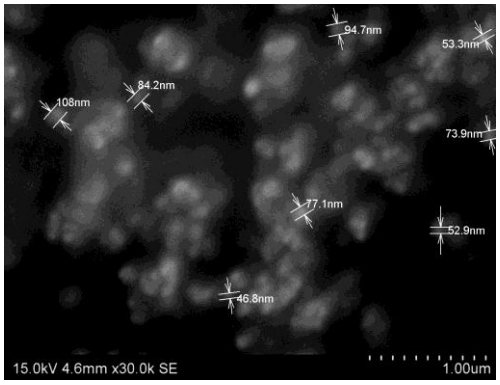
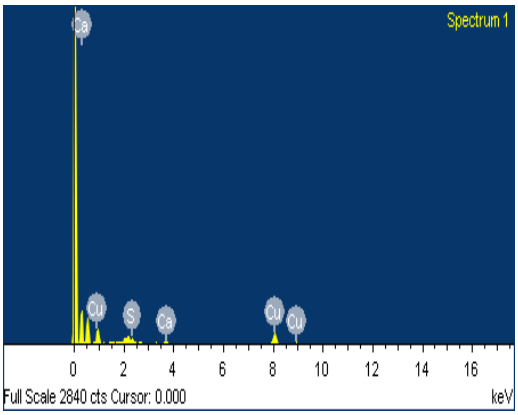


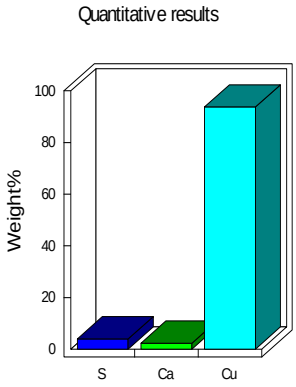
Fig.2: FT-IR spectrum [11].



.

Fig.3: SEM spectrum [11]





.

Fig.4: EDX spectrum [11].

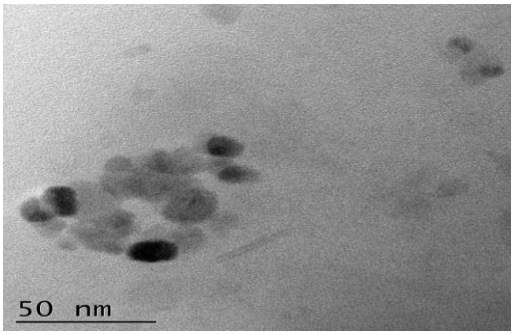


Fig.5: TEM image [11].

PHOTO KINETIC STUDIES:

The photo degradation experiments are carried out under sun light on the 30 ppm organic dye solution using 5 mg Cu-NPs acting as a catalyst. It is found that the colour of methylene blue solution which is originally dark blue slowly turned to pale blue. The colour change is indicated by Figure (6).

Fig.6: Colour change of methylene blue dye after addition of CuNPs.

Time vs absorption graph

The degradation study is evaluated via time vs light absorption graph by collecting absorption data from UV-Visible spectrum collected at various time intervals as given Figure (8).

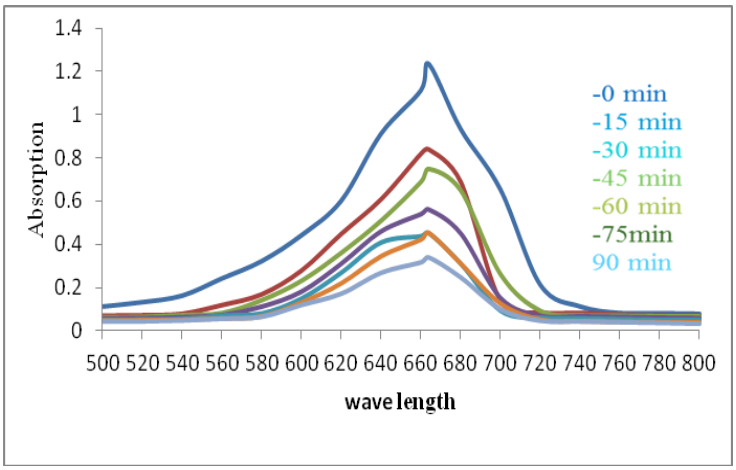


Fig.7: Degradation graph of methylene blue.

