Introduction

Explosion of population, industrialization and progress in agricultural techniques have resulted in the degradation of the environment and hazardous materials into the environment [1-3]. Textile industry is one of the important water consumers producing colored waste water [4]. Dyes have a broad spectrum of chemical structures [5,6]. The discharge of effluents of azo dyes into the water is uncontrollable because the dyes degrade to carcinogenic and toxic products [7,8]. These dyes residence time is greater in the waste water. There are techniques which are used for dye removal like chemical oxidation, microbial, microwave induced degradation, photocatalysis and adsorption. Today microwave induced degradation and photocatalytic degradation of azo dyes is the effective and economic process [9-11]. The advantage of microwave induced degradation for the control of azo dye pollution is less applied in terms of initial cost, quick operation, and recovery of the adsorbents [12]. The microwave induced degradation process leads to oxidation-reduction and production of free radical.

Nanotechnology deals with the manipulation of matter at lower size normally less than 100nm. The preparation of metallic nanoparticles can be carried out using chemical and physical
methods. These methods have certain flaws, like emission of toxic chemicals during its chemical reaction can cause serious environmental hazards which can cause pollution and serious issues for the living beings [1]. The research in green chemistry has played important role in nanotechnology in terms of the benefits to the surface area of society due to which the mass ratio absorption has increased to maximum level 2. Green synthesis has been anxious in the synthesis of highly stabilized nanoparticles. Due to the disadvantages of standard synthesis methods the synthesis of nanoparticles in collaboration with eco-friendly methods has achieved huge attention in the modern era. The nature of particles produced using green synthesis and physical or chemical methods are totally different [3]. In the green synthesis, the chemical reducing agent has been replaced with an extract of leaves of trees and fruits for the synthesis of metal or metal oxide nanoparticles. The green synthesis follows the same bottom-up approach followed by any chemical method but the use of expensive reducing agents has been replaced with the eco-friendly extracts of natural products [4]. The synthesis process starts with the natural reducing agent and the final result of the process is the synthesized nanoparticles as shown in Figure 1.

Figure 1: Green synthesis of nanoparticles.

For the synthesis of Copper nanoparticles, leaf extract of Aloe Barbadensis (Aloe Vera) plant has been used. The green synthesis of the copper nanoparticles using Aloe Vera plant has been comparatively easier, fast, and environmentally suitable [5]. Aloe Vera plant can be seen in Figure 2. The phenolic contents in plant extracts are usually dissolved in water, which is degradable and catalyzed for the synthesis of the nanoparticle as capping and reducing agent [6]. The old plant of Aloe Vera is famous for its deeper healing effects. Further, it has been mostly used in the cosmetics and skin creams due to its ability to clean skin and anti-aging effects [7]. The folic acid choline and other antioxidant vitamins including A, C and B12 are also present in Aloe Vera plant due to which its gel juice has been used as energy drink [8]. Aloe Vera contains other minerals including copper, chromium, calcium, magnesium, selenium, manganese, potassium and zinc [8]. The leaves of Aloe Vera also provides anthraquinones [9]. The Copper nanoparticles synthesis using electron microscopy represented their range up to 50nm to 130nm [10].

Figure 2: Aloe Vera plant.

