Phyto Fabricated Green Synthesis of Novel Ag-Fe Bimetallic Nanoparticles : Characterization and Photocatalytic Activity on Malachite Green Dye

[1]Anuradha Ch.S., [2]Prof. Susheela Bai G., [3]Dr. Kishore Babu B.
[1]Assistant Professor, [2]Professor, [3]Assistant Professor
[1]Visakha Government Degree College for Women,
[2]A.U.C.E.(A) , Andhra University,
[3]A.U.C.E.(A) , Andhra University

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Abstract - **An environmentally sound, facile and cost effective method was reported for green synthesis of Ag-Fe bimetallic nanoparticles by using Aerva Lanata leaf extract. The phyto molecules present in the extract are acting as reducing agents, stabilizing and capping agents for the biosynthesized nano particles. The characterization studies were done by UV-VIS , FTIR spectroscopies , SEM, XRD, EDX and HRTEM analyses. These nanoparticles were further applied as photocatalysts for degradation of Malachite Green dye by irradiation under sunlight to study optimum conditions for maximum photodegradation. It was observed that the maximum photodegradation 88.75% was achieved for 10 ppm of dye solution at pH 9 with a catalyst dose of 40 mg under irradiation for 120 minutes.**

keywords - **Bimetallic nanoparticles (BMNPs), Aerva Lanata(AL), Malachite Green (MG), photo degradation**
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INTRODUCTION

Nanotechnology involves the synthesis and application of materials having one of the dimensions in the range of 0.1-100 nm[1] . Nanoscience and nanotechnology is about the precise and purposeful manipulation of matter at the atomic level. It embraces many different fields like biology, chemistry, physics, engineering and medicine[2].There are two types of methods generally adopted for fabricating nanomaterials: top-down methods and bottom-up methods. In top down method we remove material progressively from bulk substrate until the desired nanomaterial is obtained. Bottom-up methods work starting from the atomic or molecular precursors and by gradually assembling it until the desired structure is formed (**Figure.1**)[3].
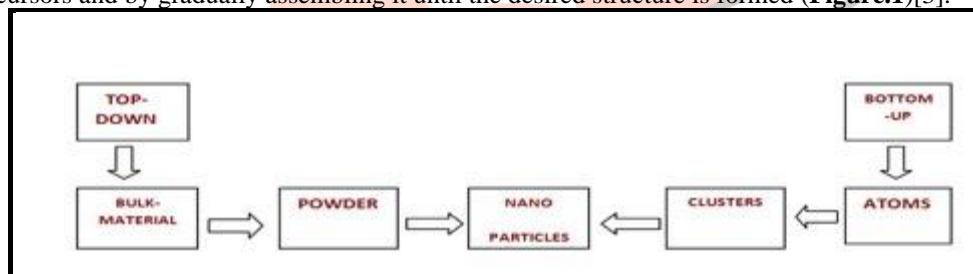
Figure.1: Different approaches for preparation of nanoparticles

Prodigious growth in nanotechnology has spread out its application in biomedical sciences, nutrition, energy sciences , nanobiotechnology, cosmetics, mechanics , optics , chemical industries, drug-gene delivery [4]. Alloying of different metals in nano size could enhance the properties of their respective monometallic nanoparticles. Bimetallic nanoparticles show greater stability, catalytic activity than monometallic nanoparticles [5]. Generally nanometals are synthesized by chemical reduction methods but they are hazardous and expensive. Green methods are ecofriendly, cheap and environmental benign methods for the synthesis of nanometals. Secondary metabolites present in plants acts as reducing and capping agents [6].Bimetallic alloy nanoparticles were synthesized in green method by using microorganisms such as yeast, bacteria and algae became one of the facile methods [7].

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[8]. One of such dye is malachite green (MG). Malachite green dye is a cationic green crystalline water soluble dye and belongs to triphenylmethane category[9] . (**Figure 1.a**). MG dye is a potential environmental contaminant and a peril to public health as it is a multi-organ toxin as proved by both experimental and clinical observations [10] .So it is necessary to exterminate the MG dye effluents from water .
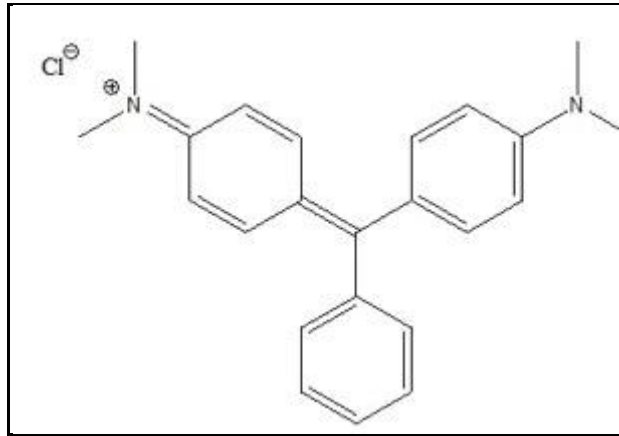
Figure 1 (a) : Structure of Malachite Green dye

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[11]. Dye removal via degradation using photocatalysts is the most scatheless and desirable among all other methods because of its sustainable and ecofriendly technology[12][13]. 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[14].