Time vs % of degradation

The efficiency of Cu-NPs as photo catalyst is evaluated by finding the percent degradation at various intervals of time. The corresponding graph is shown in Figure (8). We can see that during the initial stage of photo degradation reaction, the % degradation is very slow. But it is found to increase with time. After 90 minutes of the reaction time a maximum degradation of 72.60% is found. After which the absorption maximum is very much reduced, and hence the experiment is stopped after 90 minutes.

Many reports suggested that photo degradation of dyes is considered as pseudo-first order reaction.

$$\% \text{ of degradation} = (A_0\text{-}A)/A_0 \times 100$$

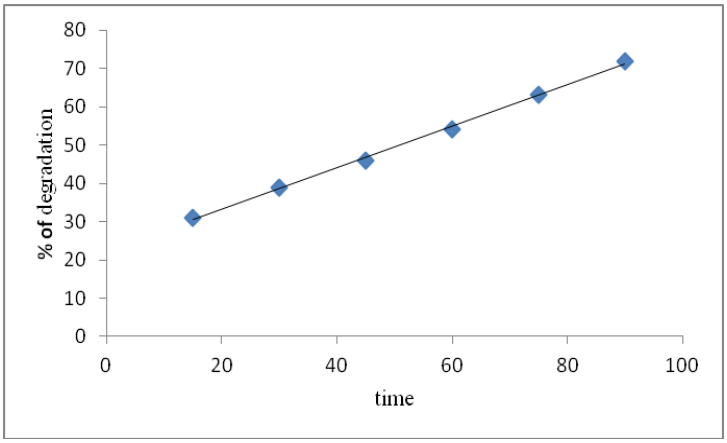


Fig.8: Time vs % degradation graph.

Time vs 2+log(A) graph

The kinetics of the photo degradation study is evaluated by plotting a graph between time and 2+log(A) values as given in Figure (9). It gives a straight line with a negative slope. The slope is found to be 0.0129.the plot indicates that photo degradation of Methylene blue solution carried out by green synthesized Cu-NPs follows pseudo first order reaction.

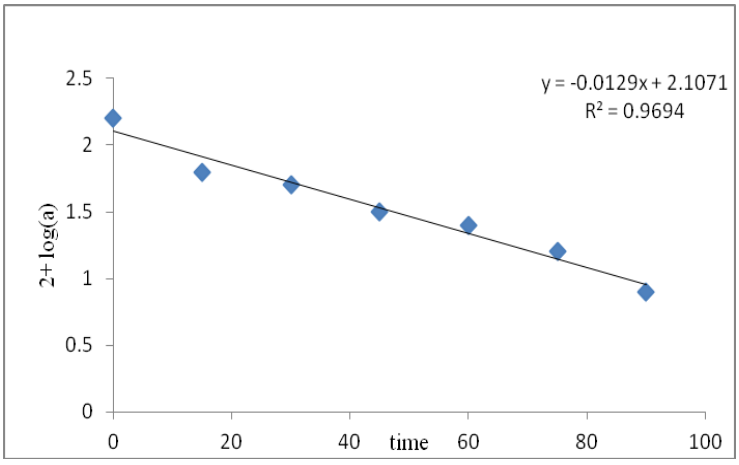


Fig.9: Time vs log(A) graph of Cu-NPs.

Time vs log(A_0/A)

We can also study the kinetics of photo degradation by drawing a graph between time and log(A_0/A). The graph is shown in Figure (10) that shows a positive slope of 0.0093.

