Green Synthesis of Ag-Ni Hybrid Nanomaterials from *Andrographis Paniculata* leaf extract and Study of their Photocatalytic Activity

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ABSTRACT

An environmentally benign cost effective method is reported for green synthesis of Ag-Ni hybrid nanomaterials by using *Andrographis Paniculata* leaf extract. The phytomolecules present in the extract are acting as reducing agents, stabilizing and capping agents for the biosynthesized nanomaterials. The characterization studies are done by UV-Visible, FTIR, SEM, XRD, EDX and HRTEM analyses. These nanoparticles are further applied as photocatalysts for degradation of Malachite Green dye by irradiation under sunlight. The optimum conditions found in the degradation of malachite green dye are pH **8**, weight of catalyst **30 mg**, dye concentration of **10 ppm** and contact time of **120 minutes**. A maximum photodegradation of **82%** is obtained under these optimum conditions.

KEY WORDS

Hybrid nanomaterials (HNMs), *Andrographis Paniculata*, Malachite Green (MG), photodegradation.

INTRODUCTION

Nanotechnology involves the synthesis and application of materials having one of the dimensions in the range of 1 nm to 100 nm and acts as a channel between bulk materials and atomic or molecular structures. In recent times hybrid nanomaterials have gained considerable attention because of their importance for magnetic, optical and catalytic applications in multiple fields [1]. Various physical, chemical and biological methods have been employed for the synthesis of hybrid nanomaterials [2]. Several advantages of biological methods over physical and chemical methods are due to the fact that they are environmentally benign, less time consuming, cost effective with almost negligible industrial waste without use of toxic chemicals [3]. Biosynthesized hybrid nanomaterials are used in several contemporary fields viz. imaging, labeling, luminescence tagging, drug delivery and biomedical field because of their superior properties. Hybrid nanomaterials synthesized from plant extracts have been found to possess extraordinary catalytic activities [4].

Dyes are used widely in various fields such as cosmetics, leather, food and textile industries. The release of these industrial dye effluents into water shows adverse effect on quality of water [5]. One of such dye is malachite green (MG).

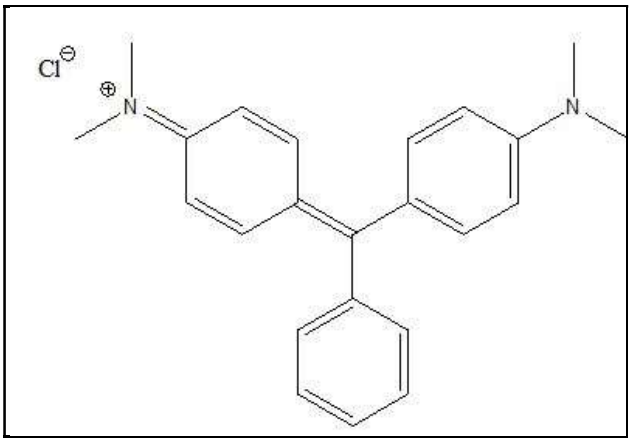

Figure 1 (a): Structure of Malachite Green dye

Malachite green dye is a cationic green crystalline water soluble dye and belongs to triphenyl methane category. (Figure1.a). MG dye is a potential environmental contaminant and a peril to public health as it is a multi-organ toxin proved as by both experimental clinical observations [6]. So it is necessary to exterminate 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 [7]. Dye removal via degradation using photocatalysts is the most scathe less and desirable among all methods because of its sustainable and ecofriendly technology [8]. Recent times nanotechnology has been extended in the waste water treatment and nanoparticles are used as photocatalysts for degradation of dyes due to their extensive surface area [9].

Herein, an effortless and robust green method for synthesis of Ag-Ni hybrid nanomaterials (HNMs) is reported by using leaf extract of *Andrographis Paniculata* as a stabilizing, reducing and capping agent. These HNMs are employed as catalysts for photodegradation of MG dye under solar light irradiation. Various reaction conditions are observed and the optimum conditions are noted for the maximum photodegradation.