Herein, an effortless and robust green method for synthesis of Ag-Fe bimetallic nanoparticles (BMNPs) by using leaf extract of *Areva lanata* as a reducing and capping agent was reported and by using these BMNPs as catalysts for photodegradation of MG dye under solar light irradiation was also studied at various reaction situations to observe the optimum conditions for the maximum degradation.

2. EXPERIMENTAL

2.1. Materials: Chemical reagents used (siver nitrate and ferrous sulphate) in this study were of analytical grade. Deionized water was used to clean glassware, to prepare chemical solutions and for experimental procedure. Fresh leaves of *Aerva lanata* were collected from agricultural fields in S.Kota, Vizianagaram district, Andhra Pradesh state, India.

2.2. Preparation of *Aerva lanata* leaf extract: 100g of fresh leaves were 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 were cut into tiny pieces and made homogenized powder by using home blender. The procured powder placed in refrigerator at 4_oC which was kept in an air tight container. Now 200 mL deionised water was taken in 500 mL beaker to this 10g stored powder was weighed and added. The contents in the beaker heated for 30 minutes at 50_oC with occasional stirring with glass rod and then cooled to acquire room temperature. The cooled concoction was filtered 2 times with Whatman No.1 filter paper and reserved in refrigerator at 4_oC. This was taken as leaf extract throughout the experiment (**Figure : 1.(b)1(c)**).

Figure 1(b): *Aerva Lanata* plant

Figure 1(c): *Aerva Lanata* leaf extract

2.3. Synthesis of Ag-Fe bimetallic nanoparticles:

Equimolar (25 mM) concentrations of silver nitrate and nickel nitrate aqueous solutions were prepared separately in 100 ml volumetric flask by dissolving 0.4246 g, 0.6950 g weight of $AgNO_3$ and $FeSO_4$ in water respectively. Synthesis of Ag-Fe BMNPs was done by taking 100mL of $AgNO_3$ solution in a 500 mL beaker, to this 90ml of leaf extract and 100mL of $FeSO_4$ solution were added drop wise by simultaneous addition process. During addition process beaker was placed on a magnetic stirrer for continuous agitation. Now this mixture was stirred at 40_oC for 50 minutes at pH 7 on magnetic stirrer. These synthesized BMNPs were separated out by doing centrifugation at 5000 rpm for 40 minutes. The obtained BMNPs were washed with using deionized water for 2 times to remove unwanted constituents and dried in oven at 90_oC for two hours. The resultant BMNPs particles were collected (**figure: 1(d)**) and used for characterization.

Mechanism of green synthesis of Ag-Fe bimetallic nanoparticles :

Aerva Lanata leaf extract + Ag(I)-Fe(II) precursor salt solutions

Reduction

Ag(0)-Fe(0) bimetallic nanoparticles

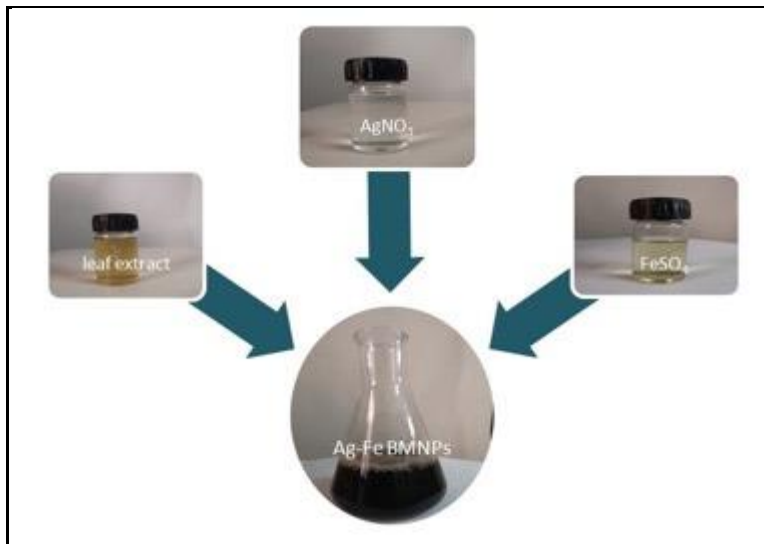Growth   and   stabilization

Capped Ag(0)-Fe(0) bimetallic nanoparticles

Figure : 1(d) . Synthesis of Ag-Fe BMNPs from precursor solutions

2.4. Characterization:

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

3. RESULTS AND DISCUSSION

3.1.UV-Visible spectral analysis:

