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Rapid Green Synthesis of Amalgamated Silver Nanoparticles and its Photocatalytic Activity of Dye Degradation

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ABSTRACT

Organic dye present in the waste water becomes a major threat to the environment. Here we focus our attention to synthesis silver nanoparticles from silver nitrate by Moringa Oleifera flower extract (Green approach). This silver nanoparticle was further amalgamated by mercurous chloride and it was used for dye removal. Here in this present work Methyl orange has been chosen as a dye (20ppm) to analyze the effective dye removal capacity of amalgamated silver nanoparticles in presence of sunlight irradiation. The particles size calculated from UV/Vis absorption study (by the effect of mass approximation) were found to be 3nm and 4nm for amalgamated silver nanoparticles and silver nanoparticles. From the above study conducted it was concluded that the effective dye removal of amalgamated silver nanoparticles (97%) was observed at 52 hrs (or 2.16 days) under photochemical degradation, shifted UV-Vis absorption peak from 520 nm to 232 nm.

Keywords: Environment; Green approach; Irradiation; Moringa; Nanoparticles; Organic dye.

GRAPHICAL ABSTRACT

1. INTRODUCTION

Nanotechnology is mainly concerned with the synthesis of nanoparticles in the range of 1 to 100nm size. Nanoparticles were found applications in various fields such as solar cell, laser, targeted drug delivery etc,. Nobel metal nanoparticles such as gold (Au), silver (Ag), platinum (pt) have recognized importance applications in the field of chemistry, physics and biology (Jain *et al.* 2008). Because of their unique physicochemical characteristics and high specific surface area to volume ratio and the properties of these nanoparticles completely differ from bulk particles. The properties of these nanoparticles such as optical, electronic, antibacterial properties and magnetic properties were studied extensively by various researchers (Catauro *et al.* 2004).

Metal nanoparticles can be synthesized by various physical and chemical methods (Namita Rajput, 2015) such as co-precipitation methods (Kandpal, 2014), micro-wave assisted process (Rathi *et al.* 2006), sol-gel techniques (Rathi *et al.* 2006), and chemical reduction methods (Maribel G. Guzmán *et al.* 2009) etc. However these methods are quite expensive and potentially hazardous to the environment and nowadays researchers are focusing to synthesis metal nanoparticles by eco-friendly green synthesis approach (Begum *et al.* 2009). Silver nanoparticles were also synthesized from biomass, such as plants, and micro-organisms (Singh *et al.* 2016). Moreover this method of synthesis has some advantage, such as simple, cost effectiveness and rapid in the production of nanoparticles in large scale and it does not require desired high temperature, pressure, and toxic chemicals (Khadeeja Parveen *et al.* 2016).

Moringa oleifera flower (family of moringaceae, English: drumstick tree) has been used as an ingredient of Indian diet since several centuries. It is cultivated all most all over the country and its leaves and fruits are used as vegetables. All most, all parts of the plant have been utilized in traditional medicine. The leaves of the plant have also been reported for antitumor, cardio productive, healing hypertension and use for eye diseases (Rathi *et al.* 2006). We report for first time using moringa oleifera flower powder extract as reducing agent and capping, stabilizing agent for the synthesis of silver nanoparticles.

Dye effluents often discharged in water bodies and it pollutes the environment. The hazardous effects of organic dyes in wastewater have a major threat to human beings and hence, the removal of these dyes from industrial effluents has great significance in connection with environmental and human safety (Mendhulkar Vijay *et al*. 2016).

Guangming et al and vindogopal et al have studied photochemical degradation of dye removal using nanoparticles (Guangming Liu and Jincai Zhao, 2000; Vinodgopal and Kamat 1995). In one study Bhakya et al (14) have phtoto degraded organic dyes using silver nanoparticles via green approach and further it was characterized by UV-Vis, FT-IR,TEM studies.

Metal nanoparticles including silver nanoparticles are known to promote degradation of dyes. Ag NPs are known to catalyze many reductions (Arviro *et al*. 2012) methods. Environmental hazards from discharge of dyes from textiles and other industries are considered to be major causes of concern due to their impact on human health. Therefore development of newer technologies for degradation of dyes before their release into the environment will always be important in the present day context (Bappi paul *et al.* 2015).