2. EXPERIMENTAL

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

2.2. Preparation of *Andrographis Paniculata* leaf extract: 100 g of fresh leaves are weighed and thoroughly washed with running tap water to remove detritus on surface of leaves followed by deionised water to get rid of other contaminants from leaves and dried up under shade for 10 days. These leaves are cut into tiny pieces and made homogenized powder by using home blender. The procured powder is placed in refrigerator at 4° C which is kept in an air tight container. Now 200 mL deionized water is taken in 500 mL beaker to this 10 g stored powder is weighed and added. The contents in the beaker heated for 30 minutes at 50° C with occasional stirring with glass rod and then cooled to acquire room temperature. The cooled concoction is filtered two 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(b), 1(c)).

Figure 1(b): *Andrographis Paniculata* plant

Figure 1(c): *Andrographis Paniculata* leaf extract

2.3. Synthesis of Ag-Ni hybrid nanomaterials:

Equimolar (25 mM) concentrations of silver nitrate and nickel nitrate aqueous solutions are prepared separately in 100 mL volumetric flasks by dissolving 0.4246 g, 0.7267 g weight of $AgNO_3$ and $Ni(NO_3)_2$ in deionized water respectively. Synthesis of Ag-Ni HNM s is done by taking 100 mL of $AgNO_3$ solution in a 500 mL beaker, to this 90 mL of leaf extract, 100 mL of Ni $(NO_3)_2$ solutions are added by drop wise in simultaneous addition process. After this addition the beaker is placed on a magnetic stirrer for continuous agitation. This mixture is stirred at 70ºC for 50 minutes at pH 8 on magnetic stirrer. These synthesized HNMs are separated out by doing centrifugation at 4500 rpm for 45 minutes. The obtained HNM s are washed with deionised water two times to remove unwanted constituents and dried in oven at 80^0 C for two hours. The resultant HNMs are collected (**Figure. 2**) and used for characterization.

Figure. 2: Ag-Ni HNMs

2.4. Characterization:

Formation of Ag-Ni HNM s is confirmed by UV-Visible absorption spectra using UV-2450 SHIMADZU double beam spectrophotometer, FTIR using Bruker, SEM, EDX studies are done by using Hitachi S-3700N machine and the morphology of HNM s is elucidated by HRTEM analysis with FEI Technai machine.

3. RESULTS AND DISCUSSION

3.1. UV-Visible spectral analysis:

UV-Visible absorption spectrum of Ag-Ni HNM s is presented in **Figure.3.** The characteristic surface plasmon resonance (SPR) band at around 437 nm is observed in Ag-Ni HNMs which confirms the nano size of the synthesized HNMs [10].

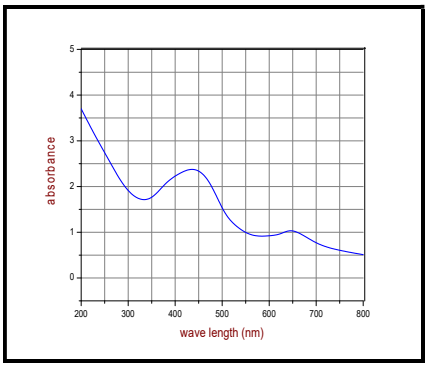

Figure. 3 : UV-Visible absorption spectrum of Ag-Ni HNM s

3.2. FTIR spectral analysis:

FTIR spectral data is used to identify different functional groups present in biomolecules of leaf extract and formed HNMs. These groups are responsible for the bioreduction of Ag^{+}, Ni^{+2} precursors and also for capping and stabilization of Ag-Ni HNMs. The FTIR spectrum of Ag-Ni HNM s exhibits major peak positions at 3210 cm^{-1}, 3414 cm^{-1} and 3384 cm^{-1} which indicate the N-H stretching vibrations of amines and O-H stretching of hydroxyl groups of alcohols and phenols. Intense peak at 1640 cm^{-1} is due to C=O stretching of amide group. Very small peak at 601 cm^{-1} indicates the presence of C-Cl group.

This spectral data clearly confirms that the surface of the nanoparticles is covered by plant secondary metabolites such as carbohydrates, glycosides, Saponin, phytosterols, phenolic compounds, tannins, flavonoids, proteins, aminoacids, diterpenes, carboxylic acids, amides, ketones and alkyl halides [11].

3.3. **SEM and EDX analysis:**

From energy dispersive X-ray analysis we can analyze all the elements present in the HNM s prepared by *Andrographis Paniculata* leaf extract. **Figure.4** shows EDX spectrum and elemental composition. This indicates the presences of Ag and Ni which confirms the formation of Ag-Ni hybrid nanomaterials. Scanning electron microscopic (SEM) images of Ag-Ni HNM s with various magnifications are given in **Figure 5**. From this it can be clearly noted that the prepared Ag-Ni HNMs are in the size range between 50 to 100 nm in diameter.