Copper nanoparticles are important due to their properties with less cost as compared to other expensive metals such as gold and silver. The cost of synthesis for the examination of catalytic activity of Copper nanoparticles by degradation of Malachite green is too much less as compared to the other metals [11]. Copper oxide particles had shown the effective catalytic removal of organic dyes such as Malachite green when particles were added into it [12]. The use of green method has been increased due to the easier preparation of materials and low manufacturing cost. Further, its starting is less toxic due to which the handling of materials is more favourable as compared to physiochemical methods [13]. Malachite green has been used for the dye of leather and textiles since decades further, it has also been used for the control of fish parasites and diseases and in aquaculture industry [14]. The Malachite green has been categorized as class II health hazard due cause of mutagenicity and genotoxicity to the organisms including fish, bacteria and algae. It has been banned by different countries due to its toxic nature [15,16]. The Malachite green dye can be seen in Figure 3. The removal of dyes and organic contaminants in
industries had remained a challenging task due to the complexity of decomposition of dye molecules. In this regard researchers have tried to remove various organic and heavy metal pollutants by using nano adsorbents [16-18]. In this paper degradation of Malachite green has been carried out using Copper nanoparticles Aloe Barbadensis leaf extracts. The green synthesis of the copper nanoparticles has been carried out using an aqueous solution of copper sulphate and extract of Aloe Barbadensis. The present work emphasis on the degradation of MG from aqueous media using microwave induced catalysis phenomenon. It is point to be noted, no study has been reported on the application of CuO/ZnO nano composite with microwave induced catalytic degradation of dye activity and compare it to metal nano oxides [19].

**Materials and Methods**

The detailed discussion of the materials and methods involved in achieving the target has been reported in subsequent subsections for the better understanding of the experimentation.

**Material**

Copper sulphate, Aloe barbadensis leaves, sodium borohydride (NaBH₄), organic dyes such as Malachite green.

**Preparation of Plant Leaf Extract**

50g of the Aloe Vera is taken from the nearby garden. The leaves of Aloe Vera are first separated from the gel part of Aloe Vera. The leaves are then washed thoroughly with distilled water to remove soil and dust particles. After washing leaves were dried and finely chopped. These finely chopped leaves were allowed to boil for 15min at 100 °C with 100mL of de-ionized water in a 250mL flask and then allow to cooled down to come at least at room temperature. The resulting solution is passed through a filter paper to remove any solid particles and then again filtered through a Whatman filter paper of pore size 0.2μm. The filtrate is stored at 6 °C as a stock for the synthesis of CuO NPs [18].

**Synthesis of CuO-ZnO nanocomposite**

For the Synthesis of CuO-ZnO nanocomposite we used the sol-gel method [11]. In first step, 25mL of ethylene glycol 1g was mixed with 5.3g of Zn(CH₃COO)₂ H₂O zinc acetate and 25mL of distilled water now 6.29g of citric acid with vigorous stirred for about an hour. After an hour 1.3g of CuSO₄·5H₂O copper sulphate was added to the suspension at 80 °C for 2 hours and quickly mixed. The solution was kept in the dark for long time and washed with water several times. The resulted gel was dried at 120 °C to and calcined at 500 °C for 4 hours to produce the CuO-ZnO nanocomposites. These nanocomposites further used for characterization and dye degradation.

**Green Synthesis of CuO Nanoparticles**

A copper sulphate solution of fifty millilitres was added to 15ml Aloe Vera leaves extract. The solution was stirred on a magnetic stirrer at 120degrees. The colour change was observed. The colour changes from deep blue to colourless and then dark red at saturation. Brick redcolour confirms the nanoparticles formation. The resultant solution was centrifuged for ten mints at speed of 50,000rpm. After discarding supernatant copper oxide nanoparticles were dried in a watch glass. After drying, black colour particles were assembled for further characterization. The process of nanoparticles synthesis can be seen in Figure 4.

**Characterization of Green Synthesis Copper Nanoparticles**

The morphological, structural and chemical composition of CuO NPs were analyzed by using SEM (jsm-6480) and XRD (XPERT-PRO) equipment. Optical properties of synthesized particles are investigated by UV spectrophotometer (DB-20). Size and shape of copper oxide nanoparticles were observed by SEM (jsm-6480). The crystal structure of synthesized nanoparticle is examined by XRD(XPERT-PRO). FTIR analysis is performed for the collection of the functional groups, present in this synthesis of CuONps. Colour changes indicate the formation of nanoparticles of copper oxide. The bluecolour solution was turned into red or brick red indicated for the formation of copper nanoparticles synthesis.