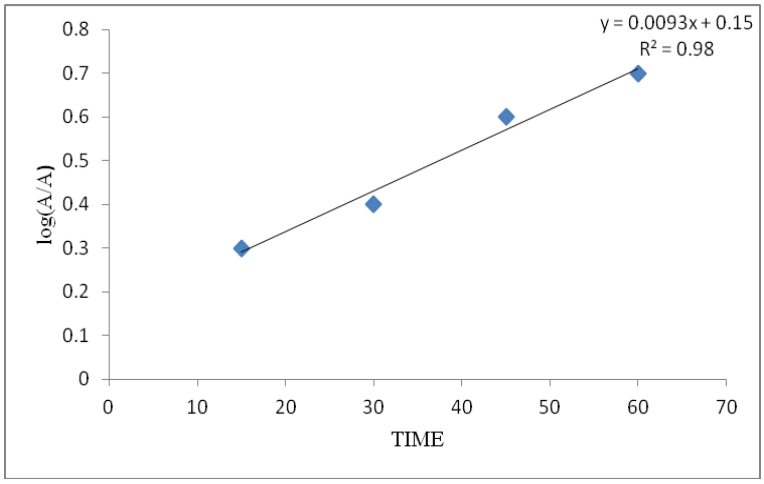


Fig.10: Time vs log(A_0/A) graph of Cu-NPs.

From the graph, it is clearly indicated that the photo degradation of the dye follows pseudo first order reaction. The rate constant of the degradation of methylene blue by green synthesized Cu-NPs is calculated by following equation.

$$\mathbf{K = (2.303 \times M) / 60}$$

$$\mathbf{K= (2.303 \times 0.009)/ 60}$$

$$\mathbf{K=3.4545 \times 10^{-4}\ Sec^{-1}}$$

The rate constant obtained as 3.4545×10^{-4} sec^{-1}.

MECHANISIM OF PHOTODEGRADATION:

In the degradation process of the organic dye structure by the photo irradiated copper nano particles. The follows mechanism could be proposed. [12,13,14,15].

(1). Absorption of radiation by the surface active copper nano particles. The nano particles gain energy and get excited leading to the generation of charge carries. i.e e^{-1} or h^{+} on the surface of nano particles.

(2). By means of scattering and delocalization of these primary electrons furthur generate a stream of secondary electrons, which are either trapped by the oxygen molecules (adsorbed on the dye structure) or directly attack the dye structure to give reduction products.

(3). Furthur more, the generated charge carriers (e^{-1} or h^{+}) in step 1can be trapped respectively by the O_2 molecules (adsorbed on the dye structure) to give radical anion of $O_2^{-\cdot}$ **or** trapped by the H_2O molecules (adsorbed on the dye structure) to finally generate the peroxy free radical intermediates. In the successive steps hydroxyl free radicals are generated which play a very crucial role in the degradation of the organic dye structure by means of interfacial charge transfer mechanism.

STEP 1: Generation of charge carries

$$CU\text{-}NP + h\nu \xrightarrow{\text{Excitstion}} (CU\text{-}NP)^{*}$$

$$(CU\text{-}NP)^{*} \xrightarrow{\text{Generation 0f charge-carriers}} e^{-} + h^{+}$$

STEP 2: Trapping of charge carries

$$H_2O + h^{+} \xrightarrow{\text{trapping of charges}} OH^{\cdot} + H^{+}$$

$$O_2 + e^{-} \xrightarrow{\text{trapping of charges}} O_2^{-\cdot}$$

STEP 3: Generation of peroxy radicals

$$O_2^{-\cdot} + H^+ \xrightarrow{\text{trapping of carriers}} HOO^{\cdot}$$

STEP 4: Recombation of radicals and generation of hydroxy free radicals

$$2\,HOO^{\cdot} \xrightarrow{\text{recombination of freeradicles}} H_2O_2 + O_2$$

$$H_2O_2 \xrightarrow{\text{generation of hydroxy freeradicles}} 2OH^{\cdot}$$

STEP 5: Degradation of dye by interfacial charge transfer

$$Dye + OH^{\cdot} \xrightarrow{\text{Degradation interfacial charge transfer}} H_2O + CO_2$$

$$Dye + h^+ \xrightarrow{\text{Oxidation}} \text{Oxidised product}$$

$$Dye + e^- \xrightarrow{\text{Reduction}} \text{Reduced product}$$

CONCLUSIONS:

Green synthesized copper nanoparticles are used to degradation of methylene blue dye in presence of sun light. Good color change observed and The % of degradation is 72.60 after 90 minutes. From the graphical information the present degradation reaction follows the pseudo-first order reaction and the rate constant value is 3.4545×10^{-4} Sec^{-1}. CU-NP are further used to catalyst in many reactions.