UV-Visible spectrum of *Aerva Lanata* leaf extract is given in **Figure2(a)**. UV-Visible absorption spectrum of Ag-Fe BMNPs is revealed in **Figure.2(b)**. The characteristic surface plasmon resonance (SPR) band at around 436 nm is observed in Ag-Fe BMNPs   which confirms the nano size of the synthesized paricles [15] .
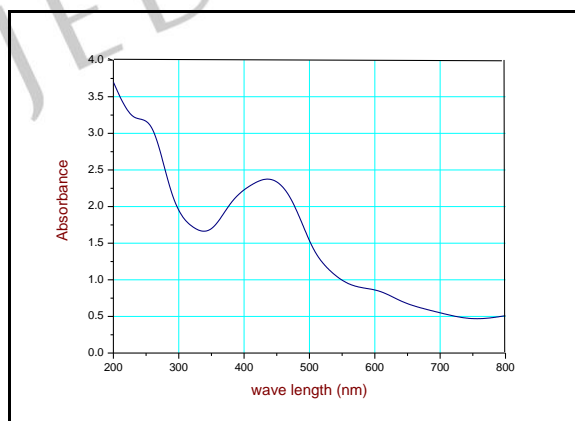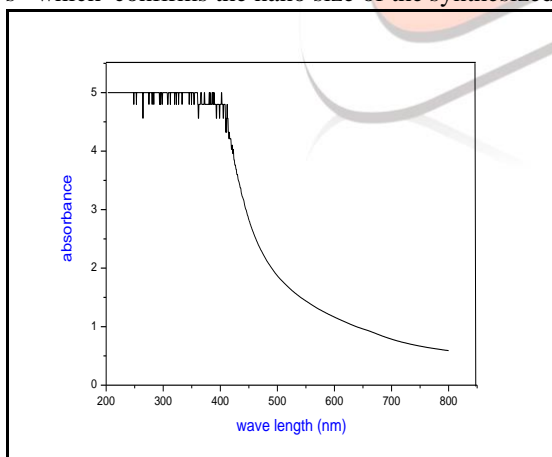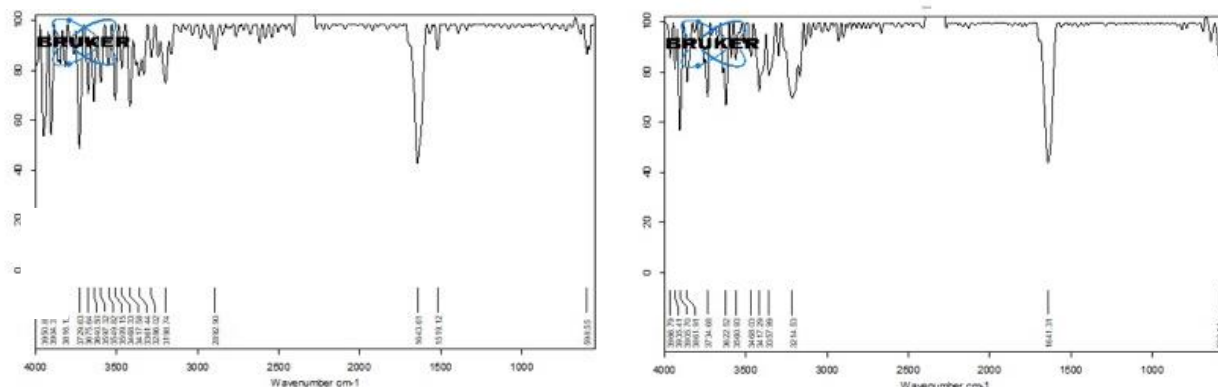

Figure 2 (a): UV-VIS Spectrum of *Aerva Lanata* leaf extract **Figure.2(b):** UV-Visible absorption spectrum of Ag-Fe BMNPs

3.2. FTIR spectral analysis:

FTIR spectral data is used to identify different functional groups present in biomolecules of leaf extract. These groups are responsible for the bioreduction of Ag_+, Fe_{+2} precursors and also for capping and stabilization of Ag-Fe BMNPs. The intense peaks were observed and compared with standard values to analyze the functional groups in *Aerva lanata* leaf extract and green synthesized Ag-Fe BMNPs. FTIR spectra of *Aerva lanata* leaf extract and synthesized Ag-Fe BMNPs by using *Aerva lanata* leaf extract were shown in **Figure.3 (a)** and **Figure.3 (b)** respectively**.** The comparison of the FTIR spectra of both Ag-Fe BMNPs and leaf extract of *Aerva lanata* clearly indicates the existence of the plant extract phytomolecules such as polyphenols ,terpenes, flavonoids, glycosides, tannins, sterols, amides, carbohydrates, amines the surface of the Ag-Fe BMNPs [15].

