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Biogenesis of Ag-Cu Bimetallic Nanoparticles from Leaf Extract of Krishna College Campus: Characterization and Photocatalytic Studies

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ABSTRACT

An environmentally benign cost effective synthesis is reported for green synthesis of Ag-Cu bimetallic nanoparticles by using *Andrographis Paniculata* leaf extract. The phyto molecules present in the extract are acting as reducing agents, stabilizing and capping agents for the biosynthesized nanoparticles. The characterization studies are done by UV-Visible, FTIR, SEM, XRD, EDX and HRTEM techniques. These nanoparticles are further applied as photo catalysts for degradation of Malachite Green dye by irradiation under sunlight. The optimum conditions obtained from these research findings in the degradation of MG dye by using bimetallic Ag-Cu nanoparticles synthesized from *Andrographis Paniculata* leaf extract are pH 9, 10 mg weight of catalyst, 10 ppm of dye concentration and 150 minutes contact time for obtaining % photo degradation is 80.5.

KEY WORDS

Bimetallic nanoparticles (BMNPs), *Andrographis Paniculata* (AP), Malachite Green (MG), photo degradation.

1.1 INTRODUCTION

Nanoparticles have gained more attention owing to the fact that their physical and chemical properties generally differ from their bulk materials due to their decreased particle size into nanoscale ie 10^{-9} m [1]. As they encompass high surface area they tend to exhibit excellent catalytic properties [2]. Research on nanomaterials has increased a lot of importance over the last ten years due to their exclusive properties and vast applications in medical, biological and electronic fields [3]. Nanoparticles can be synthesized from top-down and bottom-up methods [4]. Nanoparticles can be obtained by three methods viz chemical, physical and biological methods. The biological methods are regarded as easily scaled up techniques, eco-friendly and rapid. Currently, nanoparticles synthesized by biological methods are found to be greater pharmacologically active when compared to physic chemically synthesized ones [5]. Synthesis of nanoparticles by using eco-friendly starting materials such as plant extracts [6] and different microorganisms like fungi

[7], yeast [8] and bacteria [9] have potential applications when compared to other methods. Bimetallic nanoparticles (BMNPs) are formed from two metal elements, which have more significant interest in recent years around worldwide due to their new chemical and physical properties with the effective combination between corresponding two individual metals which are useful in industrial applications, especially as catalysts [10].

Now day's dyes are used widely in various fields such as cosmetics, leather, and food and textile industries. The release of these industrial dye effluents into water shows adverse effect on quality of water. One of such dye is malachite green (MG). MG dye is cationic green crystalline water soluble dye and belongs to family triphenyl methane category [11]. MG dye originator for public health peril and also acts as potential environmental issue and it is a multi-organ toxin proved by both experimental clinical observations [12]. It is necessary to get rid of the MG dye effluents from water. Many chemical, physical and biological treatment methods including adsorption, precipitation filtration, electrodialysis, coagulation, oxidation and membrane separation are used in the treatment of dye effluents [13]. Dye removal by photocatalysts more admire among all methods because of sustainable and ecofriendly technology [14].

Herein, facile method for synthesis of Ag-Cu BMNPs by using leaf extract of *Andrographis Paniculata* as a reducing and capping agent is reported and by using these BMNPs photodegradation of MG dye by solar light irradiation is also studied.

1.2 MATERIALS AND METHODS

1.2.1 Chemicals and collection of *Andrographis Paniculata* leaves

Chemical reagents used (copper sulphate and silver nitrate) in this study are of analytical grade. Deionised water is used to clean glassware, prepare chemical solutions and throughout experimental procedure. Fresh leaves of *Andrographis Paniculata* are collected from botanical garden of Dr.V.S. Krishna Government Degree College, Maddilapalem, Visakhapatnam, Andhra Pradesh, India.

1.2.2 Preparation of plant leaf extract

100 g of leaves are weighed and thoroughly cleaned with running tap water to eliminate debris on surface of leaves followed by deionized water to remove other contaminants from leaves and dried up under shade for seven days i.e., until the weight of the dried leaves remains constant. These leaves are sliced into tiny pieces and made homogenized powder by using home blender. The obtained powder is stored in an air tight container for further usage.