**Results**

**X-rays Diffraction Studies**

Copper oxide nanoparticles were examined by X-ray diffractometer (XPERT-PRO). 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, a pattern which is compared 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 the cubic crystal structure. The average size of the particle calculated by Scherrer equation was 60-100nm. The XRD pattern of CuO nanoparticles has been graphically represented in Figure 5.

![Figure 5: XRD pattern of CuO nanoparticles.](image)

**FTIR Analysis:**

In this analysis, FTIR (IPRrestige-21) spectrum was analyzed. The analysis confirms the presence of copper nanoparticles. Different peaks were observed at 1100cm⁻¹ confirm the formation of Copper oxide nanoparticles peaks 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. The peak at 1601.2cm⁻¹ is due C=C aromatic bending. The absorption peak at 1038.0cm⁻¹ stretching vibrations of C=O group of primary and secondary alcohols (C=O), while smaller peaks at 900–700cm⁻¹ were also assigned to the aromatic bending vibration of C-H group [20]. For better elaboration, the FTIR spectra of the Copper oxide nanoparticles is shown in Figure 6.

The peaks have been observed in FTIR, the same has been reported in Table 1.

**Table 1:** FTIR spectra peaks.

| Sr. No. | Groups | Stretching or Bending | Peaks |
|--------|--------|-----------------------|-------|
| 1.     | OH- stretch | stretching | 3250.8 |
| 2.     | C-H     | stretching | 2860.1 |
| 3.     | C=O     | aromatic bending | 1650.7 |
| 4.     | C-Cl    | stretching | 2250.1 |
| 5.     | CuO stretch | stretching | 1100 |
| 6.     | C-Cl    | stretching | 550-850 |

**Ultraviolet 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 Aloe vera leaves extracts proved feasible, coast free and successful method. UV-Vis spectra analysis has apparently shown the formation of copper oxide nanoparticles. Nanoparticles synthesized have a variety of application in the different field. The maximum absorption peak is between 265-285nm. The peak at about 280nm was achieved. This peak confirmed the formation of the copper oxide nanoparticles as shown in figure 7.

![Figure 6: FTIR spectra of Copper oxide nanoparticles.](image)
SEM Analysis:

The average particle size of copper nanoparticle was analyzed by SEM model (JSM-6480). 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 spherical shape. The images of Copper Oxide nanoparticles with different ranges of 2Mm, 5Mm and 100Mm are shown in (Figure 8a-8c).

Characterization of CuO/ZnO Nanocomposites

X-ray diffraction analysis (XRD) of the nano composite material was calculated by using Cu Ka radiation (k = 1.54 Å). The SEM (S-3400N, Hitachi) image of metal oxide nanocomposite was recorded at different magnifications. The UV-vis spectra (DB-20) of cuo/zno nanocomposite were recorded for wavelength. The spectrum showed absorption in the range of 200-600nm regions. Fourier transforms infra-red spectra of cuo/zno nanocomposite were taken by KBr disc method. CuO/ZnO nanocomposite exhibit the excellent photodegradation of malachite green dye. The adsorption and microwave induced catalysis was more effective, the percentage efficiency of degradation of dye was observed efficiently increase by nanocomposites rather than metal oxide nanoparticles. So, we reviewed comparative potential of copper nano oxide and its composites degradation efficiency, which was observed in nano composite due to reduce size particles.
Preparation of 1000mg/l dye S.S

1000ppm solution of Malachite green dye was prepared by dissolving dye in 1-litre distilled water. Different concentration of dyes was prepared from stock solution. 100ppm solution was prepared from 1000ppm solution after dilution. After that, 150, 200, 250-ppm solution was prepared. 18g of NaBH₄ is made up to 10mL and kept aside. Different concentrations of NaBH₄ and catalyst are tested on the methylene blue dye. The catalytic degradation of organic dyes was observed by measuring UV-Visible spectra at regular time intervals [19].

