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# PHOTO KINETIC STUDIES OF METHYL ORANGE DYE BY USING GREEN SYNTHESISZED SILVER NANOPARTICLES FROM *AREVA LANATA* STEM EXTRACT.

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**Abstract:**

*Green synthesized silver nanoparticles are applied to photodegradation of methyl orange organic dye and their photo-kineics also studied. silver nanoparticles are prepared from green method by using Areva lanata stem extract. The kinetic studies are carried out at different time intervals under sun radiatuin of expourse of time is 180 minutes. The degradation percentage is 74.02. the rate constant obtained from this studies is 3.0706 $\times 10^{-4}$ $Sec^{-1}$. The synthesized silver nanoparticles were characterized by using various techniques like UV-Visible, FT-IR, SEM, TEM.*

**Keywords:***Silver nanoparticles (Ag-NPs), Areva lanata, methyl orange, photodegradation*

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## INTRODUCTION:

Metallic nanoparticles play major role in the field of nanomedicine and Nanotechnology because of their variety and large applications. nanoparticles used in almost all fields. Several methods have been used for the synthesis of nanoparticles. But green method is best suitable method. Due to nontoxic chemicals were not used.

Recent results were found to synthesis of nanoparticles and their photo degradation effect of dyes are studied from *Amaranthus gangeticus Linn* (Chinese spinach) leaf extract [1], *Vishanika* or Indian screw tree [2], *Hypnea musciformis* [3], *Ulva lactuca* (seaweed) [4], the leaf extract of Neem [5], aqueous extract of SDKP [6], brown seaweed *Padina tetrastromatica* leaf extract [7], *A.niger* [8], *Brassica oleracea capitata* (Cabbage) [9], *Zanthoxylum armatum* [10], *Casuarina equisetifolia* leaf extract[11], *tangerine peel* extract [12], bacterial [13].

Dyes are belongs to organic compounds [14]. Dyes are mainly used as a coloring agent in textile and paper industries. They are non-degradable and carcinogenic agents. Moreover, to unique in their products most of the industries uses colour dyes, without any treatment the coloring material are liquidated in water leads to contamination of resources [15]. The release of dyes effluents in aquatic system is major environmental concern because coloration not only decreases sunlight penetration and toxic compounds during chemical or biological reaction pathway that effects aquatic flora and fauna [16].

In this present study, we discuss photo catalytic degradation of green synthesized silver nanoparticles against methyl orange dye.

## MATERLS AND METHODS:

All the chemical were used in this experiment are sigma Aldrich.

**Preparation of Silver Nano Particles:**

Preparation method and characterization of green synthesized silver nanoparticles was already reported [17].

**Fig. 1: *Areva lanata* plant**

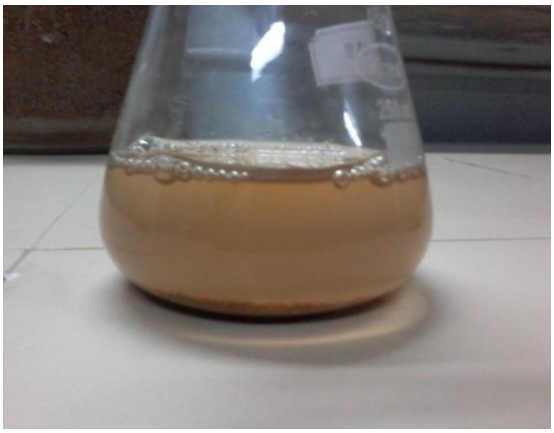

**Fig. 2: Plant extract**

**Fig. 3: silver nanoparticles**

*Areva lanata* extract is prepared by 10 gm of dried leaves are taken in clean and dry conical flask.
To it add 100 ml of double distilled de ionized water. The colour of the extract is light brown. 10 ml of leaves extract is added to 90 ml of 1 mM silver nitrate solution. the colour of solution is changes from light brown to dark brown, indicates the formation of silver nanoparticles. the reaction mixture incubated 24 hours in dark room at room temperature. The mixture is centrifuged 20 minutes at 10,000 RPM and washed double distilled de ionized water, dried at $60^0$ C.

**Characterization:**
UV-Visible absorption spectra are measured suing shimdzu uv-2203 doublem beam spectrophotometer. FTIR spectra are obtained with IR-prestige-21shimaduz, FTIR spectrophotometer, using Kbr pellet method. SEM studies of silver nanoparticles are done by using jsm-6610lv machine. The morphology of silver nanoparticles is done by TEM analysis, by using x-pert pro machine.