250 mL deionized water is taken in 500 mL beaker to this 10 g stored powder weighed and added. The contents in the beaker boiled for 20 minutes with occasional stirring with glass rod and then cooled to attain room temperature. The cooled leaf broth is filtered 2 times with Whatman No.1 filter paper and reserved in refrigerator at 4°C. This is taken as leaf extract throughout the experiment (**Figure 1.1**).

Figure 1.1: Image of *Andrographis Paniculata* leaf extract

1.2.3 Synthesis of Ag-Cu BMNPs

Equimolar (25 mM) concentrations of copper sulphate and nickel sulphate solutions are prepared separately in 100 ml volumetric flask by dissolving 0.6242 g, 0.4246 g weight of $CuSO_4$ and $AgNO_3$ respectively. Synthesis of Ag-Cu BMNPs is done by taking 90 mL of copper sulphate solution in beaker. To this 90 mL of leaf extract is added drop wise through burette. 90 mL of $AgNO_3$ solution is added to contents in the beaker by drop wise. During addition process beaker is placed on a magnetic stirrer for continues agitation at pH 7. Now this mixture is heated up to 50^{o} C for 50 minutes then cooled and kept undisturbed overnight. These synthesized BMNPs are obtained by centrifugation at 5000 rpm for 20 minutes. The obtained BMNPs are washed by using deionised water two times to remove unwanted constituents. The resultant BMNPs particles used for characterization.

Figure 1.2: Ag-Cu BMNPs in solution

1.2.4. CHARACTERIZATION

Formation of Ag-Cu BMNPs is confirmed by UV-Visible absorption spectra measured by using UV-2450 SHIMADZU double beam spectrophotometer, FTIR by Bruker, SEM and EDX studies by using Hitachi S-3700N machine and the morphology of BMNPs is done by TEM and SAED analysis Jeol/JEM 2100 machine.

1.2.5. PHOTODEGRADATION EXPERIMENT

Photo catalytic activity of Ag-Cu BMNPs is examined for degradation of MG dye. Initially, 50 ppm of malachite green stock solution prepared. Then reaction mixtures are prepared by adding predetermined amount of Ag-Cu BMNPs to 100 mL of malachite green distinct concentrations. The pH of the reaction mixtures are altered by adding H_2SO_4 or NaOH solutions when required. Now this mixture is agitated for 30 minutes in dark condition to attain adsorption-desorption between MG dye and Ag-Cu BMNPs. Sun light used as irradiating source to reaction mixture for study degradation during 11 am to 2 pm. At regular 10 minutes time intervals aliquot of the reaction mixture is collected, centrifuged to remove the photocatalyst particles and analysed for absorbance using UV-Visible Spectrophotometer (200 nm to 800 nm). The effect of BMNPs catalyst amount and also concentration of dye is observed. MG dye shows the highest absorption at 617 nm [15]. To determine the percentage of degradation of MG dye solution following equation (1) is used.

$$\%\ \text{degradation} = \left(\frac{A_0 - A_t}{A_0}\right) \times 100 \quad \rightarrow (1)$$

Where, A_0 is the initial absorbance of the MG dye solution at 0 minutes and A_t is the absorbance of the degraded solution after time t minutes [16].

1.3 RESULTS AND DISCUSSIONS

1.3.1 UV-Visible spectral analysis

UV-Visible absorption spectrum of Ag-Cu BMNPs reveals a band at ~ 440 nm as shown in Figure 1.4. This clearly indicates the nanoscale structure of BMNPs [17]. The particles are obtained as brownish powder. This is also supported by EDX spectroscopy studies with absence of oxygen content.