Figure.3 (a): FTIR spectrum of *Aerva lanata* leaf extract **Figure 3(b)**. FTIR spectrum of Ag-Fe BMNPs in leaf extract

The strong intense peaks between 3200 cm-1 to 3950-1may be due to N-H ,O-H stretching of 1o amines and polyhydroxy groups present in the extract. The strong absorption at 1643 cm-1indicates the presence of C=O group of amides. This result gives the evidence about the high protein content of the extract. The small peak at 2892 cm-1 is may be due to C-H symmetrical stretching of methylene groups. The peak position at 1519 cm-1 may be due to C=C stretch of aromatic ring. The peak at 598 cm-1 is denoting the presence of C-Cl group.

The FTIR spectrum of Ag-Fe BMNPs exhibits major peak positions at 3214 cm-1,3417 cm-1, 3622 , 3905 cm-1 and 3935 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 1641 cm -1is due to C=O stretching of amide group. Very small peak at 588 cm-1 connotes the presence of C-Cl group [16],[17].

FTIR analysis clearly confirms that all the aforementioned absorption peaks of the extract are barely shifted in the FTIR spectrum of Ag-Fe BMNPs as the phyto molecules of the extract act as bioreducing agents, capping and stabilizing agents for the synthesized nanoparticles. The existence of these IR bands also in the Ag-Fe BMNPs confirmed that the surface of the nanoparticles was covered by plant secondary metabolites such as carbohydrates, glycosides, Saponin, phytosterols, phenolic compounds, tannins, flavonoids, proteins, aminoacids, diterpenes with functional group phenols, carboxylic acids, amides, ketones, alkyl halides.[18]

3.3.SEM and EDX analysis:

From energy dispersive X-ray analysis we can analyze all the elements present in prepared BMNPs by *Aerva lanata* leaf extract. **Figure.4** and **Table.1** show EDX spectrum and elemental composition of Ag-Fe BMNPs respectively. EDX study which gives the quantitative data of silver and Iron elemental compositions in the synthesized BMNPs **.** Scanning electron microscopic (SEM) images of Ag-Fe BMNPs with various magnifications are given in **Figure 5**. From this it can be clearly noted that the prepared Ag-Fe bimetallic nanoparticles are within the size range of 50 to 100 nm in diameter.

Table: 1. Quantitative results of Ag-Fe BMNPs

Element	Weight %	Atomic %
Fe L	33.93	49.80
Ag L	66.07	50.20
Totals	100.0	100.0
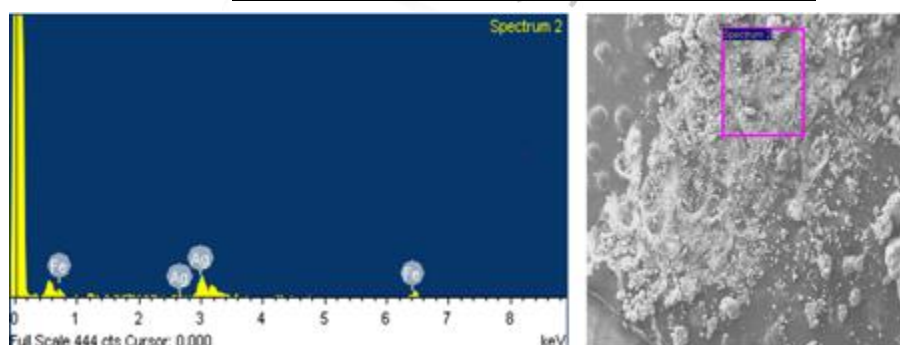
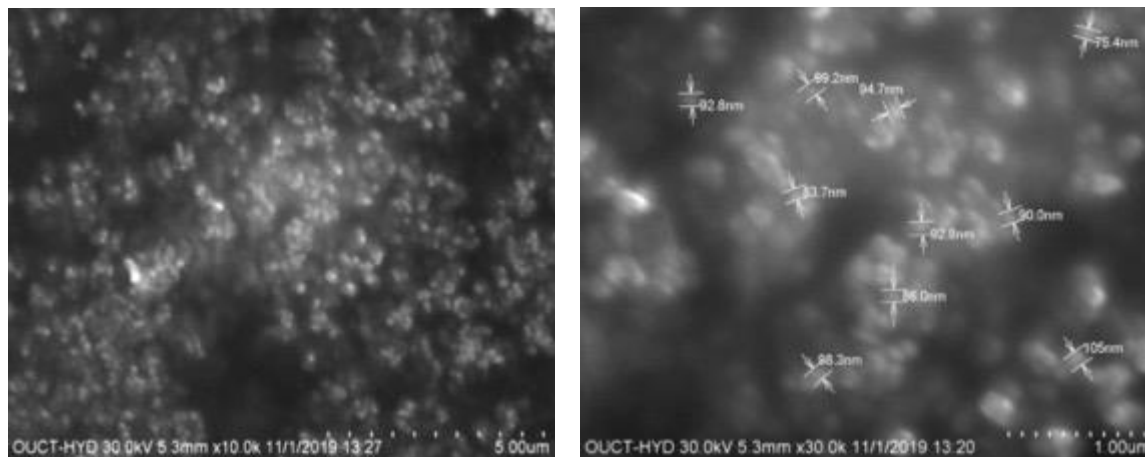**Figure 4 :** EDX Analysis of Ag-Fe BMNPs