Malachite Green

Malachite green is extensively used in many industries as a dye for leather, textiles and also in aquaculture industry to control fish parasites and disease. The use has increased so much because of its easy preparation and low manufacturing cost [17]. The detailed description of the Malachite green dye is provided in Table 2.

Table 2: Malachite green dye description.

| Dye      | Malachite green                                      |
|----------|------------------------------------------------------|
| IUPIC Name | [4-[[4-(Dimethylamino)phenyl]phenyl]methylidene]cyclohexa-2,5-dien-1-ylidene]dimethylazanium; chloride |
| Common Name | Malachite green chloride                             |
| Chemical formula | C₂₃H₂₅ClN₂ (chloride)                               |
| Molar mass   | 364.911 g/mol (chloride)                             |
| Main hazards | Moderately toxic, Extreme irritant                  |

Structure:

The chemical formula of the Malachite green is C₂₃H₂₅N₂, the basic use of this organic component is in dye industry where it has been used for the dye of materials like silk, leather and paper. The structure of the Malachite green is elaborated in Figure 9.

![Figure 9: Nanoparticle UV at 620nm.](image)

Dye Degradation

The degradation of malachite green in the absence and presence of CuO NPs were studied spectrophotometrically by using DB-20 UV-Vis spectrophotometer determining the decrease in the absorbance at 631nm. The reaction was to study spectrophotometrically at room temperature (25°C). The colour of the reaction mixtures faded, indicating that degradation had occurred. The same procedure was followed for uncatalyzed reactions, in absence of CuO NPs.

Time Effect on Dye Removal

Decolourization of dye Malachite Green at room temperature was analyzed. Initially 20ml dye solution was taken and 1mg of greenly synthesized copper nanoparticles using Aloe Vera leaves extract dissolved in it. 0.1mg of NaBH₄ was dissolved as a reducing agent. The solution was heated for 10-20mint at 100 degrees. The time interval was taken in consider gradually during the reaction. The removal percentage of decolourization was calculated and draw graphically. The maximum time was 120mints with 70% colour removal. This confirms the rapid reaction of copper oxide nanoparticles (CuO NPs). The time effect on dye removal has been graphically represented in Figure 10.

![Figure 10: Images of cuo/zno nanocomposites.](image)


**PH Effect on Dye Removal**

PH of the solution also majorly affected the de-colourization of dye. pH effect on the decolourization of copper oxide nanoparticles was analyzed in this research. Aloe Vera synthesized copper oxide nanoparticles showed maximum percentage de-colourization as pH was increased at a certain limit after more increase has a negative effect. This may be happened due to the formation of more positive ion competition. Maximum decolourisation 70% was at pH [5]. The effect of pH on dye removal has been graphically represented in Figure 11.

![Figure 11: FTIR analysis of cuo/zno.](image)

**The Concentration of Dye Effect on Decolourization of Dye:**

The increase or decrease in the concentration of Malachite green MG dye is also considerable in decolourization efficiency. The graph was obtained after experimenting with various concentration of dyes. The maximum amount of dye taken was 20mg/l. After increasing concentration, no effect on decolourization of dye was observed. The concentration of dye effect on decolourization on dye has been graphically represented in Figure 12.

![Figure 12: xrd pattern of cuo/zno.](image)

**Effect of copper oxide nanoparticles amount on dye removal**

The number of copper oxide nanoparticles exhibits positive results on decolourization. The number of nanoparticles 1 gram was taken, showed maximum de-colourization power. This confirmed from the experiments that increasing the of nanoparticle showed no effect on de-colourisation. This concentration of nanoparticles was used in further experimentation of research. The effect of the amount of copper oxide nanoparticles on dye removal has been elaborated in Figure 13.