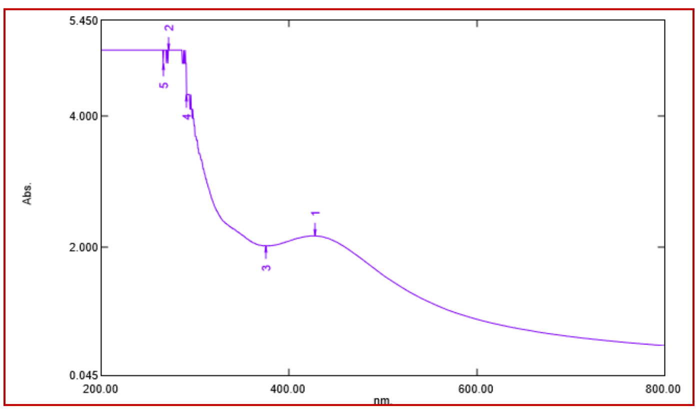

Figure 1.4: UV-Visible spectrum of Ag-Cu bimetallic nanoparticles

1.3.2 FTIR spectral analysis

FTIR describes chemical bonds in molecules by generating an infrared absorption spectrum. FTIR measurements are used to identify different functional groups present in biomolecules responsible for the bioreduction of Cu^{+2}, Ag^{+} precursors and capping/stabilization of BMNPs. The intense, broad bands are observed and compared with standard values to analyze the functional groups in *Andrographis Paniculata* leaf extract and biosynthesized Ag-Cu BMNPs. FTIR spectrum of synthesized Ag-Cu BMNPs by using *Andrographis Paniculata* leaf extract are shown in and **Figure 1.5**. This clearly indicates phytochemical like carbohydrates, alkaloids, phenolic compounds, amino acids, alkaloids and tannins are able to protect the Ag-Cu from aggregation and for more stability [18]. The FTIR spectrum of Ag-Cu BMNPs shows major peak positions at 3296, 2707, 1637, 1104, 659-576 cm^{-1}. Broad band around 3296 cm^{-1}corresponds to O-H vibrations of phenols, alcohol and carboxylic acid group or N-H stretching vibration of primary amines.

2707 cm^{-1}corresponds to vibrations of C-H of aldehyde, 1104 cm^{-1}corresponds to C-O stretching of alcohols. Small peaks in the region 659-576 cm^{-1} are due to C-Cl group.

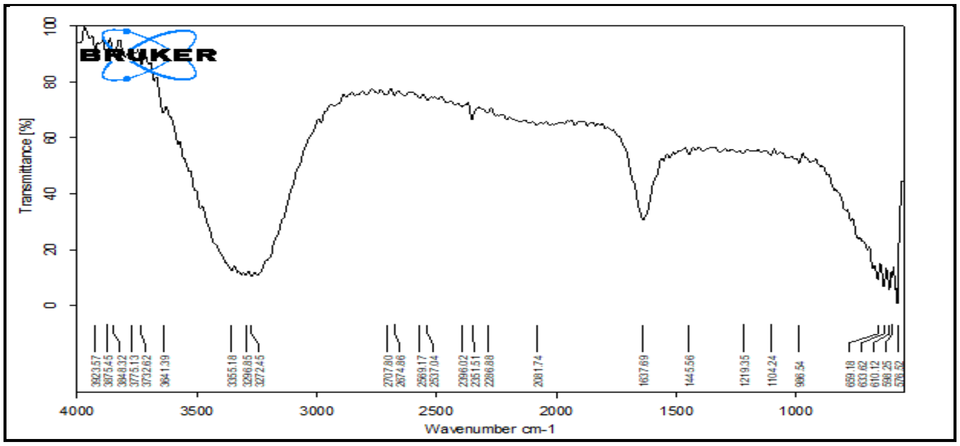

Figure 1.5: FT-IR spectra of Ag-Cu bimetallic nanoparticles

1.3.3 SEM and EDX analysis

Figure 1.6 shows SEM images of Ag-Cu BMNPs with various magnifications. From this, it can be clearly noticed that bimetallic nanoparticles prepared are spherical shaped. From EDX it can be analysed that all the elements present in prepared BMNPs by *Andrographis Paniculata* leaf extract. **Figure 1.7** shows EDX spectrum and quantitative results of Ag-Cu BMNPs indicates the presence of Cu and Ag which confirms the formation of Ag-Cu bimetallic alloy nanopaticles.