Figure.5 : SEM images of Ag-Fe BMNPs

3.4.   **HRTEM analysis: Figure.6** shows the high resolution transmission electron microscopy (HRTEM) images   for synthesized Ag-Fe BMNPs from *Areva lanata* leaf extract. From these images, it was observed that Ag-Fe BMNPs were formed with spherical morphology and crystalline structure below 100 nm in size. More specifically, the two metal nanospheres seem to be positioned side by side, providing an overall bilobal structure. It is also in strong accordance with the images from SEM analysis.
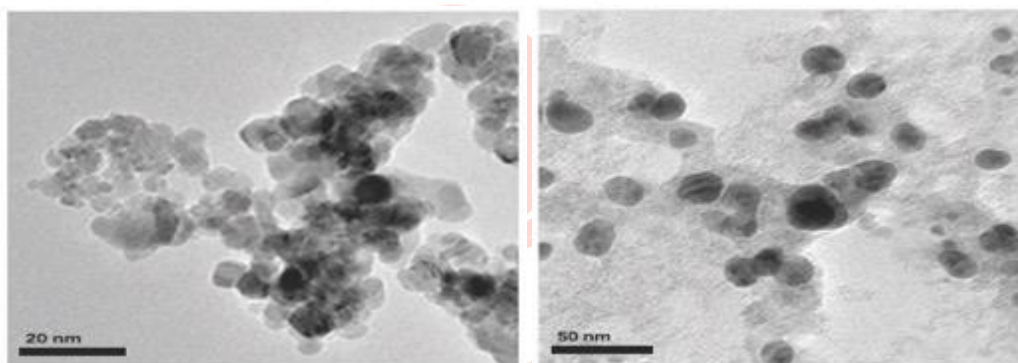

Figure .6 : HRTEM images of Ag-Fe BMNPs

   3.5. XRD analysis :

The XRD spectrum of green synthesized Ag-Fe BMNPs from leaf extract is shown in figure: 7. The peaks appeared at 2θ values of 37.96^0, 44.22^0, 64.32^0, 77.26^0 corresponding to the Bragg's reflections of Ag(111), Ag(200), Fe(110), Ag(220), Fe(220) , Ag (311)   planes respectively of face centered cubic crystal structure [19] as shown in the **Figure:7**
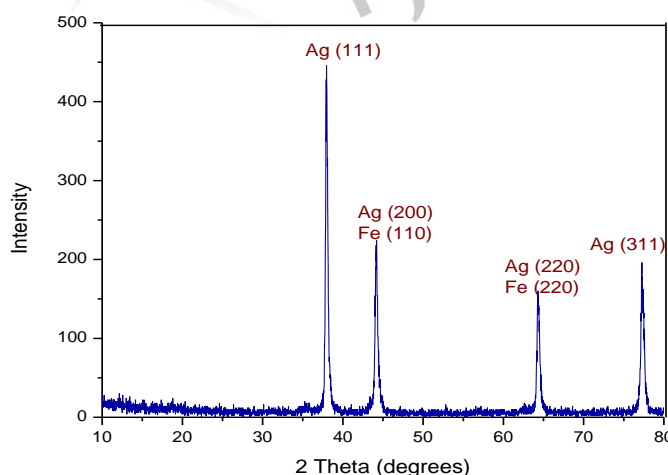

Figure:7 . XRD spectrum of Ag-Fe BMNPs

The average size D (in nm) of Ag-Ni bimetallic nanoparticles was calculated by using Debye-Scherrer equation (1).