ACKNOWLEDGEMENT:

Authors are very thankful to prof. G Susheela bai and B. kishore babu for giving their valuble suggestions, department of engineering chemistry, college of engineering, Andhra university, Visakhapatnam for providing facilities and also thankful to Teqip for providing funding.

COMPETING INTERESTS:

Authors declare that no competing interests.

LIST OF ABBREVATIONS:

CU-NP	: copper nanoparticles
UV-VISIBLE	: ultraviolet-visible spectrum.
FT-IR	: Fourier transform infrared spectrum
SEM	: Scanning electron microgram
TEM	: Transmission electron microgram
EDX	: Energy dispersive X-ray spectrum

REFERENCES:

1. Tanur S, Ahmaruzzaman M (2015) Green synthesis of copper nanoparticles for the efficient removal(degradation) of dye from aqueous phase.*Environ Sci Pollut Res*. 22:20092-20100.
2. Ganapathy GS, Sivakumar K (2015) Phycosynthesis of silver nanoparticles and photocatalytic degradation of methyl orange dye using silver (Ag) nanoparticles synthesized from Hypnea musciformis (Wulfen) J.V. Lamouroux. *Appl Nanosci*. 5: 617–622.
3. Saranya V T K , Uma G , S (2016) photocatalytic reduction of methylene blue dye using biogenic silvernanoparticles from the aqueous cladode extract of Casuarina equisetifolia. *Indo American Journal of Pharmaceutical Research,* 6(2).
4. Jyoti K , Ajeet S (2016) Green synthesis of nanostructured silver particles and their catalytic application in dye degradation. *Journal of Genetic Engineering and Biotechnology.*
5. Sankar R, Perumal M , Viswanathan M , Tajudeennasrin F , Subramanian K , Shivashangari , Ravikumar V (2014) Green synthesis of colloidal copper oxide nanoparticles using Carica papaya and its application in photocatalytic dye degradation. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 121: 746–750.
6. Devi S H, David Singh T (2014) Synthesis of Copper Oxide Nanoparticles by a Novel Method and its Application in the Degradation of Methyl Orange. Advance in Electronic and Electric Engineering. 4(1):83-88.

7. Sundaramurthy N, Parthiban C (2015) bio synthesis of copper oxide nano particles using pyrus pyrifolia extract and evolve the catalytic activity. *IRJET*.2(6):332-338.
8. Habibi M H, Askari E (2011) Photocatalytic degradation of an azo textile dye with manganese doped ZnO nanoparticles coated on glass, *Iranian Journal of Catalysis*, 1: 41-44.
9. Robinson T, McMullan G, Marchant R, Nigam P (2004) Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative .*Bioresour. Technol*. 77247-255
10. Predesc, A, Nicolae A (2014) efficient Method for nanomagnetite synthesis, *U.P.B. SciBull. Ser. B*, 74 :1454–2331
11. Hariprasad Seeram, Susheela Bai G, Santhoshkumar J, Madhu CH, Sravani D (2016) Greensynthesis of Copper Nanoparticles by Arevalanata Leaves Extract and their Anti Microbial Activites. *International Journal of ChemTech Research*, 9(2) 98-105.
12. Ajmal A, Majeed I, Malik R.N, Idriss H, Nadeem MA (2014) Principles and mechanisms of photocatalytic dye degradation on TiO_2 based photocatalysts: a comparative overview. *RSC Adv* 4:37003–37026.
13. Dong F, Li Q, Sun Y, Ho WK (2014) Noble metal-like behavior of plasmonic Bi particles as a cocatalyst deposited on $(BiO)_2CO_3$ microspheres for efficient visible light photocatalysis. *ACS Catal* **.** 4: 4341–4350.
14. Dong F, Xiong T, Sun Y, Zaiwang Z, Ying Z, Feng X, Wu Z (2014) A semimetal bismuth element as a direct plasmonic photocatalyst. *Chem Commun*. 50:10386–10389.
15. Sun Y, Zhao Z, Dong F, Zhang W (2015) Mechanism of visible light photocatalytic NOx oxidation with plasmonic Bi cocatalyst-enhanced $(BiO)_2CO_3$ hierarchical microspheres. *Phys Chem Chem Phys.* 17:10383–10390.