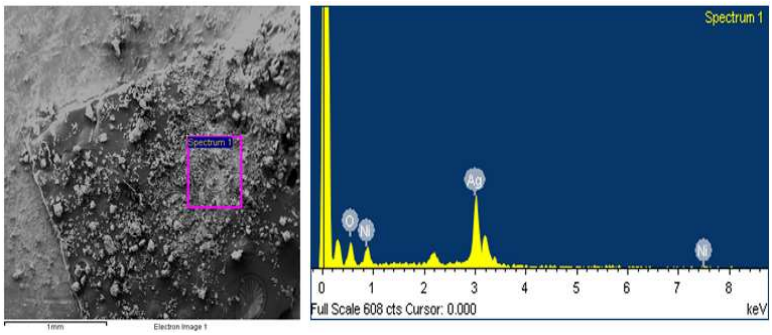

Figure. 4: EDX Analysis of Ag-Ni HNMs

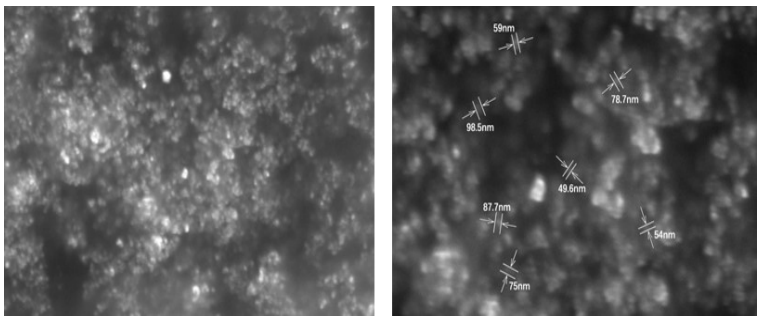

Figure. 5 : SEM images of Ag-Ni HNMs

3.4. HRTEM analysis: **Figure.6** shows the high resolution transmission electron microscopy (HRTEM) images for synthesized Ag-Ni HNMs. From these images, it is observed that Ag-Ni HNMs are formed with spherical morphology and crystalline structure below the size of 100 nm. It is also observed that, the two metal nanospheres emerge to be positioned adjacent to each other. It is also in strong accordance with the images from SEM analysis.

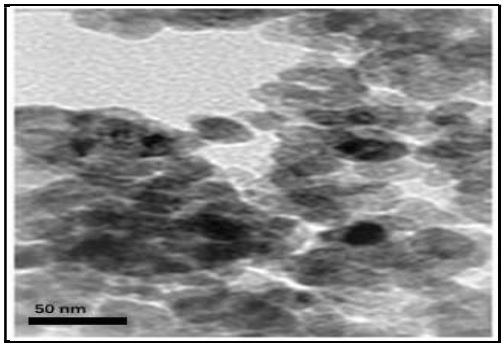

Figure .6: HRTEM image of Ag-Ni HNMs

3.5. Powder XRD analysis :

The XRD spectrum of green synthesized Ag-Ni HNM s from leaf extract is shown in **Figure: 7.** The peaks appeared at 2θ values of 38.30^0, 44.28^0, 64.38^0, 77.39^0 correspond to the Bragg's reflections of Ag(111), Ag(200), Ni(111), Ag(220), Ni(222) , Ag (311) planes respectively of face centered cubic crystal structure [12] as shown in the **Figure:7.** The numerically calculated value of the synthesized Ag-Ni HNMs materials corresponds to an average particle size of **23.35 nm**.