Similar study was reported by Hammami et al (Hammami *et al*. 2007) in their study, they were bio synthesized silver nanoparticles using Neem leaf extract and confirm the formation of silver nanoparticles by UV-Vis spectrum of maximum absorption peak at 420nm and succeeded photochemical degradation of methyl violet dye after 50 hrs in sun irradiation

In this present work we focus our attention to develop an effective technique to remove dye in water phase using amalgamated silver nanoparticles as a photo catalyst. Here we choose methyl orange dye because it is used extensively as a component in dye industries and was chosen as a model compound for photochemical degradation and also the method of photo catalytic degradation has found significant advantage over conventional methods in terms of quick oxidation, oxidation of pollutants (Sobana *et al*. 2006) and leaving less organic bi-products.

2. EXPERIMENTAL PROCEDURE

2.1 Preparation of *Moringa oleifera* Flower Powder Extract

The fresh flowers of ***moringa oleifera*** were collected, thoroughly washed several times with distilled water to remove impurities. The cleaned flowers were subsequently dried under sunshade for 2days and using mechanical grinder; it was crushed into powder and then stored. The 2g of flower powdered were taken into a beaker along with 100ml of distilled water and allowed to boil at 60°C for 30 minutes under water path. Then it was cooled down to room temperature. The prepared solution initially filtered through normal filter paper repeated several times to get clear solution and then the filtrate was stored at 4°C.

2.2 2.2 Green Synthesize of Silver Nanoparticles

To synthesis silver nanoparticles from *moringa oleifera* flower extract, 10ml of flower powder extract was carefully added to 90ml of 1mM silver nitrate solution in 250ml Erlenmeyer flask. The reaction mixture was stirred well in a rotary orbital shaker for 24 hrs at 200rpm. A change of color from pale yellow to brown red color suspension was spotted after 24 hrs. This color change confirms the reduction of Ag^{+} to Ag^{0} and the appearance of brown red color confirms the formation of silver nanoparticles (AgNPs).

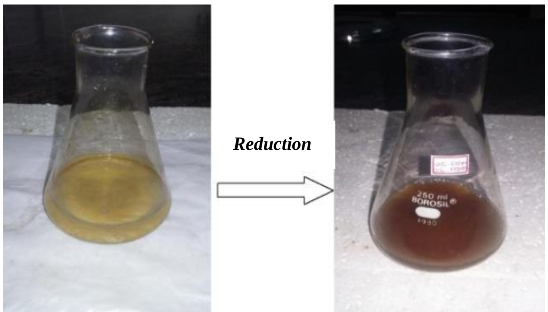

Fig. 1: (a) Flower extract + silver nitrate solutions (b) formation of silver nanoparticles.

2.3 Synthesis of Amalgamated silver Nanoparticles

The stock solution of Hg^{2+} (1000ppm) has been prepared using de-ionized water; from this 100ppm Hg^{2+} solution was made. 20ml of silver nanoparticles solutions and 30ml of Hg^{2+} prepared solution was mixed well and the formation of amalgamated silver nanoparticles was confirmed by UV-visible absorbance study.

2.4 Purification of Amalgamated Silver Nanoparticles

The biosynthesized silver nanoparticles followed by formation of amalgamated AgNPs were purified by centrifuge method. One part of AgNPs / amalgamated AgNPs was centrifuged at the rate of 500rpm by 30 mints. The supernatant solution was discarded and the settled AgNPs / amalgamated AgNPs pellet were washed several times with de-ionized water.

2.5 pH – Analysis

The pH was measured by digital pH meter (model Systronics-335**)**. The pH of the solution was found to be 4.50 before formation AgNPs. But the pH of the solution after formation AgNPs was found to be 3.49. The amalgamated silver nanoparticles were found to be 3.25**.**

Table 1. p^{H}-analysis of flower extract/AgNPs/amalgamated AgNPs.

S. No.	Plants/Nanoparticles	pH
1	Moringa flower extract	4.50
2	Silver nanoparticles (AgNPs)	3.49
3	Amalgamated silver nanoparticles (Hg-AgNPs)	3.25

2.6 Photo Catalytic Dye Degradation of Amalgamated AgNPs

2mg of methyl orange dye was dissolved into 100ml of de-ionized water used as stock solution. About 50ml green synthesized of amalgamated silver nanoparticles was added to 50ml of methyl orange dye solution. A control was prepared in similar manner without addition of amalgamated silver nanoparticles.

