PHYTO-BIOLOGICAL AG-CU BIMETALLIC NANOPARTICLES SYNTHESIS, CHARACTERISATION AND ITS APPLICATION FOR PHOTODEGRADATION OF MALACHITE GREEN DYE

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Abstract: Single pot, simple, clean and green approach was established for synthesis of Ag-Cu bimetallic nanoparticles by using *arevalanata* leaf extract. Leaf extract was found to reduce the metal ions into nanosized particles and stabilize them by avoiding more aggregation. Characterisation of the prepared nanoparticles was done by UV-Visible spectroscopy, FT-IR, SEM, EDX and TEM. These synthesized Ag-Cu bimetallic nanoparticles were used as photocatalyst for 83.3% degradation of Malachite Green dye under sunlight irradiation under optimum conditions.

Index Terms - **Bimetallic nanoparticles, arevalanata, photodegradation, malachite green dye.**

I. Introduction:

The research on the structures and properties of tiny sized particles is blooming topic for more than a century [1-3]. The of branch technology which deals with tiny particles size below 100 nanometres is called as nanotechnology. Nanoparticles can be synthesized by two different approaches, which are top-down and bottom-up processes [4]. Majority of these methods are bound with one or more limitations which have resulted in a gradual shift towards developing facile and eco-friendly processes to synthesize nanoparticles by using biotic sources like plants and microorganisms [5]. Nanoparticles synthesized by biological methods are having greater advantages when compared to chemical and physical methods [6]. Furthermore, biosynthesis of nano metallic particles is an eco-friendly method doesn't need of harsh, toxic and expensive chemicals [7-10]. Bimetallic nanoparticles have technologically superior than their monometallic analogues owing to their enhanced catalytic, optical and electronic properties [11]. The biosynthesis of bimetallic nanoparticles may be produced by more compounds such as terpinoids, phenolic, carbonyl groups, flavonones, amines, proteins, amides, pigments, alkaloids and extra reducing agents existing in the plants extracts, plant virus, fungi, bacteria, yeast and algae [12 and 13]. Nanoparticles synthesized by using plants is cost-effective, simple and one- pot synthesis process where in the phyto-components present in plants act as both reducing and stabilizing (capping) agent to synthesize desire nanoparticles [14].

With the increase of industrialization, the release of effluents consists of dyes, pesticides, phenols and other constant organic pollutants are growing at a fast rate. They are causing hazard to the living organisms due to their toxic and hazard effects [15 and 16]. All wings of the consumer goods industry use synthetic dyes. Undoubtedly, these dyes releases around 12% of used amount during processing and manufacturing. It is needed to be remitted these effluents into environment before released [17]. Different methods such as physical, chemical, biological methods, membrane, adsorption, coagulation processes and oxidation-ozonation are presently usable for treatment of dye in wastewater. Photocatalytic degradation process can be able to degrade any type of complex organic chemical and cost effective when compared to other purification techniques [18]. An organic dye, malachite green (MG) is cationic, toxic with triphenylmethane structure usually used in the tinting of silk, leather and paper industries [19].Researchers recognized that MG and its reduced forms are persistent, highly toxic, carcinogenic and mutagenic[20]. Therefore, biological processes should be developed will have more advantages to degrade MG. The present study describes the synthesis of Ag-Cu bimetallic nanoparticles (BMNPs) from *arevalanata* leaf extract and their photocatalytic activity on MG.

II. Materials and methods:

Materials:

Chemical reagents used (silver nitrate and copper chloride) in this study were of analytical grade. Deionised water was used to clean glassware, prepare chemical solutions and throughout experimental procedure. Fresh leaves of *arevalanata* were collected from agricultural fields located at Neelavathi village in Vizianagaram district, Andhra Pradesh, India.

Preparation of leaf extract:

100g of fresh leaves were weighed and thoroughly cleaned with running tap water to eliminate debris on surface of leaves followed by deionised water to remove other contaminants from leaves and dried up under shade for 9 days. These leaves were sliced into tiny pieces and made powder by using home blender. The obtained powder placed in refrigerator at $4^{o}c$ which was taken in air tight container. Now 200mL deionised water was taken in 500mL beaker to this 10g stored powder weighed and added. The contents in the beaker boiled for 30 minutes with occasional stirring with glass rod and then cooled to acquire room temperature. The cooled leaf broth was filtered 2 times with Whatman No.1 filter paper and reserved in refrigerator at $4^{o}c$. This was taken as leaf extract throughout the experiment.