**Photo Degradation**:
Aqueous stock solution of a commonly obtained organic dye i.e methyl orange. 30 ppm methyl orange solution is prepared and100 ml of the aqueous solution of the dye is taken out in 250 ml clean and dry beaker. To this 2 mg of green synthesized silver nanoparticles is added. The solution mixture is exposed to sun light for about 180 min. Experiments are done between 10 am to 2 pm (temperatures 35-39$^o$C).

In every 30 minutes of time intervals, 5 ml of reaction mixture is taken out into centrifuging tubes and centrifuged, after that the filtrate is studied to monitor the absorption maximum values using UV-visible spectrophotometer. The readings were noted in Table (4.3). Before exposure to sun light the aqueous Methyl orange solution gives UV-visible absorption maximum value at 464nm. The orange colour of the solution is found to slowly decolourise within an exposure time of 180 min. the reported values for degradation correspond to the maximum rate of degradation, after which the degradation rate slow down taking very long time for complete degradation. This may be due to saturation of the adsorption sites of the nanoparticles surface.

**RESULTS AND DISCUSSIONS**:
The VU-Visible, FT-IR, SEM, TEM, XRD spectral studies of green synthesized silver nanoparticles from *Areva lanata* stem extract was reported [17].

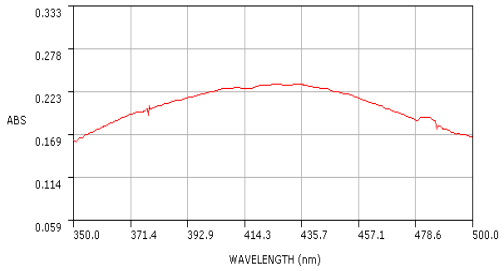


**Fig. 4: UV-visible spectrum [17]**

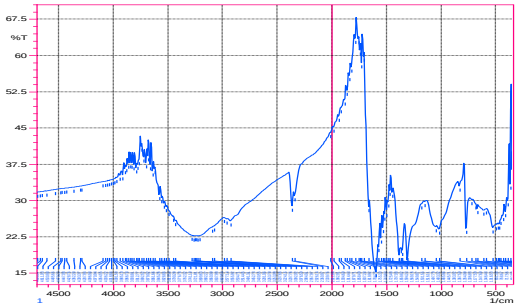


**Fig. 5: FT-IR spectrum [17]**

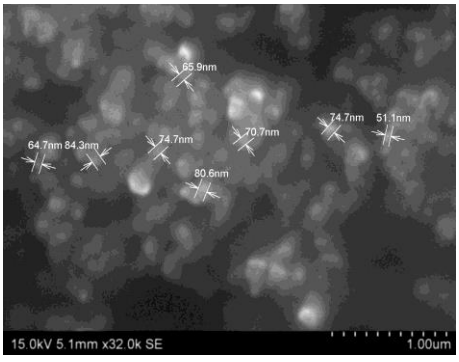


**Fig. 6: SEM image[17]**

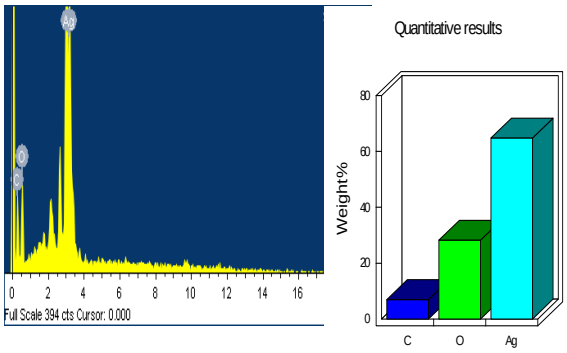


**Fig. 7: EDX image[17]**

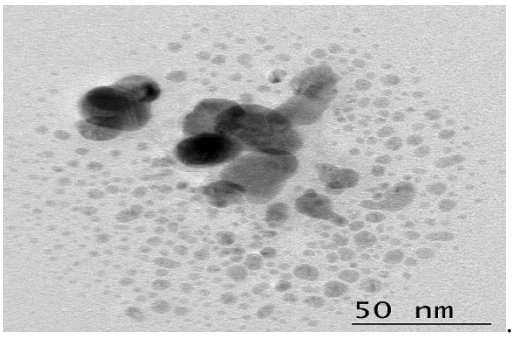


**Fig. 8: TEM image [17]**

**Photo kinetic studies:**

The photo degradation experiments were carried on the organic dye using green synthesized silver nanoparticles acting as a catalyst. It was found that the colour of Methyl orange solution which was originally dark orange eventually turned to pale orange colour on the addition of silver nanoparticles with in a time period of 180 min, as shown in Figure (10).