Before exposing to sunlight irradiation the reaction suspension was well mixed and magnetically stirred for 30mints. Then the test solution were subjected to sunlight irradiation until its complete color change and monitored from morning to evening sunset. The absorbance spectrum of the irradiated test solutions were subsequently measured using UV-Visible absorbance from 200-700nm.

Percentage of dye degradation was estimated by following formula:

$$\% \text{ dye} = (C_0 – C/C_0) \text{ X } 100$$

Where

C_0 – is the initial concentration of dye solutions , C- is the concentration of dye solution after photo catalytic degradation.

3. RESULTS & DISCUSSION

3.1 UV-Visible Spectrophotometer Analysis of *Moringa Oleifera* Flower Extracts, AgNPs/Amalgamated AgNPs

The green synthesized of *moringa oleifera* flower extract and silver nanoparticles, amalgamated silver nanoparticles were characterized by using UV-Visible spectrophotometer and the wavelength ranging from 200-700nm operated at resolution at 1nm. The maximum absorbance peak observed at 409nm, 439nm and 218nm. Confirm the reduction silver ions (at 439nm) and the formation of green synthesized amalgamated silver nanoparticles (at 218nm).

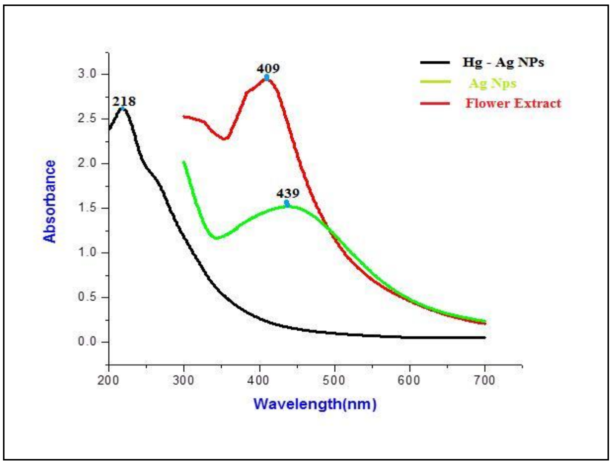

Fig. 2: UV/Visible absorption study for (a) flower extract (b) green synthesized silver nanoparticles (c) green synthesized amalgamated silver nanoparticles.

3.1.1 Measurement of Particle Size by UV/Vis Mass Approximation Methods

The green synthesized silver nanoparticles and amalgamated silver nanoparticles were confirmed by absorption spectrum of UV-Vis spectroscopy (Model JASCO-V-630). Size of the AgNPs/Hg-AgNPs was also analyzed using effect mass approximation calculation method.

Effect of mass approximation

$$E\ (g) = hC/\lambda = 1250/\lambda_{\text{low}}\ eV$$

Where

h- Planks constant
C- Light scattering
λ – Wave length

λ_{low} - Minimum absorbance

$$d(E) = \frac{0.32 - 2.9\sqrt{E(g) - 3.49}}{3.50 - E(g)}$$

Where

d (E) - particle size

E (g) - Effect of mass approximation

Particle size analyzed using from effect of mass approximation calculation method

Table 2. Particle size calculation for silver nanoparticles and amalgamated silver nanoparticles from UV/Vis absorption spectrum.

S. No.	Nanoparticles	Absorbance		Particles size d(E) nm
		Min. (nm)	Max. (nm)	
1	Silver nanoparticles	350	439	7
2	Amalgamated silver Nanoparticles	264	212	3

3.1.2 Band Gap Energy Calculation of AgNPs and Amalgamated AgNPs using UV/Vis Absorption Spectrum

a.) Silver Nanoparticles (AgNPs)

Band gap energy of silver nanoparticles was calculated from maximum absorption UV/Vis spectrum wavelength of

λ_{max} =439nm.

Eg = 1240/ λ eV,

Eg = 1240/439 = 2.82Ev

The calculated Band gap energy for this silver nanoparticle is 2.82 eV.

b.) Amalgated Silver Nanoparticles (Ag/Hg-NPs)

Band gap energy of amalgamated silver nanoparticles was calculated from maximum absorption UV/Vis spectrum wavelength of

λ_{max} =232nm.

Eg = 1240/ λ eV

The calculated Band gap energy for this amalgamated silver nanoparticle is 5.34 eV.

The shifted in band gap energy from 2.82 eV to 5.34 eV confirm the formation of amalgamated silver nanoparticles and its photocatalytic activity of methyl orange dye degaradation.