Synthesis of Ag-Cu bimetallic nanoparticles:

Equimolar concentration of silver nitrate and copper chloride solutions were prepared by weighing 0.1698g of silver nitrate in 250mL deionised water and 0.1705g of copper chloride in 250mL water. Synthesis of Ag-Cu BMNPs was done by taking 90mL of silver nitrate solution in beaker to this 10ml of leaf extract was added drop wise through burette. 90mL of copper chloride solution was added to contents in the beaker by drop wise again 10mL extract was added to it drop by drop by using burette. During addition process beaker was placed on a magnetic stirrer for continues agitation. Now the mixture was heated up to $50^{o}c$ for 40 minutes with stirring and cooled to room temperature. These synthesized BMNPs were accomplished by doing centrifugation at 6000 rpm for 15 minutes. The obtained BMNPs were washed by using deionised water 2 times to remove unwanted constituents. The resultant BMNPs used for characterisation

III. Characterization:

Formation of Ag-Cu BMNPs was confirmed by UV-Visible absorption spectra are measured using UV-2450 SHIMADZU double beam spectrophotometer, FT-IR(Fourier Transform Infrared spectroscopy) using Bruker, SEM(Scanning Electron Microscope) and EDX(Energy Dispersive X-ray)studies are done by using Hitachi S-3700N machine and the morphology of BMNPs was done by TEM analysis Jeol/JEM 2100 machine.

IV. Photodegradation experiment:

Photocatalytic activity of Ag-Cu BMNPs was examined for degradation of malachite green. Initially, 50ppm of malachite green stock solution prepared. Then Reaction mixtures were prepared by adding certain amount of Ag-Cu BMNPs to 100mL of malachite green with distinct concentrations. The P^{H} of the reaction mixtures were altered by adding H_2SO_4 or NaOH solutions when required. Now this mixture was agitated for 30 minutes in dark condition to attain adsorption-desorption equilibrium between malachite green and Ag-Cu BMNPs. Sun light used as irradiating source to reaction mixture for study degradation during 11am to 2pm. At regular 15 minutes time intervals aliquot of the reaction mixture is collected, centrifuged to remove the photocatalyst particles and analyzed for absorbance using UV-Visible Spectrophotometer (200nm to 800nm). The effect of contact time, concentration of dye, p^{H} and catalyst dose loaded are observed on photodegradation of MG. Generally, Malachite green shows the highest absorption peak at 617nm [21]. To determine the percentage of degradation of MG solution following equation (1) was used.

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

Where, A_0 is the initial absorbance of the MG solution at 0 minutes and A_t is the absorbance of the degraded solution after time t minutes [22].

V. Results and discussions:

1. UV-Visible spectral analysis:

UV-Visible absorption spectra of Ag-Cu BMNPs is revealed in Figure.1.The characteristic surface Plasmon resonance (SPR) band observed at 401 nm represents Ag contribution is more in Ag-Cu BMNPs which is not observed for bulk materials [23-25].

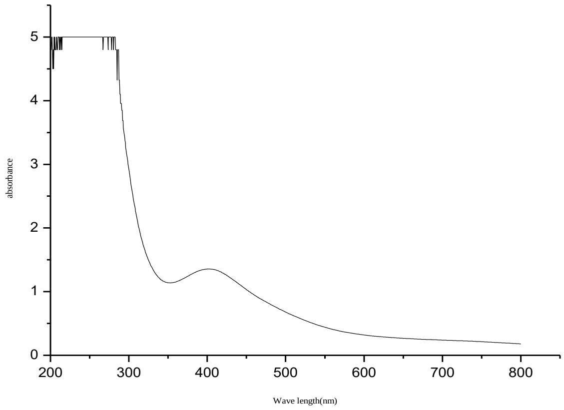


Figure.1: UV-Visible absorption spectra of Ag-Cu bimetallic nanoparticles

2. FT-IR spectral analysis:

FT-IR describes chemical bonds in molecules by generating an infrared absorption spectrum. FTIR measurements were carried out in order to identify the presence of various functional groups in biomolecules responsible for the bioreduction of Ag^+, Cu^{2+} precursors and capping/stabilization of silver copper BMNPs. The intense, broad bands were observed and compared with standard values to analyze the functional groups in *arevalanata* leaf extract and biosynthesized Ag-Cu BMNPs. FTIR spectrum of *arevalanata* leaf extract and synthesized Ag-Cu BMNPs by using *arevalanata* leaf extract were shown in figure.2 (a) and Figure.2 (b). The infrared spectra shows common and mild shift of absorption bands in isolated samples even after centrifugation and washing that indicates the adsorption of the secondary metabolites likes carbohydrates, proteins, terpenoids and Flavonids with functional group phenols, carboxylic acids, ketones, aldehydes, alkyl halides and others on the surface of the BMNPs [26]. The spectrum of *arevalanata* leaf extract shows major peak positions at 3329, 3290, 2860, 1640, 1556, 1019, 825 and 690-570cm^{-1}.A broad and intense band at 3329 and 3290cm^{-1} are due to O-H vibrations of phenols, alcohol and carboxylic acid group or N-H stretching vibration of primary amines present in the extract the other peaks at 2860, 1640, 1556, 1019, 825 and 690-570cm^{-1}corresponds to vibrations of C-H of aldehyde, C=O stretching, N-H bending of primary amines, C-O stretching, C-Cl groups respectively. The spectrum of Ag-Cu BMNPs shows major peak positions at3311, 2067, 1636, 1094 and 690-550cm^{-1}.