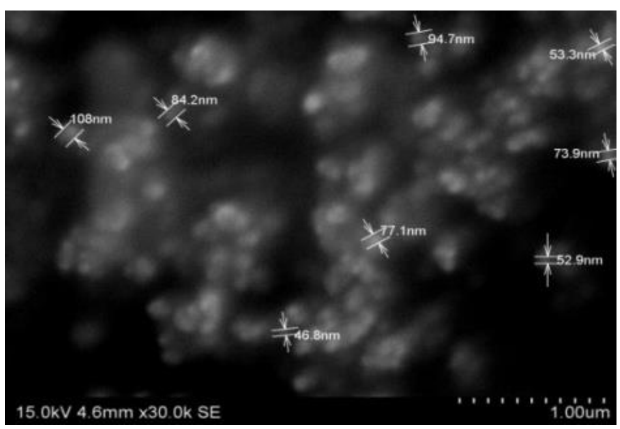

Figure 1.6 SEM images of Ag-Cu BMNPs

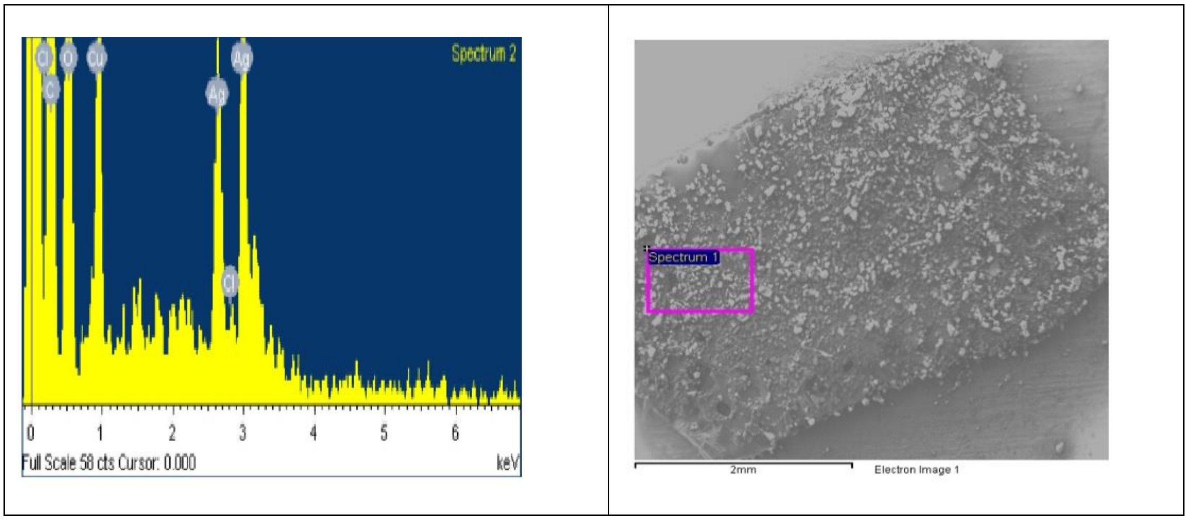

Figure 1.7: EDX spectra and quantitative results of Ag-Cu BMNPs

1.3.4 TEM analysis

Figure1.8 shows the TEM images and (SAED) pattern for synthesized Ag-Cu BMNPs from *Andrographis Paniculata* leaf extract. From these images, it is observed that amorphous Ag-Cu BMNPs are formed with size 10-20 nm in diameter, which is good agreement with SEM images.

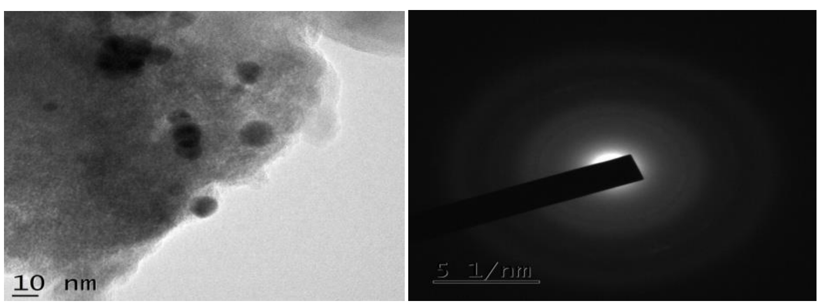

Figure 1.8: TEM and SAED images of Ag-Cu BMNPs

1.3.5 Photo degradation of MG dye

To study the photo catalytic activity of the Ag-Cu BMNPs on malachite green visible region in UV-visible spectrophotometer is used. Absorption spectrum of 10 ppm malachite green has highest absorption peak at 617 nm (**Figure 1.9 (a)**) and taken as to monitor the photo degradation of MG dye (**Figure 1.9 (b)**).