**Fig. 10: Color change of methyl orange dye after addition of silver nano particles.**

**Time vs absorption graph**

The degradation study is analyzed via time vs light absorption graph by collecting absorption data using UV-Visible spectrum at various time intervals as shown in Figure (11).

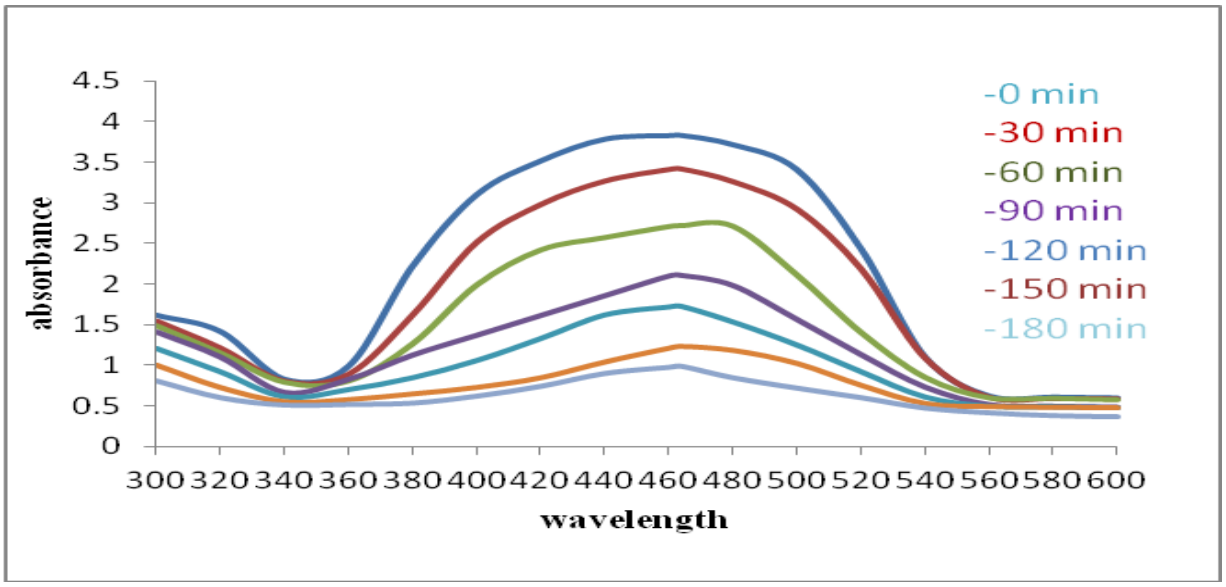


**Fig. 11: Degradation graph of Methyl orange**

**Time vs % degradation**

The efficiency of silver nanoparticles as photo catalyst is evaluated by noting the percent degradation at various intervals of time. The corresponding graph is shown in Figure (12). We can see that during the initial stage of photo degradation reaction, the % degradation is very slow. But it increases along with time. After 180 minutes of the reaction time the degradation is 74.02%. thus the graph indicates that % degradation increases with time.

Many reports suggested that photo degradation of dye follows pseudo-first order reaction.