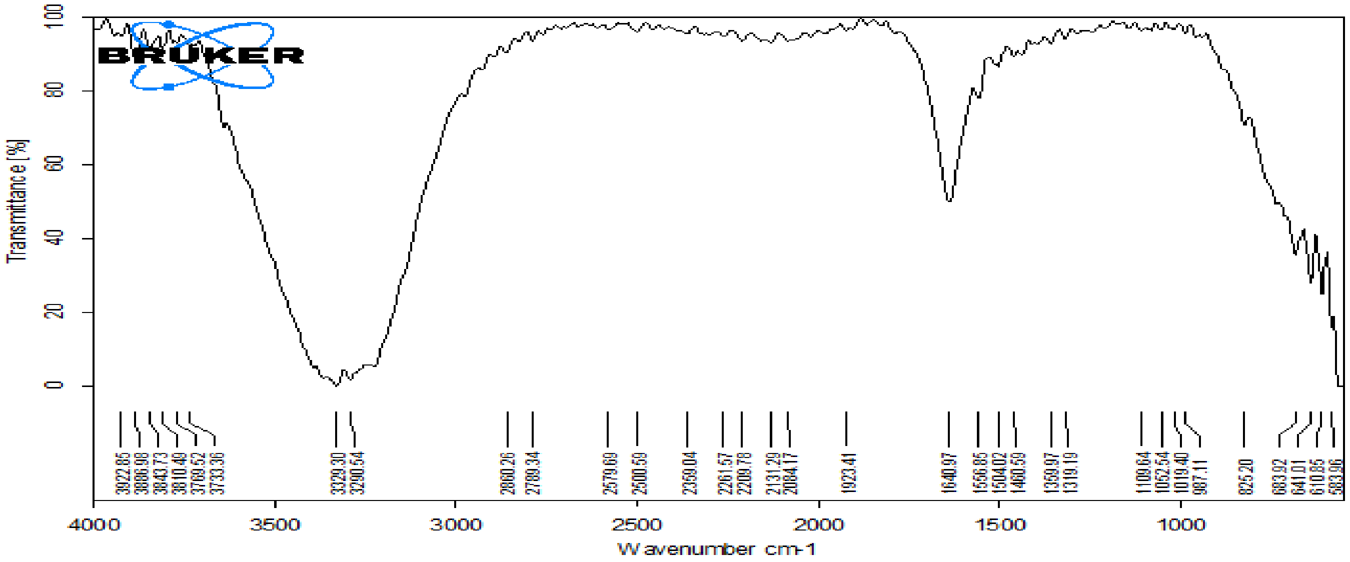


Figure.2 (a): FT-IR spectra of *arevalanata* leaf extract

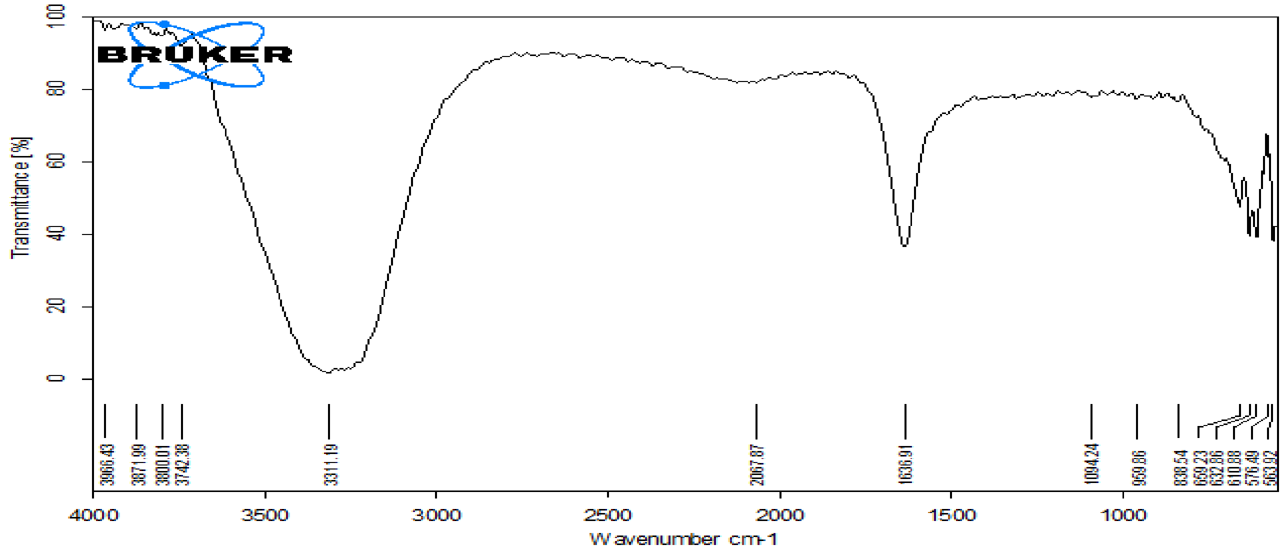
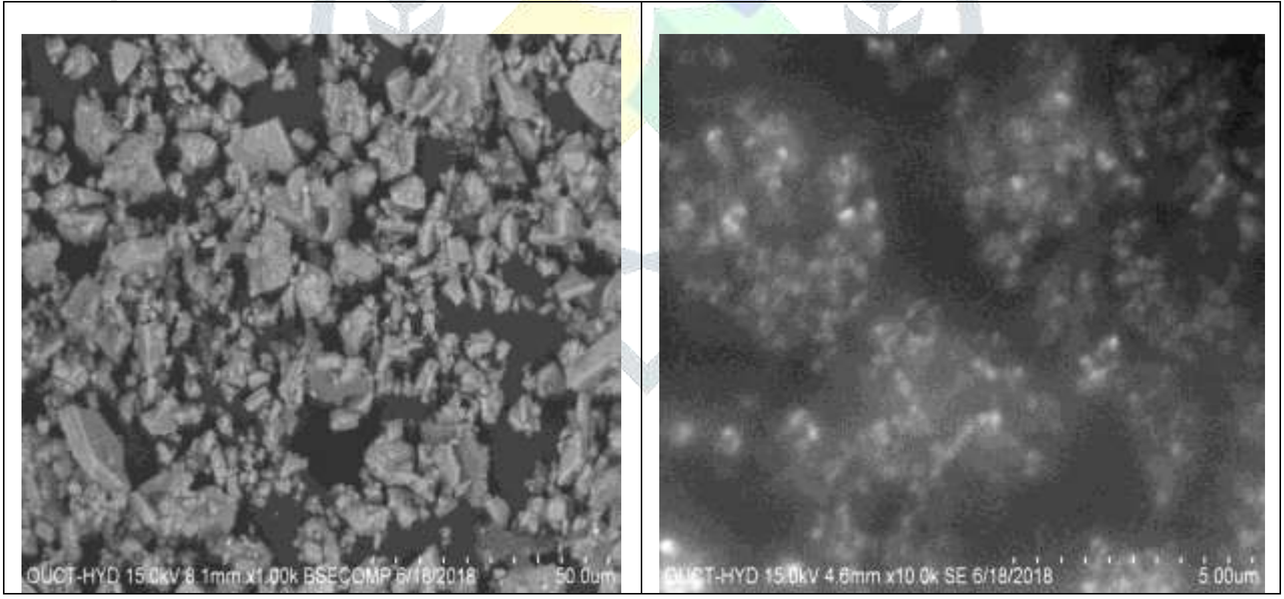


Figure.2 (b): FT-IR spectra of Ag-Cu bimetallic nanoparticles

3. SEM and EDX analysis:

Figure.3 shows SEM images of Ag-Cu BMNPs with various magnifications. From this, it can be clearly noticed that bimetallic nanoprticles prepared are in size of<100 nm in diameter.

From EDX, we can analyse all the elements existing in the prepared BMNPs by *arevalanata* leaf extract. Figure.4 shows EDX spectrum and elemental composition indicates the presence of Ag, Cu, C, O and Cl which confirms the formation of Ag-Cu bimetallic nanopaticles.