$$D = \frac{K\lambda}{\beta \cos\theta} \ldots\ldots\ldots(1)$$

D = crystalline size of Ag-Fe BMNPs

λ = wavelength of x-ray source (0.15406 nm) used in XRD

β = full width at half maximum (FWHM) of the diffraction peak

K = Scherrer constant = 0.9

θ = Bragg's angle

| S.no.	2θ (degrees)	θ (radians)	Cos θ	β (radians)	D (nm)
1	37.960	0.2876	0.9589	0.005501	26.2856
2	44.220	0.3859	0.9264	0.005864	25.5235
3	64.320	0.5613	0.8466	0.005658	28.9462
4	77.260	0.6742	0.7812	0.005642	31.4584

The numerically calculated value of the synthesized Ag-Ni BMNPs materials corresponds to an average particle size of **28.0534 nm**.

4. Photodegradation studies on Malachite Green dye using Ag-Fe BMNPs :

The photodegradation experiments are carried on Malachite Green dye using green synthesized Ag-Fe BMNPs acting as a photocatalyst. . Initially, 50 ppm of malachite green stock solution was prepared. Then reaction mixtures were prepared by adding certain amount of Ag-Fe BMNPs (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 was altered (for 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 was agitated for 20 minutes in dark condition to attain adsorption-desorption equilibrium between malachite green and Ag-Fe BMNPs. Sun light was used as irradiating source to reaction mixture for studying degradation during 11.00 am to 3.00 pm. At regular 30 minutes of time intervals , aliquot part of the reaction mixture is taken, centrifuged to remove the photocatalyst particles and optical absorption properties were analyzed by using UV-Visible Spectrophotometer . The absorbance was 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, dosage of the catalyst. Malachite green shows the highest absorption at 617 nm. [19].To determine the percentage degradation of MG solution following equation (2) was 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.
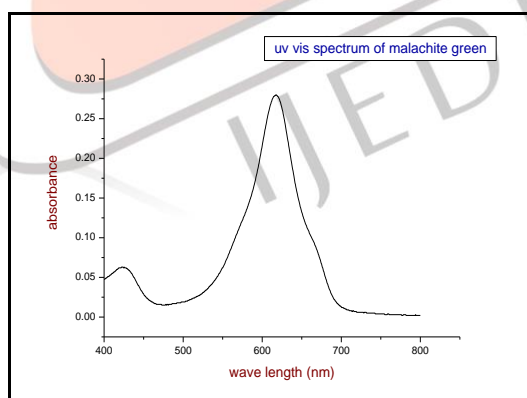
Figure 8(a): UV- VIS spectrum of Malachite Green

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

4 (a) . Probable Mechanism of Photocatalytic degradation of MG dye with Ag-Fe BMNPs
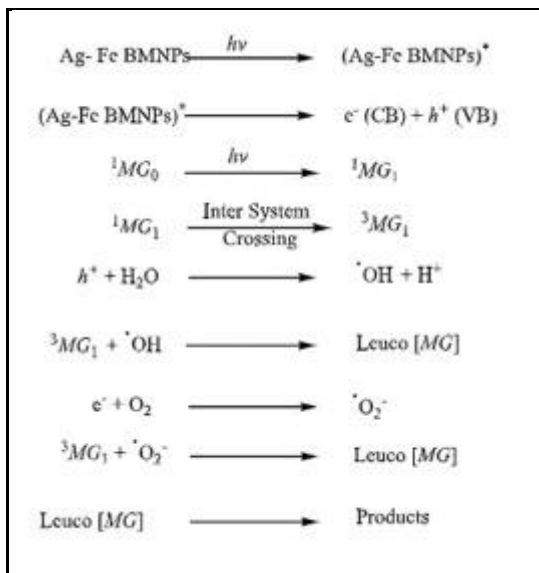
By absorbing suitable wavelength radiations MG dye goes to its first excited singlet state. Then by undergoing intersystem crossing (ISC), it enters into to the triplet state. In the intervening time Ag-Fe BMNPs also absorb the radiant energy to excite its electron from valence band to the conduction band. The hole abstracts an electron from H_2O to generate $\cdot$OH radical and H_+. $\cdot$OH radical oxidizes the MG dye to its leuco form degrades into colourless product. The electron will be abstracted by oxygen molecule generating superoxide anion radical ($\cdot O_{2-}$). The formed anion radical reduce the MG dye to its leuco form, which on degradation forms products.