![Figure 13: The catalytic activity of the CuO NPs analyzed by the degradation of malachite green dye.](image)

**Microwave Induced Catalytic Studies of CuO/ZnO Nano Composites**

The adsorption and photo catalytic efficiency of cuo/zno nanocomposite were examined for Malachite Green dye degradation. In start 100mg of cuo/zno nano composite were added into 1.8 X 10^-5M solution of Malachite green dye [21]. The degradation studies were examined by using a glass beaker and stirred for agitation. During degradation experiments, the suspension was retained in dark to desorption of MG dye, when the equilibrium was gained, the suspension was exposed to microwave for further degradation. The suspension of dye and composite were stirred continuously and exposed to microwave directly. The reaction was compared to study the effect of the conditions with metal nano oxides. In the progress of reaction, 5mL solution was taken at different time intervals and centrifuged. The catalytic degradation of the dye was performed at 620nm uv wavelength. The degradation percentage of dye was calculated using formula as: A-B/A×100 where A and B are the concentrations of MG dye at equilibrium and at time dye degradation uv graph shown below in Figure 4 microwave induced dye degradation by cuo/zno nanocomposites.

**Microwave Induced Degradation of Dye by Nanocomposites**

Microwave induced photo degradation of CuO/ZnO nanocomposite were studied at different condition such as adsorption in dark followed by catalysis. In this process of catalysis process, the MG dye solution containing nanocomposite were kept in dark. for next experiment for microwave induced degradation process, the solution was exposed to microwave light to react with...
dye. The absorption band intensities decrease with irradiation time was observed for malachite green showed that the dye was degraded by nanocomposite. It was examined that only 31% MG dye was degraded in dark while 91% by MG Dye degraded in microwave irradiation. The nano copper oxide nanoparticles efficiency of dye degradation was 70%. The photo degradation of MG dye using cuo/zno nanocomposite plot of ln Ao/At vs irradiation time predict a linear correlation shown in graph. The MG dyes degradation was pseudo-first-order kinetics. The microwave catalytic degradation of MG dyes by nanocomposite was examined to be 90% in 90min of microwave irradiation. This research indicated the greater degradation of malachite green as compared to MNPs and MN-composites microwave catalysis. The process generate free radicals to disturb the conjugation in free dye molecules present. The dye adsorption can enhance the degradation process and increases the rate and decrease the time [20].

The supposed mechanism for degradation of dye is shown:

\[
\text{nanocomposite} + \text{Dye} \rightarrow \text{nanocomposite -Dye adsorbed (microwave light)}
\]

\[
\text{-Dye adsorbed} + \text{O}_2 \rightarrow \text{cuo/zno composites (O}_2 \cdot \text{-Dye O}_2 \cdot \text{ or OH}\cdot}
\]

Thus degradation was studied in dark and microwave induced condition. The kinetics of MG dye degradation resulted a linear correlation a. The value of rate constant and rend pseudo first order type. The comparison of degradation of dye by microwave induced catalysis of nano composites and nanometals undoubtedly prove that the catalysis using metal oxide nanocomposites due to small size has greater percentage removal efficiency than nano oxide metal (Figures 14-19).

Figure 14: Structure of Malachite green dye.

Figure 15: Time effect on dye removal.

Figure 16: Effect of pH on dye removal.
**Conclusion**

Here, in conclusion, we concluded a method of green synthesis of Cu nanoparticles by leaf extract of Aloe Vera barbadensis 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 analysis on nanotechnology for the synthesis of nanoparticles, it is declared that it is safer and best by using natural plants. With the huge plant variety, much more plants are still not known for the synthesis of nanoparticles. 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, Malachite green dye was removed by nanoparticles and its time, pH, contact time was observed. The maximum contact time was 120min, pH was observed 5, nanoparticle amount 1mg which proved green synthesized copper nanoparticles, as best removal of carcinogenic dye like Malachite green. CuO/ZnO nanocomposite exhibit the excellent photodegradation of malachite green dye. The adsorption and microwave induced catalysis was more effective. the percentage efficiency of degradation of dye was observed efficiently increase by nanocomposites rather than metal oxide nanoparticles. So, we reviewed comparative potential of copper nano oxide and its composites degradation efficiency, which was observed in nano composite due to reduce size particles.
References

1. White RJ, Luque R, Budarin VL, Clark JH, Macquarrie DJ (2009) Supported metal nanoparticles on porous materials. Methods and applications. Chemical Society Reviews 38(2): 481-494.