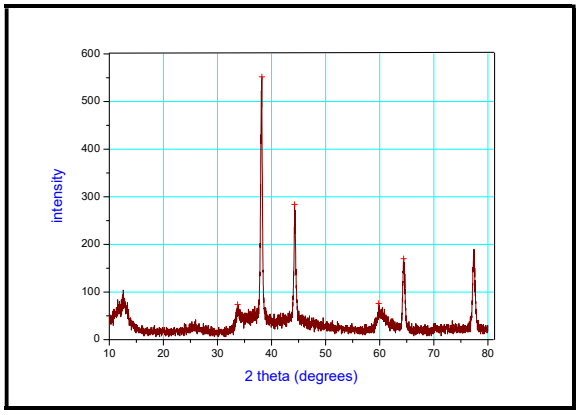

Figure:7 . XRD spectrum of Ag-Ni HNM s

4. Photodegradation studies on Malachite Green dye using Ag-Ni HNMs:

The photo degradation experiments are carried on Malachite Green dye using green synthesized Ag-Ni HNM s acting as a catalyst. Initially, 50 ppm of malachite green stock solution is prepared. Then reaction mixtures are prepared by adding certain amount of Ag-Ni HNM s (10 mg, 20 mg, 30 mg, 40 mg, 50 mg, 60 mg,70 mg, 80 mg) to 100 mL of malachite green for distinct concentrations(5 ppm, 10 ppm, 15 ppm, 20 ppm, 25 ppm, 30 ppm, 35 ppm). The pH of the reaction mixtures is maintained in the experiments at various values for both acidic and basic range

(i.e. pH 3,4,5,6,7,8,9,10,11) by adding 0.1 N H_2SO_4 or 0.1 N NaOH solutions when required. Now this mixture is agitated for 20 minutes in dark condition to attain adsorption-desorption equilibrium between malachite green and Ag-Ni HNM s. Sun light is used as irradiating source to reaction mixture for studying photodegradation during 11.00 am to 3.00 pm. At regular 30 minutes time intervals, aliquot part of the reaction mixture is taken, centrifuged to remove the photocatalyst particles and optical absorption properties are analyzed by using UV-Visible Spectrophotometer. The absorbance is observed by varying parameters like changing the time of contact between the catalyst and the dye, pH of the reaction mixture, concentration of the dye solution and dosage of the catalyst. Malachite green shows the highest absorption at 617 nm [13]. To determine the percentage degradation of MG dye solution following equation (2) is used.

$$\% \text{ degradation} = \left(\frac{A_0 - A_t}{A_0}\right) \times 100 \quad \ldots \quad (2)$$

Where, A_0 is the initial absorbance of the MG solution at zero minutes and A_t is the absorbance of the degraded solution after time t minutes.

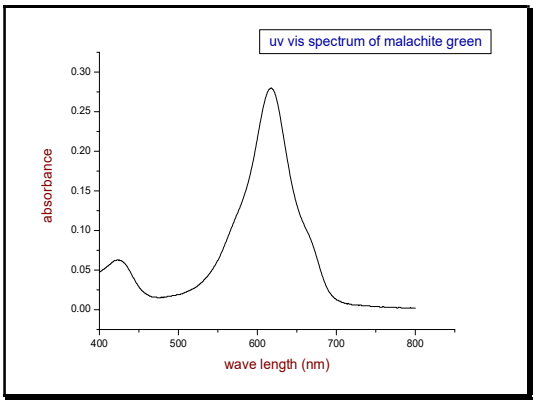

Figure 8(a): UV- Visible spectrum of Malachite Green

To study the photocatalytic activity of the Ag-Ni HNM s on malachite green visible region of the light source is selected on UV-visible spectrophotometer. Absorption spectrum of 10 ppm malachite green solution is shown in **Figure 8(a).** Highest absorption peak at 617 nm is observed and this maximum absorption peak is considered to monitor the photodegradation reaction of MG dye for all further studies in this paper.

4.1. Effect of time of contact:

Photodegradation capacity of the Ag-Ni HNMs on malachite green dye is studied in the presence of sunlight by batch mode experiments. The efficiency of HNMs photocatalyst on degradation of MG is expected to be increased by increasing contact time. The effect of contact time is carried out by taking 10 ppm of 100 mL MG dye solution and 10 mg of HNM s (pH at 7) as catalyst load which is shown in **Figure 8(b).** From the initial part of the graph i.e upto 120 min, % photodegradation is exhibiting rapid rise. However, above 120 minutes the slope is relatively less steeper although % photodegradation remains still considerably predominant thus shows higher values.

Thus, upto 120 min, the % photodegradation of the dye by using the HNMs photocatalyst is found to be rapid, and above 120 min it becomes relatively less rapid although active even upto 180 min. This is due to strong adsorption forces that predominate between the dye and the HNMs as the number of the reactive sites on the photocatalyst are largely vacant during initial periods of contact time. But after 120 minutes of contact period, equilibrium between the number of vacant sites of adsorption and the dye molecules appears to be established although at slower rate, hence exhibit slightly slower rise of % photodegradation [14].