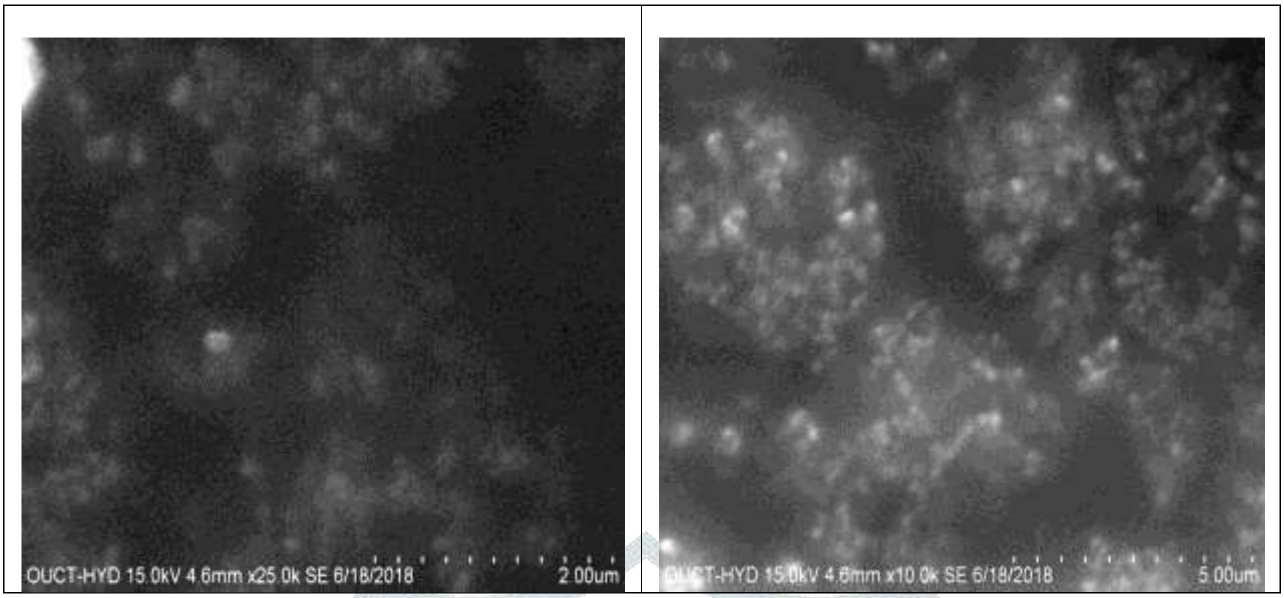


Figure.3: SEM images of Ag-Cu bimetallic nanoparticles

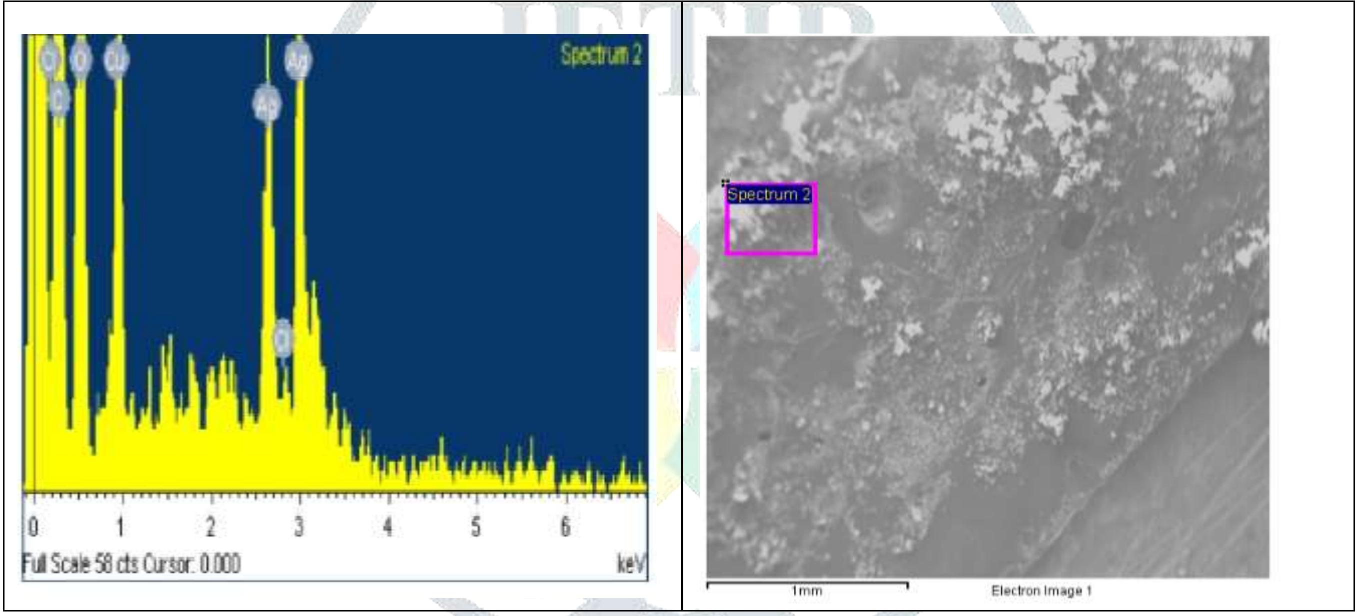


Figure.4: Ag-Cu bimetallic nanoparticles EDX spectra

Table 1: Quantitative results of Ag-Cu bimetallic nanoparticles

Element	Weight%	Atomic%
C K	-56.26	-996.92
O K	60.17	808.37
Cl K	16.17	97.09
Cu L	25.38	85.02
Ag L	53.94	106.44
Total	100	