4.1. Effect of time of contact :

 Efficiency of photodegradation of the Ag-Fe BMNPs on malachite green dye was studied by batch mode experiments. The efficiency of BMNPs on degradation of MG is expected to be increased by increasing contact time. The effect of contact time was carried out by taking 10 ppm of 100 ml MG dye solution and 10 mg of BMNPs (at pH 7) as catalyst load (**Figure 8(b)** and **Figure 8 (c)**). Initially, degradation of dye by using BMNPs was found to be rapid and then it almost settles down as % degradation attains more or less constant value with this increase in contact time. This is due to strong adsorption forces predominate between the dye and the BMNPs and as the number of the reactive sites on the catalyst were vacant during initial periods of contact time. But after 120 minutes of contact time, percent degradation gradually approached a constant value to some degree when equilibrium was almost reached because the number of vacant sites available for further dye adsorption is inevitably diminishing[20].
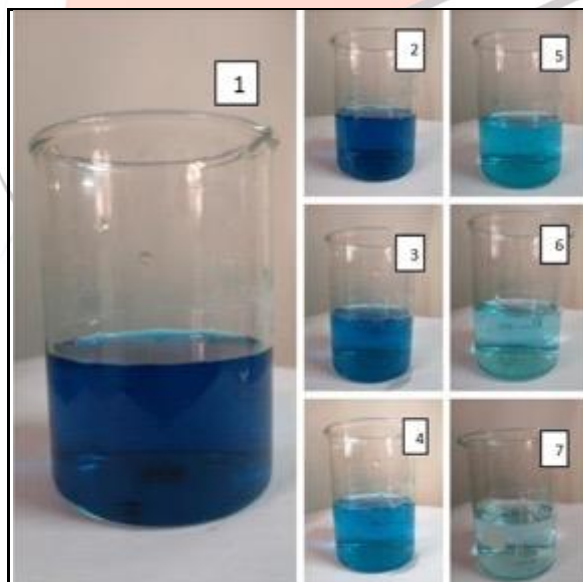
(1) 0 mins (2) 30 mins (3) 60 mins (4) 90 mins (5) 120 mins (6) 150 mins (7) 180 mins
Figure 8(b): Colour change in MG dye after addition of Ag-Fe BMNPs at various time intervals
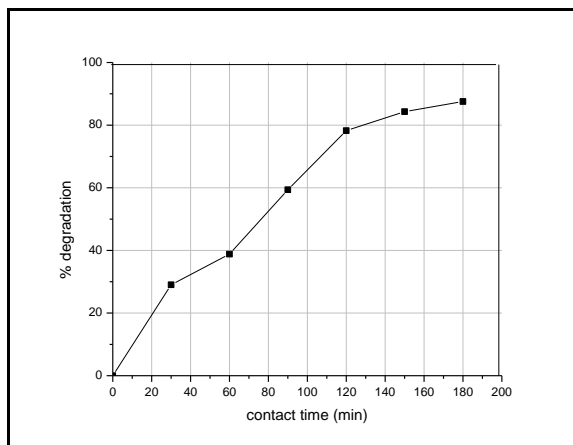
Figure 8(c): Effect of contact time on photo degradation

4.2. Effect of initial concentration of MG dye solution :

Initial concentration of MG dye solution is also expecting to effect the rate of photo degradation. To investigate this fact, dosage of BMNPs nano-catalyst was kept constant at 10 mg , keeping solution pH at 7 and the time of irradiation was maintained as 180 minutes. Whereas the initial concentrations of the MG dye solutions were 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(d)**. From the figure it can be observed that the highest degradation is located at 5 ppm, and the photodegradation decreases gradually with increase in the concentration of MG dye solution. This finding can be explained by the fact that as the concentration of the dye increases, the dye continues to act as a barrier for the incident light and does not allow the light intensity to touch the BMNPs surface and thus the %photodegradation decreases.[21]
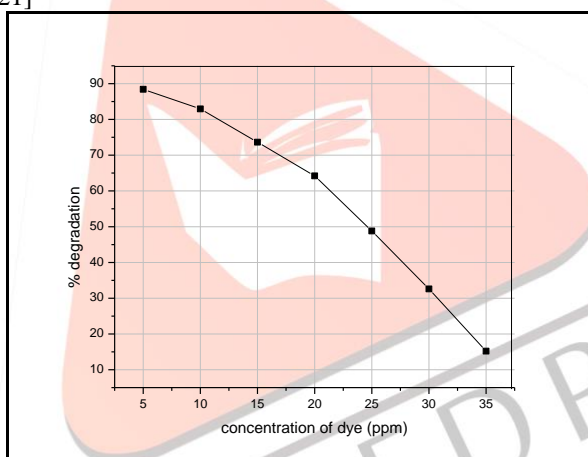

