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Green synthesis, characterization and catalytic degradation studies of metal nanoparticles against malachite green

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Abstract
Silver, copper and zirconium dioxide nanoparticle have been synthesized from green method by reducing corresponding salt using Spicy Jatropha flower extract as a reducing agent at room temperature in an aqueous medium. The instant formation of above metal nanoparticle (MNPs) was analyzed by visual observation and UV-Visible spectrophotometer. Further, the synthesized MNPs were characterized by FT-IR and XRD. These nanoparticles have been used as a catalyst for the degradation of malachite green (MG) in the presence of sodium borohydride ($NaBH_4$). Silver nanoparticles have a drastic catalytic effect as compared to copper or zirconium dioxide nanoparticles on the degradation of malachite Green in the presence of sodium borohydride. From the kinetic data it is concluded that the rate constant follows the order: $k_{AgNPs} > k_{CuNPs} > k_{ZrO2NPs} > k_{uncatalyzed\ reaction}$.

Keywords: Spicy Jatropha, Metal nanoparticle, Malachite Green (MG), Sodium borohydride, Green method.

1. Introduction
Nanoparticle is a microscopic particle of matter that is measured on the nanoscale usually in the range of 10-100 nanometers with the large surface area. It is highly reactive and can be used as a good catalyst [1]. It has interesting optical and electronic effects [2].Several methods have been developed for the synthesis of metal nanoparticles (MNPs), which follow either top-down (physical) approach or bottom-up (chemical) approach. Most popular chemical methods produce nanoparticles along with the existence of toxic chemicals, which lead to some adverse effect in medical applications [3]. Recently attention has been given to green routes for the synthesis of metal nanoparticles because of its environmental friendly and secure technology is the ultimate need for the production of nanoparticles. Making use of plant extracts becomes the ultimate method for the production of MNPs due to its cost effective, easy scale up and environmental benign steps.
Spicy Jatropha oil is converted into biodiesel for use in diesel engines and also used as a reducing agent to reduce noble metal salts into metallic nanoparticles as well as it works as a capping and stabilizing agent. Here we have reported nanoparticles of Silver, Copper and ZrO_2 from Spicy Jatropha flower extract that is used as a good catalyst.
The electron transfer step plays a dynamic role in the degradation of dyes because there may be a large redox potential difference between the electron donor and acceptor species, which can obstruct electron transfer [4]. The MNPs are Ag, Cu and ZrO_2 with an intermediate redox potential between the electron donor and acceptor species can assist in the transfer of electrons, and act as an electron relay system [5,6]. Gold, silver and platinum nanoparticles are well-known examples of this type of redox catalyst, and it is known that when metal particles become nanoparticles, their electrode potential differs from each other. The turnover frequency (TOF) of metal nanoparticles increases as the size decreases [7].
In this study we have synthesized Ag, Cu and ZrO_2 metal nanoparticles using Spicy Jatropha flower extract and shown by application as a catalyst in the degradation of dye Malachite Green (MG) in the presence of UV-Visible light [8,9] $NaBH_4$ is a well-known reducing agent. Reduction of dyes (MG) by $NaBH_4$ in the absence of a catalyst is kinetically difficult but thermodynamically favorable. Nanoparticles can achieve this by providing an alternate path by reducing the activation energy, thereby decreasing kinetic barrier, making it kinetically favorable [10,11].

2. Materials and Methods

2.1 Materials

The Spicy Jatropha flower samples were collected from sawyerpuram, situated in Tuticorin district. Silver nitrate, zirconium oxy chloride and Copper sulphate pentahydrate and malachite green (MG) were purchased from Standard Scientific Supplies chemicals (P) Ltd, Tirunelveli. All the chemicals were used for AR grade.

2.2 Methods

2.2.1 Preparation of plant extract

10 g of the collected flower samples were washed thoroughly with distilled water, mixed with 100 ml distilled water and boiled for 15-20 minutes. The extract was filtered through whatmann no.1 filter paper and stored in an air tight container under 4ºC for further use.