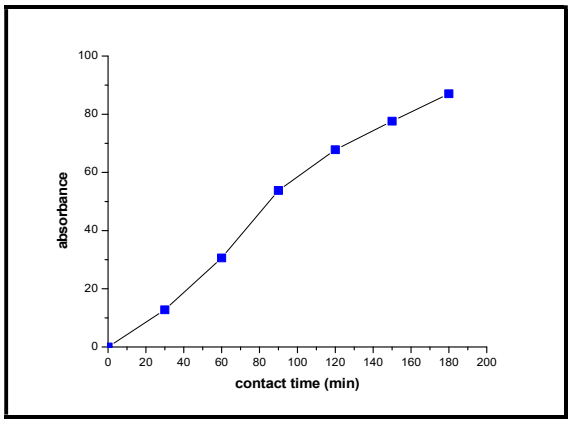

Figure 8(b): Effect of contact time on photo degradation

4.2. Effect of initial concentration of MG dye solution:

Initial concentration of MG dye solution is also expected to affect the rate of photo degradation. To investigate this fact, dosage of HNM s nanocatalyst is kept constant at 10 mg, maintaining the dye solution pH at 7 and the time of irradiation as 180 minutes. However one parameter (the initial concentration of the MG dye solutions) is varied at 5 ppm, 10 ppm, 15 ppm, 20 ppm, 25 ppm , 30 ppm and 35 ppm. The rate of photodegradation can be represented graphically in **Figure 8(c).**

It can be observed from the figure that, the maximum photodegradation is found at 5 ppm, and then it decreases with further rise in the concentration of MG dye solution. Thus as the initial concentration of the dye increases beyond 5 ppm, % photodegradation decreases [15]. This observation can be explained by the fact that at the low initial concentration of the dye solution, large number of dye molecules could be adsorbed on the surface of HNMs. Increasing the initial concentration of the dye can result competitive adsorption among the dye molecules while the area of active reaction sites on the catalyst is fixed. Consequently the % photodegradation of MG dye decreases.

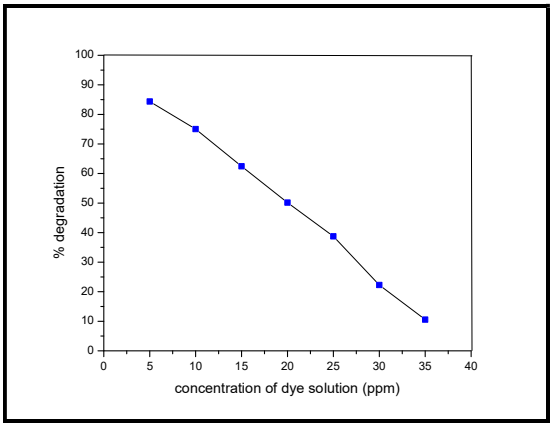

Figure.8(c): Effect of concentration of MG dye solution on photodegradation

4.3. Effect of pH:

pH of dye solution can influence the adsorption of dye on the photocatalyst. Keeping pH as variable, all other parameters are kept constant viz. the initial concentration of the malachite green solution is taken as 10 ppm, the concentrations of the photocatalyst as 10 mg and with time of irradiation 120 minutes. Different solutions of various pH values from 3 to 11 are prepared. Photodegradation efficiencies are compared which is shown in **Figure: 8(d).**