4. TEM analysis:

Figure.5 shows the transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) pattern for synthesized Ag-Cu BMNPs from *arevalanata* leaf extract. From these images, we can observe that spherical morphology and crystalline structure of Ag-Cu BMNPs with size below 50nm.

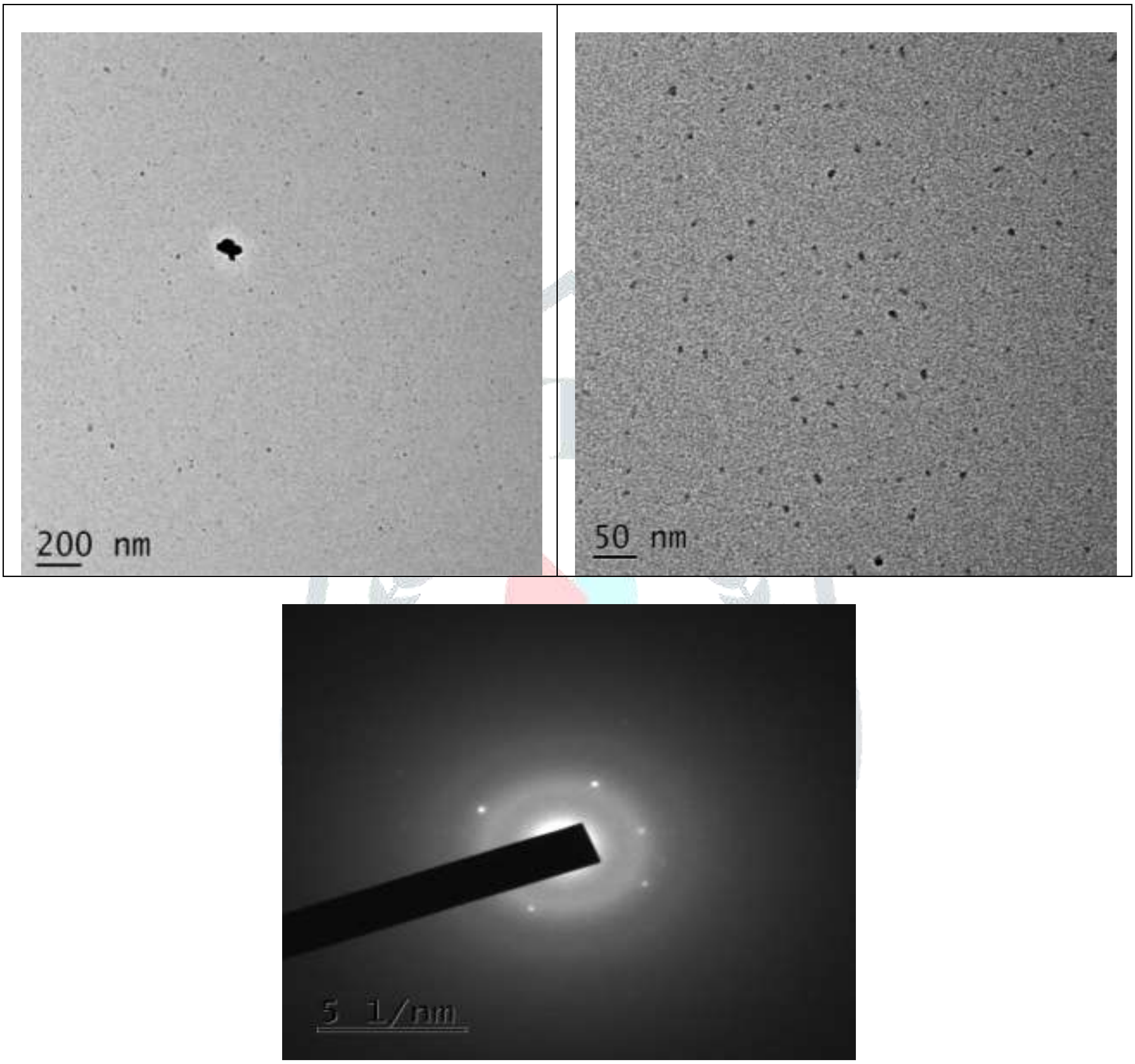


Figure. 5: TEM and SAED images of Ag-Cu bimetallic nanoparticles

5. Photodegradation of MG:

To study the photocatalytic activity of the Ag-Cu BMNPs on malachite green visible region in UV-visible spectrophotometer was used. Absorption spectrum of 10ppm MG was shown in Figure 6(a). Highest absorption peak at 617nm was observed and taken as to monitor the photodegradation of MG.