3. Synthesis of silver, Copper and Zirconium dioxide nanoparticle using Spicy Jatropha flower extract

To 10 ml of Spicy Jatropha flower extract, 5 ml of $AgNO_3$ (1mM), 40 ml of $CuSO_4.5H_2O$ (4mM) and 40 ml of $ZrOCl_2.8H_2O$ was mixed to synthesized silver, copper and Zirconium dioxide nanoparticles respectively. The mixture was stirred for 15 minutes at room temperature for silver nanoparticles and five minutes for zirconium dioxide nanoparticles, while kept in incubator at 60ºC for 24 hrs for copper nanoparticles and five minutes stirred for zirconium dioxide nanoparticles. The solution changes to yellowish brown, reddish brown and violet for the respected silver, copper and zirconium dioxide nanoparticles. The synthesized metal nanoparticles are used as catalyst for the degradation of malachite green by $NaBH_4$ and the rate constants (k) were determined.

4. Characterization of the metal nanoparticles

The green synthesized Metal NPs was analyzed using UV-visible, FT-IR and XRD analyses. Jasco V-550 spectrophotometer at the range of 200-800nm was used to get absorption maximum. Metal NPs was centrifuged at 9,500 rpm for 20 minutes, dried in a hot air oven and ground to get powder. FT-IR spectrum of the powdered sample was recorded with Jasco 5300 model FTIR instrument using KBr pellet at the spectral range of 400-4000 cm^{-1}. The xrd pattern of the air dried MNPs was analyzed by PAN analytical X'PERT-PRO powder X-ray diffractometer (XRD) using Cu-Kα radiation (1.5406Å) in the 2θ range 20-80°.

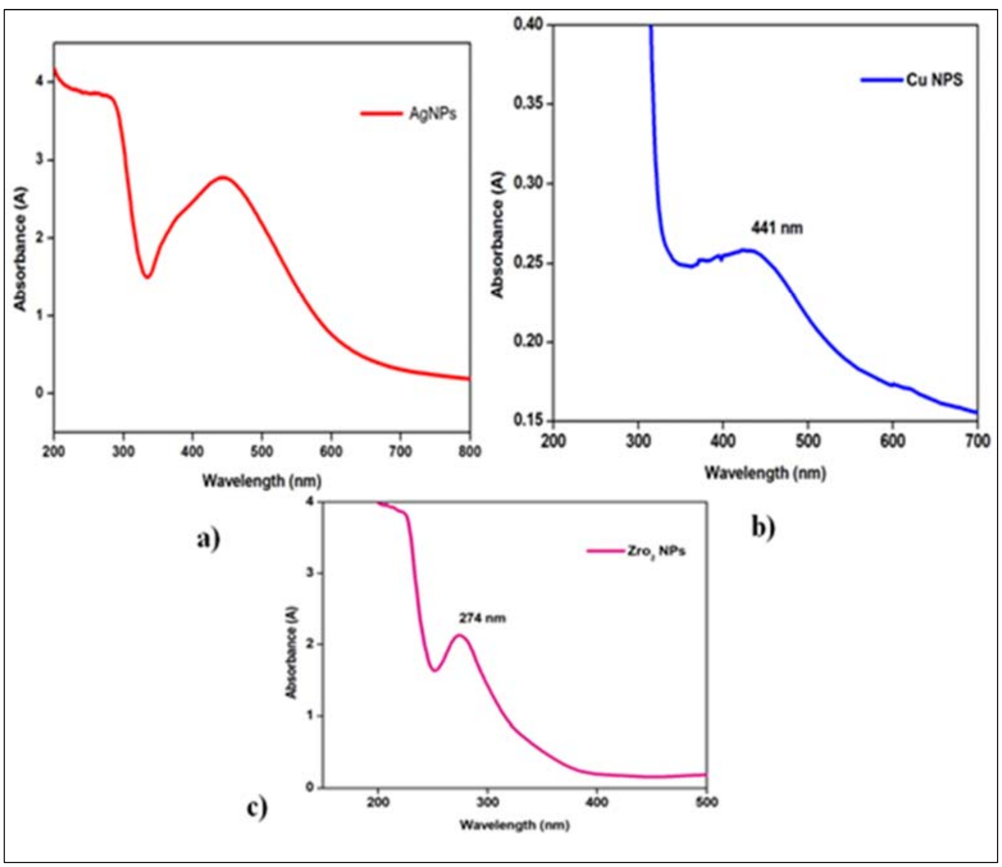
5. Kinetic study for the degradation of malachite green