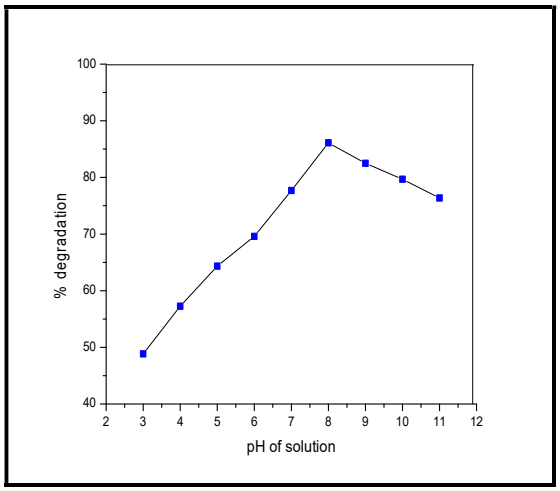

Figure:8(d): Effect of pH on photodegradation

It is observed that by increasing pH of the MG dye solution, the % photodegradation of MG dye on the photocatalyst enhances up to pH 8 and on further increase of pH, the rate of photodegradation is diminished. At pH less than four, lower values of % photodegradation are observed. Solution pH may influence both solution chemistry and surface active sites of the adsorbent. At acidic pH, H^+ ions of the water molecules, may race with dye ions for the adsorption sites of the catalyst surface, there by hindering the adsorption of the dye. As the pH value increases, the number of H^+ ions of the aqueous solution reduces, hence the cationic dye molecules could approach the catalyst surface at a faster rate, thus exhibit an fast increase in the rate of % photodegradation. At pH 8 the adsorption is maximum, hence the photo degradation is found to be maximum. At pH >8, the malachite green dye may not be maintained

in its cationic form due to high concentration of OH^- ions in the aqueous dye solution. Consequently, the electrostatic repulsion increases between the MG dye and negatively charged catalyst surface. As a result the photodegradation slowly decreases from pH 8 to 11.

4.4. Effect of dosage of photo catalyst:

In photodegradation process, one of the important parameters of decolourizing of dye solution is dosage of the photocatalyst. To avoid splurge of costly catalyst and attain the maximum absorption of photons optimization of the catalyst dosage is important. For this, dosage amount is varied from 10 mg to 80 mg taken in 100 ml of 10 ppm MG dye at pH 8 with contact time 120 minutes. The degradation of MG is shown in **figure 8(e).**

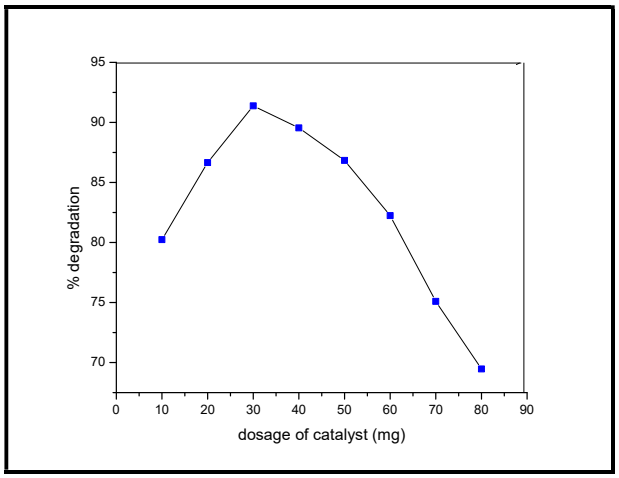

Figure 8(e): Effect of dosage of catalyst on photo degradation

From the graph it can be concluded that, by increasing dosage of catalyst from 10 mg to 80 mg in 100 ml dye solution, the % photodegradation of the MG dye shows an increasing trend up to 30 mg. This is because the increase in amount of catalyst up to 30 mg would increase the number of reactive sites that produce more reactive species [16]. On further increase of catalyst dosage, % photodegradation of MG dye decreases because the catalyst particles form more turbid suspensions at higher loadings, which increase the scattering of the solar light and reduce the penetration of light into the reaction mixture.

CONCLUSION

An ecologically safe method is projected in this report to synthesize Ag-Ni hybrid nanomaterials from *Andrographis Paniculata* leaf extract. From UV-VIS spectral analysis it is confirmed that the particles are in nanoscale as per the positions of the Surface Plasmon Resonance (SPR) bands. FTIR data confirms the presence of secondary metabolites of phyto molecules that act as the bio reducing and capping agents of the formed nanoparticles. Results of XRD, SEM and TEM analyses proved that Ag-Ni HNM s are in spherical morphology and cubic crystalline structure with size between 20-100 nm. The photocatalytic activity of these nanomaterials is examined under sunlight for degradation of MG dye which is an environmental pollutant. The % photodegradation of MG dye changes with parameters such as contact time, concentration of MG dye, pH and photocatalyst dosage. From this research study on bimetallic Ag-Ni HNM s synthesized from *Andrographis Paniculata* leaf extract, the optimum conditions found in the degradation of MG dye is pH **8**, weight of catalyst **30 mg**, dye concentration of **10 ppm** and contact time of **120 minutes**. A maximum photodegradation of **82%** is obtained under these optimum conditions.

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