Effect of contact time:

Photodegradation capacity of the Ag-Cu BMNPs on malachite green can be studied by batch mode experiments. The efficiency of BMNPs on degradation of MG is increased by increasing contact time. The effect of contact time is carried out by taking 10ppm of 100ml MG and 10mg of BMNPs which is shown in Figure 6(b). At 120minutes which is set as optimum contact time for MG dye degradation onto BMNPs. When the contact time increases the removal efficiency of MG is also increased. The degradation is high or low consistent later contact time 120minutes. This may be arise due to the initial stage of degradation and the possibility of more surface area sites and once saturation is arrived, the uncovered sites are ambitious to be filled, which is induced by the impenetrable forces among the cationic dye molecules and BMNPs [27].

Effect of concentration of MG:

Initial concentration of MG effects photodegradation rate. For this, concentration of BMNPs was kept constant at 10mg and time of irradiation 120 minutes. Different initial concentrations 5ppm, 10ppm, 15ppm, 20ppm and 25ppm of MG solutions were prepared. The rate of degradation can be shown graphically in Figure 6(c). The maximum degradation observed at5ppm then decreases by increase in the concentration of MG [28]. This may be due to the availability of excess of dye molecules to be degraded by a small amount of catalyst and it will be up to optimum concentration of dye. If higher concentration of dye is taken, it makes the solution darker color and decreases the penetration of light into depth which reduces the photocatalytic activity of catalyst. As a result, malachite green photodegradation rate decreases [29 and 30].

Effect of P^H:

P^H of dye solution can influence the adsorption of dye on photocatalyst. Originally, Malachite green dye solution is having P^H value at 5. The initial concentration of malachite green solution 10ppm and the concentrations of the photocatalyst 10mg were kept constant with time of irradiation 120 minutes. Different solutions of various p^H values of 3-10 were prepared. Degradation efficiencies were compared after 120 minutes which was shown in Figure 6(d).

It is observed that by increasing p^H of the MG solution, enhances the degradation of MG on the photocatalyst up to p^H 8 and then onwards decreases. This may be explained as, at lower pH the number of positively charged adsorbent surface sites increased at the expense of the number of negatively charged surface sites. At lower p^H, carboxylic groups of MG had more positive charge density and protonated [31]. At higher p^H, surface of the photocatalyst was negatively charged which favoured for electrostatic force of attraction of the dye having positive charge. The degradation of MG increased with an increase of pH values [32 and 33].

On further increasing pH above 8, the degradation was decreased because there was more possibility for the formation of oxygen anion radical ($O^{2-\bullet}$), which are produced from the reaction between O_2 molecule and electron (e^-) of the photocatalyst. Which is may be due to the fact that cationic form of malachite green is converted to its neutral form, there is no attraction towards the negatively charged photoctalyst surface since to the absorption of OH^- ions [34].

Effect of dose of photo catalyst:

The catalyst dosage is also major parameters for the photodegradation studies. In order to prevent excess usage of catalyst it is required optimize the dosage of catalyst for effective removal of pollutant [35]**.**For this dosage amount was varied from 10mg to 100mg taken in 100ml of 10ppm MG at p^H 8 with contact time 120 minutes. The degradation of MG was shown in figure 6(e).

This concluded that, by increasing dosage of catalyst from 10mg to 50 mg in 100ml, the degradation of MG enhances because the increase in amount of catalyst would increase the reactive sites that produce more reactive species. Further increase in dosage of catalyst from 50mg to 100mg will develops light scattering and reduces light consumption [36].Many authors examined, in photocatalytic degradation technique the reaction rate also depends on catalyst loading [37-39].