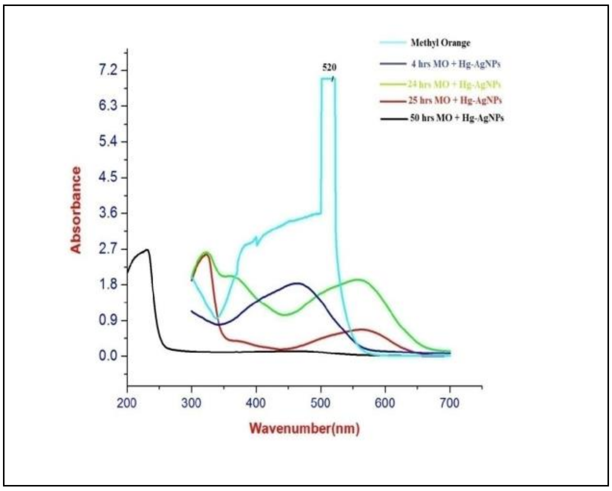

Fig. 3: UV/Vis absorption spectrum of dye gradation of methyl orange with respect to time.

Fig. 4: Photographic observation of dye removal of methyl orange by amalgamated silver nanoparticles under sunlight irradiated upto 52 hrs.

Table 3. Photo catalytic activity of methyl orange dye degradation (%) by green synthesized amalgamated silver nanoparticles.

Exposure time (hrs)	Amount dye degradation (%)
4	11.5%
24	35.7%
25	38.4%
50	55%
52	97%

Fig. 2 confirms the formation of silver nanoparticles from aqueous solution of silver nitrate by green synthesis at 439nm absorption and for amalgamated silver nanoparticles it was confirmed at 218 nm. The dye degradation in presence of sunlight irradiation was observed from the UV/Vis absorption peak and the time taken for this degradation was found to be 4hrs to 52 hrs shown in Table.3 and Fig.5. The maximum degradation 97% was observed at 52hrs and it was confirmed by visual observation as shown in Fig.4.

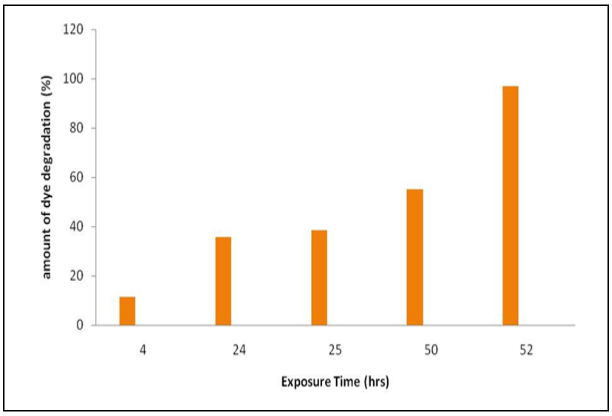

Fig. 5: Bar chart diagram of percentage of methyl orange dye degradation vs Exposure time in (hrs).

3.3 Hypothetical Mechanisms of Dye Degradation

We propose hypothetical mechanism for dye degradation of methyl orange by amalgamated silver nanoparticles.

Step-1

$$Ag^{+} + e^{-} \longrightarrow Ag^{0}$$

Step-2

$$Hg^{2+} + Ag^{0} \longrightarrow Hg\text{-}Ag^{2+}$$

Step-3

$$Hg\text{-}Ag^{2+} + MO \xrightarrow{h\upsilon} \text{dye degradation}$$

$$e^{-}$$

5. CONCLUSION

Silver nanoparticles (AgNPs) have been synthesized from moringa oleifera flower extract then it is modified into amalgamated silver nanoparticles (Hg-AgNPs).

Methyl orange dye (20ppm) was chosen dye stuff and photo catalytic activity of amalgamated silver nanoparticles (20ppm) was tasted in sun light irradiation up to 3 days.

The complete degradation of methyl orange in water phase occurs at 52 hrs (2.16 days) and noted color change from orange to colorless. This decolonization of methyl orange is due to the oxidation reaction occurs in methyl orange by amalgamated silver nanoparticles.

The shifted in band gap energy from 2.82 eV to 5.34 eV confirm the formation of amalgamated silver nanoparticles and its photocatalytic activity of methyl orange dye degaradation.

This dye degradation is also due the redox reaction involving in the valence shell electron transfer between silver and mercury ions that oxidize the dye effectively.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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