Figure.8(d): Effect of concentration of MG dye solution on photodegradation

4.3. Effect of pH:

pH of dye solution can influence the adsorption of dye on photocatalyst. The initial concentration of malachite green solution 10 ppm and the concentrations of the photocatalyst 10 mg were kept constant with time of irradiation 120 minutes. Different solutions of various pH values of 4 to 11 were prepared. Degradation efficiencies were compared which was shown in **Figure 8(e).**
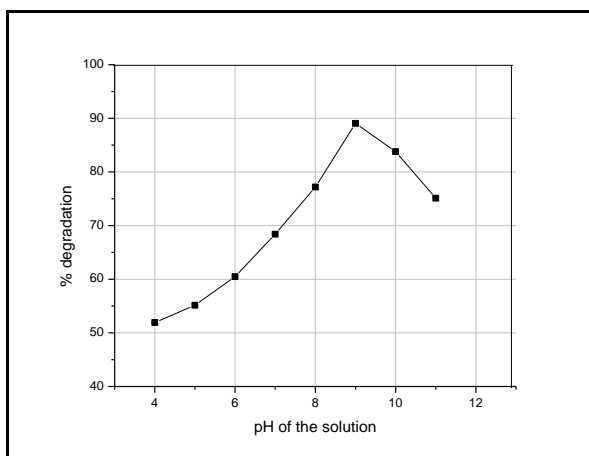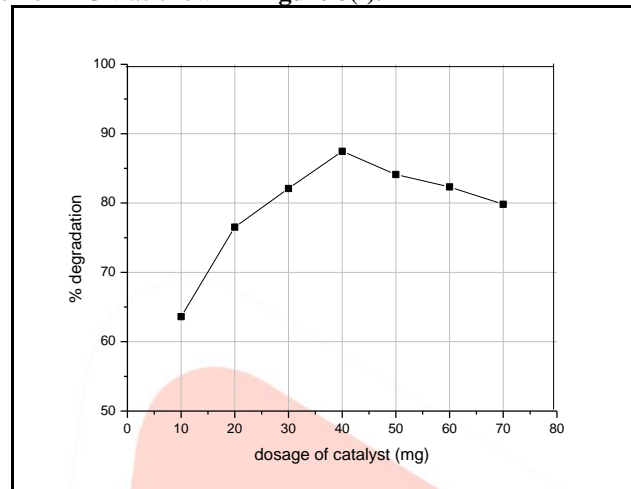

Figure.8(e): Effect of pH on photo degradation

It was observed that at initial pH values the degradation was minimum .This is due to the fact that at low solution pH Fe may undergo corrosion to form iron oxides (Fe_2O_3, Fe_3O_4) and hydroxides on the surface of Fe nanoparticles. So MG dye undergoes less degradation. Also in acidic condition the H+ ions were made to compete with cationic MG dye and hence the adsorption of dye was decreased. In contrast at pH > 9 in the more alkaline medium, the surface of the catalyst contains a huge number of –OH ions that may provide negative charge to the adsorbent resulting to a high efficiency for the removal of MG dye.[22]

4.4. Effect of dosage of photo catalyst:
In photodegradation process, one of the important parameters of decolourizing of dye solution is photocatalyst dosage. To avoid unnecessary wastage of expensive catalyst and attain the maximum absorption of photons optimization of the catalyst dosage is essential. For this, dosage amount was varied from 10 mg to 70 mg taken in 100 ml of 10 ppm MG dye at pH 8 with contact time 120 minutes. The degradation of MG was shown in **figure 8(f).**

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

It was concluded that, by increasing dosage of catalyst from 10 mg to 80 mg in 100 ml, the degradation of MG dye enhances because the increase in amount of catalyst upto 40 mg would increase the reactive sites that produce more reactive species. On further loading of catalyst ,% degradation of MG dye decreases. This can be rationalized by the fact that, the addition of excess catalyst results in more turbid suspensions and decelerates the light penetration into the solution . Due to particle-particle interactions (agglomeration) and sedimentation of the catalyst there will be significant decrease in the active surface area and hence the degradation falls down.[23]

CONCLUSION
An ecologically innocuous method is projected to synthesize Ag-Fe bimetallic nanoparticles from *Areva lanata* leaf extract. From UV-VIS spectal 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 as the bio reducing and capping agents of the formed nanoparticles. Results of XRD, SEM and TEM analyses evinced that Ag-Fe BMNPs are in spherical morphology and cubic crystalline structure with size between 20-100 nm. The photocatalytic activity of these nanoparticles is examined under sunlight for degradation of MG dye which is environmental pollutant. The % photodegradation of MG dye changes with parameters such as contact time, concentration of MG dye, pH, photocatalyst dosage. From this research study on bimetallic Ag-Fe BMNPs synthesized from *Areva lanata* leaf extract, the optimum conditions found in the degradation of MG dye is pH **8**, weight of catalyst **40 mg**, dye concentration of **10 ppm** and contact time of **120 minutes**. The maximum degradation is obtained as **88.75%** under these optimum conditions.

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