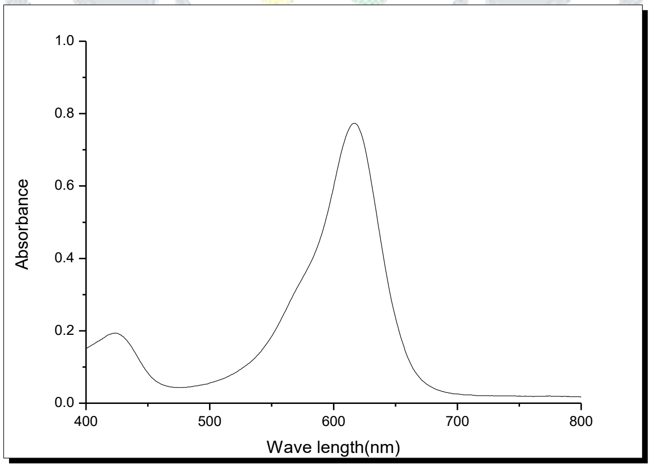


Figure.6 (a): Absorption spectrum of 10ppm Malachite Green dye

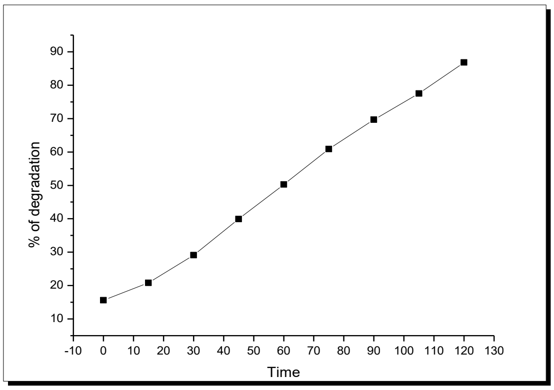


Figure.6 (b): The effect of contact time on % of degradation

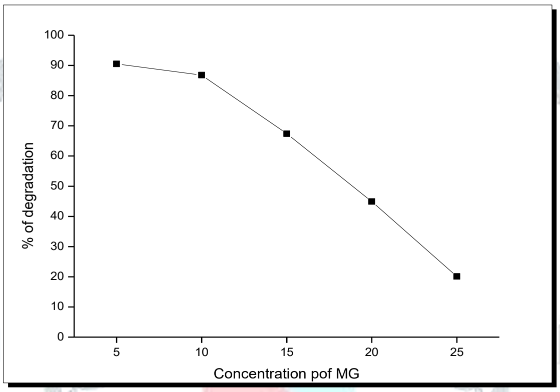


Figure.6 (c): The effect of concentration of dye on % of degradation

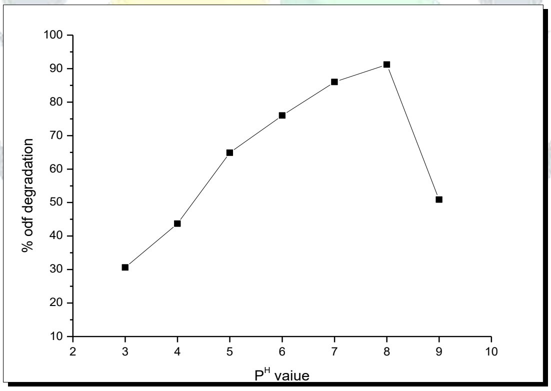


Figure.6 (d): The effect of p^H on % of degradation

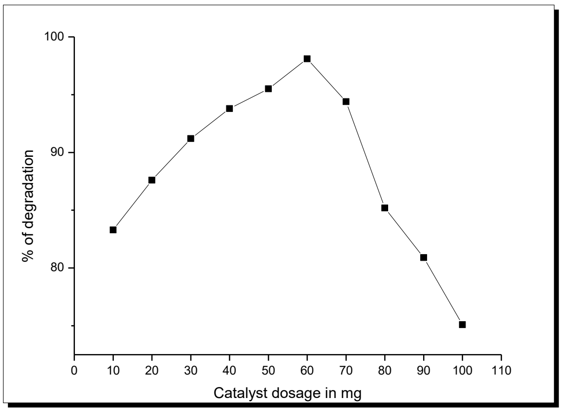


Figure.6 (b): The effect of dosage of catalyst on % of degradation

VI. Conclusions:

An environmentally friendly method was projected to synthesize bimetallic Ag-Cu nanoparticles from *arevalanata* leaf extract. Surface Plasmon resonance (SPR) band observed at 401 nm in UV-Visible absorption spectra. From SEM and TEM analysis results, the formed Ag-Cu BMNPs were crystalline and spherical in shape with size below 50 nm. The photocatalytic activity of these nanoparticles is examined under sunlight for degradation of Malachite green dye which is environmental pollutant. The % of photodegradation of Malachite green changes with parameters such as increase in contact time, increase in concentration of Malachite green, increase in p^H, increase in photocatalyst dosage. The optimum conditions for the degradation of Malachite green by using bimetallic Ag-Cu nanoparticles synthesized from *arevalanata* leaf extract was pH=8,10mg weight of catalyst 10ppm of dye concentration with 120 minutes contact time. The % of degradation is 83.3 during optimum conditions was observed.

VII. Acknowledgements:

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