**% of degradation = $(A_0-A)/A_0 \times 100$**

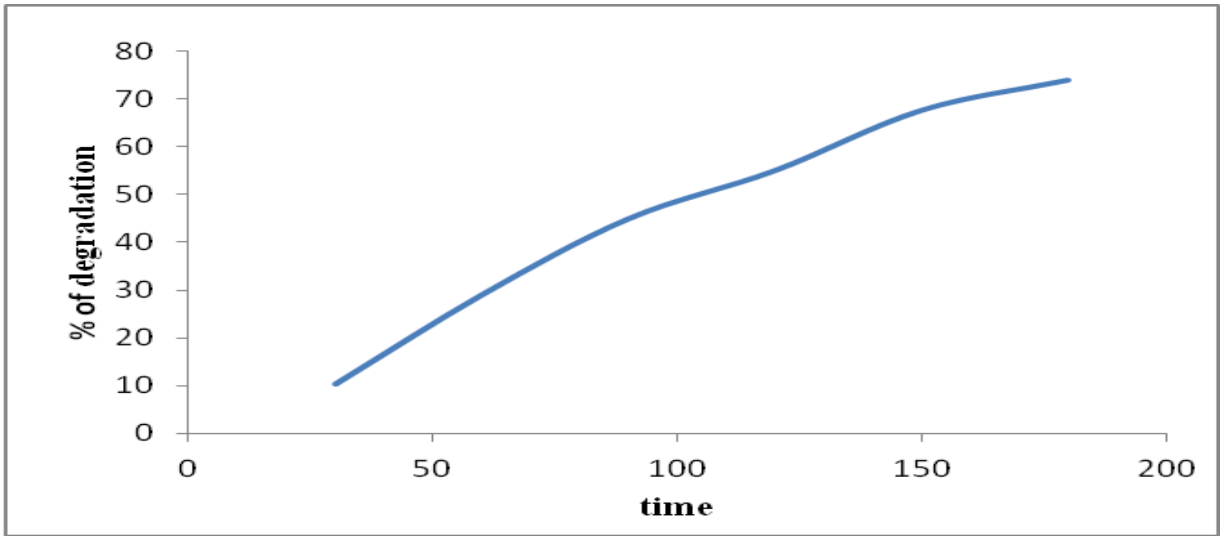


**Fig. 12: Time vs % degradation graph**

**Time vs log(A) graph**

The kinetics of the photo degradation study are evaluated by plotting a graph between time and log(A) values, is shown in Figure (13). It gives a straight line with a negative slope. The slope is found to be 0.0076. The plot indicates that photo degradation of Methyl orange solution carried out by green synthesized silver nanoparticles follows pseudo first order reaction.

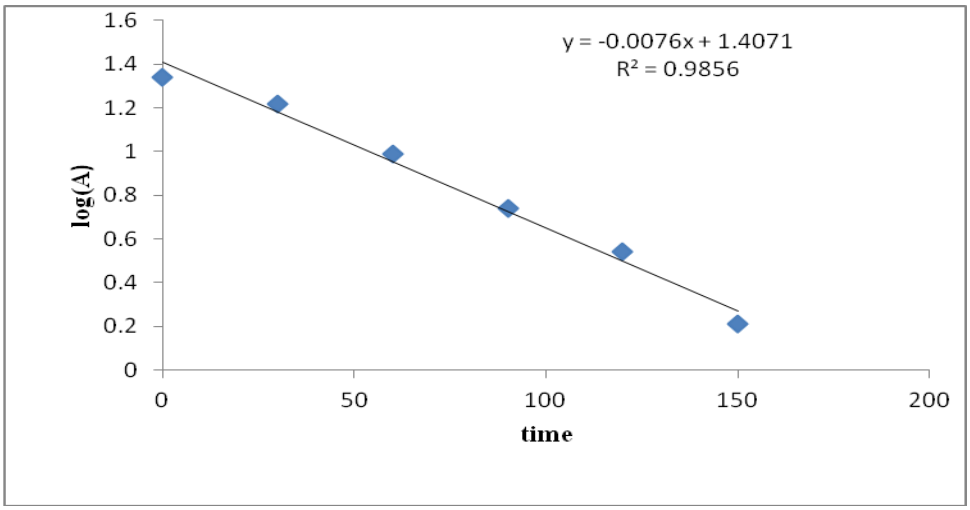


**Fig. 13: Time vs log(A) graph of silver nanoparticles**

**Time vs log ($A_0/A$)**

We can also study the kinetics of photo degradation by drawing a graph between time and log($A_0/A$). The graph has shown a positive slope of 0.0084. The graph is shown in Figure (14).