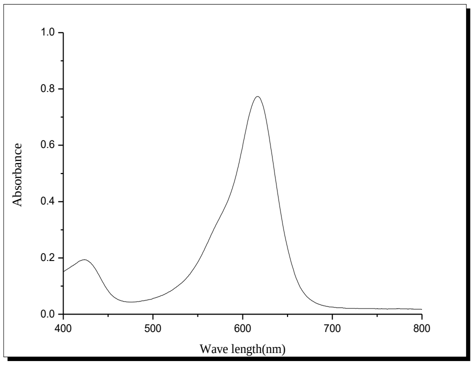

Figure 1.9(a): Absorption spectrum of 10 ppm MG dye **Figure 1.9 (b):** 10 ppm MG dye solution

1.3.5 (a) Effect of contact time

Photo degradation capacity of the Ag-Cu BMNPs on MG dye is studied to observe the effect of contact time between the dye molecules, sunlight and the catalyst reactive surface by batch mode experiments. The efficiency of BMNPs on degradation of MG dye is studied by increasing contact time from 0 to 180 min. The effect of contact time is carried out by taking 10 ppm of 100 mL MG dye and 10mg of BMNPs as constant which is shown in **Figure 1.10**. Degradation of MG dye by BMNPs is found to steeply increase with increase in contact time upto 140 min, afterwards delay in degradation process is found at 150 min and thereafter remains constant at 80%. This could be explained with the following reason. Initially when the contact time increases the degradation efficiency of MG dye is also increased. This may arise due to greater possibility of penetration of light on to the catalyst surface, increasing availability of more reactive surface area sites of the BMNP catalyst for the dye molecules to contact, adsorb and degrade in the initial contact time from 0 min to 150 min. But any further increase in the contact time (from 150 min onwards) saturation of reactive sites on the catalyst is arrived for active participation in the degradation process. Thus the degradation process remains constant after 150 min. Thus 150 minutes is taken as optimum contact time for MG dye degradation onto Ag-Cu BMNPs.

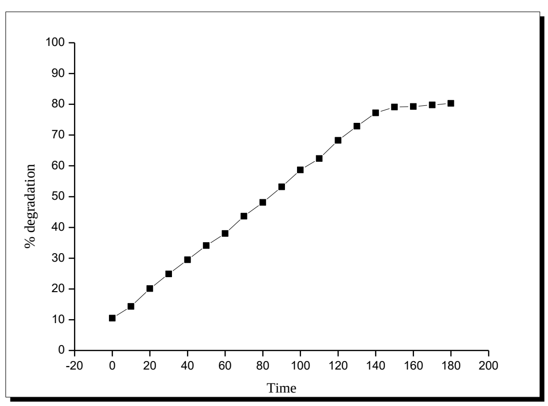

Figure 1.10: The effect of contact time on % degradation

1.3.5 (b) Effect of concentration of MG dye

Initial concentration of MG effects photo degradation rate. For this, concentration of BMNPs is kept constant at 10 mg and time of irradiation as 150 minutes. Different initial concentrations 5 ppm, 10 ppm, 15 ppm, 20 ppm and 25 ppm of MG dye solutions are prepared. The rate of degradation can be shown graphically in **Figure 1.11**. The maximum 87 % degradation observed at 5 ppm then decreases with an increase in the concentration of MG dye. This is may be because of dye molecules attached to the surface of Ag-Cu photo catalyst. With increasing dye concentration, more dye molecules will be covering the active sites of Ag-Cu BMNPs. At the same time higher concentrations of dye solution shield the penetration of light which in turn reduces the number of photons entering into solution hence penetration of solar light to the catalyst decreases [19]. From this study 10 ppm concentration which exhibits 80% degradation, is taken as optimum concentration for degradation of MG dye.

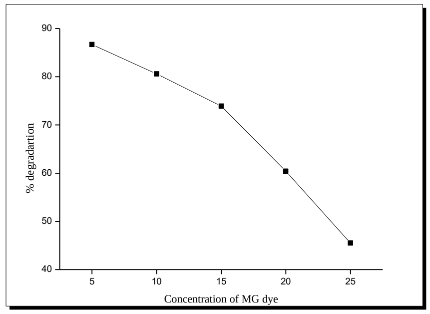

Figure 1.11: The effect of concentration of MG dye on % degradation

1.3.5 (c) Effect of pH

The pH of dye solution can influence the adsorption of dye on photo catalyst. Originally, MG dye solution is having pH value at 5. By keeping the initial concentration of MG dye solution as 10 ppm and the amount of photo catalyst 10 mg as constant with maximum time of irradiation 150 minutes. Different dye solutions of varying pH values of 4-11 are prepared. Degradation efficiencies are compared after 150 minutes which is shown in **Figure 1.12**.