2. Daniel MC, Astruc D (2004) Gold nanoparticles: assembly, supramolecular chemistry, quantum-size-related properties, and applications toward biology, catalysis, and nanotechnology. Chemical reviews 104(1): 293-346.

3. Vaidyanathan R, Kalishwaralal K, Gopalram S, Gurunathan S (2009) RETRACTED: Nanosilver-The burgeoning therapeutic molecule and its green synthesis.

4. Hussain I, Singh NB, Singh A, Singh H, Singh SC (2016) Green synthesis of nanoparticles and its potential application. Biotechnology letters 38(4): 545-560.

5. Iravani S (2011) Green synthesis of metal nanoparticles using plants. Green Chemistry 13(10): 2638-2650.

6. Dipankar C, Murugan S (2012) The green synthesis, characterization and evaluation of the biological activities of silver nanoparticles synthesized from Iresine herbstii leaf aqueous extracts. Colloids and Surfaces B: Biointerfaces 98: 112-119.

7. Sharma H (2008) Innovative approaches in cosmeceuticals developing anti-aging topical application forms.

8. Joseph B, Raj SJ (2010) Pharmacognostic and phytochemical properties of Aloe vera and an overview. International journal of pharmaceutical sciences review and research 4(2): 106-110.

9. Nandai U, Bhardwaj RL (2012) Aloe vera: A valuable wonder plant for food, medicine and cosmetic use-a review. Int J Pharm Sci Res 13(1): 59-67.

10. Agnihotri S, Mukherji S, Mukherji S (2014) Size-controlled silver nanoparticles synthesized over the range 5-100 nm using the same protocol and their antibacterial efficacy. Rsc Advances 4(8): 3974-3983.

11. Kharissova O, Dias HR, Kharisov B, Pérez BO, Pérez VMJ (2013) The greener synthesis of nanoparticles. Trends in biotechnology 31(4): 240-248.

12. Sun H, Cao L, Lu L (2011) Magnetite/reduced graphene oxide nanocomposites: one step solvothermal synthesis and use as a novel platform for removal of dye pollutants. Nano Research 4(6): 550-562.

13. Tomasic C (1992) Chemistry & technology of fabric preparation & finishing NC: North Carolina State University pp. 13-30.

14. Alderman DJ (1985) Malachite green: a review. Journal of Fish Diseases 8(3): 289-298.

15. Sudova E, Machova, J Svobodova Z, Vesely T (2007) Negative effects of malachite green and possibilities of its replacement in the treatment of fish eggs and fish: a review. Veterinarni Medicina-Praha 52(12): 527.

16. Vergis BR, Hari Krishna R, Kottam N, BM Nagabhushana, R Sharath, et al. (2018) Removal of malachite green from aqueous solution by magnetic CuFe2O4 nano-adsorbent synthesized by one pot solution combustion method. J Nanostruct Chem 8(1): 1-12.

17. Carmen Z, Daniela S (2012) Textile organic dyes–characteristics, polluting effects and separation/elimination procedures from industrial effluents—a critical overview. In: Organic pollutants ten years after the Stockholm convention-environmental and analytical update. In Tech.

18. Palajonna Narasiah, Badal Kumar Mandal, NC Sarada (2017) Biosynthesis of Copper Oxide nanoparticles from Drypetes sepiaria Leaf extract and their catalytic activity to dye degradation. IOP Conf. Series: Materials Science and Engineering 263(2017): 022012.

19. Sadia Saif, Arifa Tahir, Tuyaba Asim, Yongsheng Chen (2016) Plant Mediated Green Synthesis of CuO Nanoparticles: Comparison of Toxicity of Engineered and Plant Mediated CuO Nanoparticles towards Daphnia magna. Nanomaterials 6(11): 205.

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