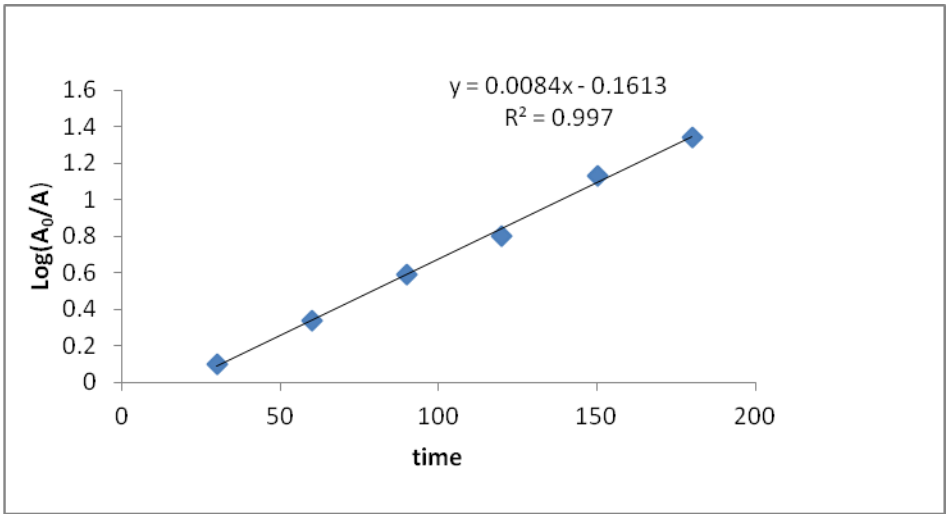


**Fig. 14: Time vs log($A_0/A$) graph of silver nanoparticles**

From the graph, it is clearly indicated that the photo degradation of the dye follows pseudo first order reaction The rate constant of the degradation of methyl orange reaction by using green synthesized silver nanoparticles (2mg) is calculated by following equation.

$K = (2.303 \times M) / 60$

$K = (2.303 \times 0.008) / 60$

$K = 3.0706 \times 10^{-4}\ Sec^{-1}$

The rate constant obtained as 3.0706 ×$10^{-4}$ $sec^{-1}$.

**Mechanisim of Photodegradation**

In the degradation process of the organic dye structure by the photo irradiated silver nanoparticles. The follows mechanism could be proposed. [18,19,20,21]

(1). Absorption of radiation by the surface active copper nanoparticles. The nanoparticles gain energy and get excited leading to the generation of charge carries. i.e. $e^{-1}$ or $h^{+}$ on the surface of nanoparticles.

(2). By means of scattering and delocalization of these primary electrons further generate a stream of secondary electrons, which are either trapped by the oxygen molecules (adsorbed on the dye structure) or directly attack the dye structure to give reduction products.

(3). Further more the generated charge carriers ($e^{-1}$ or $h^{+}$) in step 1can be trapped respectively by the $O_2$ molecules (adsorbed on the dye structure) to give radical anion of $O_2^{-\cdot}$ **or** trapped by the $H_2O$ molecules (adsorbed on the dye structure) to finally generate the peroxy free radical intermediates. In the successive steps hydroxyl free radicals are generated which play a very crucial role in the degradation of the organic dye structure by means of interfacial charge transfer mechanism.

**STEP 1:** Generation of charge carriers

$$Ag - NP + h\nu \xrightarrow{\text{Excitstion}} (Ag - NP)^{*}$$

$$(Ag - NP)^{*} \xrightarrow{\text{Generation 0f charge - carriers}} e^{-} + h^{+}$$

**STEP 2:** Trapping of charge carriers

$$H_2O + h^{+} \xrightarrow{\text{trapping of charges}} OH^{\cdot} + H^{+}$$

$$O_2 + e^{-} \xrightarrow{\text{trapping of charges}} O_2^{-\cdot}$$

**STEP 3:** Generation of peroxy radicals

$$O_2^{-\cdot} + H^{+} \xrightarrow{\text{trapping of carriers}} HOO^{\cdot}$$

**STEP 4:** Recombation of radicals and generation of hydroxy free radicals

$$2\,HOO^{\cdot} \xrightarrow{\text{recombination of freeradicles}} H_2O_2 + O_2$$

$$H_2O_2 \xrightarrow{\text{generation of hydroxy freeradicles}} 2OH^{\cdot}$$

**STEP 5:** Degradation of dye by interfacial charge transfer

$$Dye + OH^{\cdot} \xrightarrow{\text{Degradation interfacial charge transfer}} H_2O + CO_2$$

$$Dye + h^{+} \xrightarrow{\text{Oxidation}} \text{Oxidised product}$$

$$Dye + e^{-} \xrightarrow{\text{Reduction}} \text{Reduced product}$$

## CONCLUSIONS:

Green synthesized silver nanoparticles are used to degradation of methyl orange dye in presence of sun light. Good color change observed and The % of degradation is 74.02 after 180 minutes. From the graphical information the present degradation reaction follows the pseudo-first order reaction and the rate constant value is 3.0706 ×$10^{-4}$ $Sec^{-1}$. Silver nanoparticles are used to good catalyst for degradation.

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