It has been observed that by increasing pH value of the MG dye solution from 4 to 9, degradation of MG dye on the photo catalyst enhances from 45 % to 80 % and then onwards decreases. This could be reasoned out as the following. Ag-Cu BMNPs catalyst surface is able to withstand not only in acidic medium but even in basic medium upto pH 9. Thus we find very good photo catalytic activity in this particular range of pH in the degradation of MG dye. Whereas, after pH 9, the surface of the BMNPs catalyst appears to be chemically modified so that the original cationic structure and the corresponding photo catalytic activity of the catalyst is lost slowly with increasing basic conditions, thus leading to a decreasing trend in the light induced degradation. A comparison of the effect of pH on the dye degradation using all the three nanocatalyst prepared in this research work, ascertains that the MG dye structural changes with the pH of the medium, appear to play a very minor role during the degradation process.

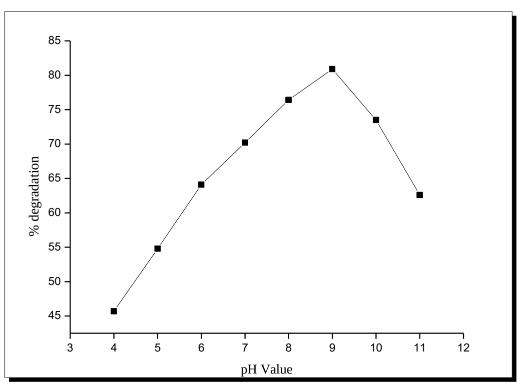

Figure 1.12: The effect of pH on % degradation

1.3.5 (d) Effect of amount of photo catalyst

Photo catalyst dosage is one of the main parameters to influence % degradation. The amount of catalyst is varied from 10 mg to 80 mg by keeping constant volume of dye solution as 100 mL with a concentration of 10 ppm at pH 9 with a constant contact time of 150 minutes. The degradation of MG dye is shown in **Figure 1.13**.

It is observed that, % degradation of MG dye increases from 10 mg to 50 mg of photo catalyst BMNPs. The increase in % degradation with increase in amount catalyst up to 50 mg is because of availability of more number of active sites onto BMNPs surface. Further enhance of the photo catalyst dosage from 50 mg to 80 mg will gradually decrease the % degradation of the dye due to increase in light scattering, which hinders the passage of light to approach the catalyst surface [20]. Thus an optimum dose of photo catalyst is needed to ensure maximum absorption of solar light for an efficient photo catalytic activity. The optimum dosage is taken as 10 mg.

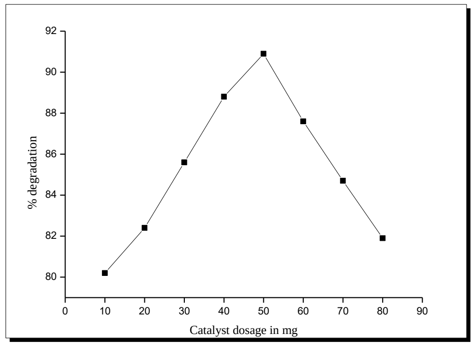

Figure 1.13: The effect of dosage of catalyst on % degradation

1.4 CONCLUSIONS

An environmentally friendly method is projected to synthesize bimetallic Ag-Cu nanoparticles from *Andrographis Paniculata* leaf extract. From SEM and TEM analysis results, the formed Ag-Cu bimetallic nanoparticles are in amorphous state with 10-20 nm size. The photo catalytic activity of these nanoparticles is examined under sunlight for degradation of MG dye which is an environmental pollutant. The % photo degradation of MG dye is found to change with parameters such as contact time, concentration of MG dye, pH, photo catalyst amount. The optimum conditions obtained from these research findings in the degradation of MG dye by using bimetallic Ag-Cu nanoparticles synthesized from *Andrographis Paniculata* leaf extract are pH 9, 10 mg weight of catalyst, 10 ppm of dye concentration and 150 minutes contact time. The % of degradation is 80.5 during optimum conditions is observed.

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