To a mixture containing 50μL of MG (5×10^{-3}M) and 50μL of $NaBH_4$ (0.5% w/v) solution, 50μL of 0.001M aqueous dispersion of bio-synthesized AgNPs, CuNPs and ZrO_2 NPS were added in quartz cuvette (3.5mL capacity). Total volume of the mixture was made up to 3.2mL by adding the required amount of double distilled water. The reaction was studied in UV-Vis spectra by keeping the cuvette kept at a desired temperature. A blank reaction was carried out by using 50μL of water instead of catalysts. The reaction was followed by studying the time-dependent absorbance (A) in a UV-Vis spectrophotometer.

6. Result and Discussion

6.1 UV-Vis absorption spectra of synthesized Metal nanoparticles

UV-Vis absorption spectra of Ag, Cu and ZrO_2 nanoparticles were shown in fig 1. The λ_{max} of the prepared metal nanoparticles was observed at 440 nm for Ag, 441 nm for Cu and 274 nm for ZrO_2 [12-14]



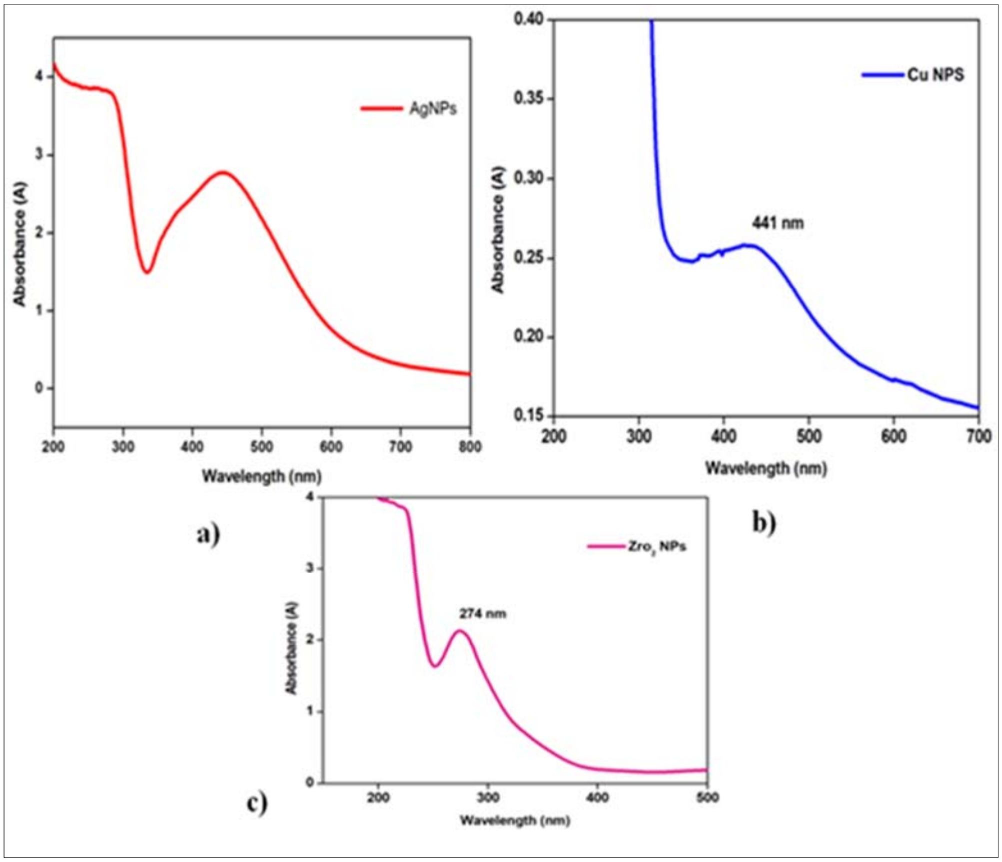


Fig 1: UV-Visible spectra of a) AgNPs b) CuNPs and C) ZrO_2NPs

6.2 FT-IR spectra of synthesized Metal nanoparticles

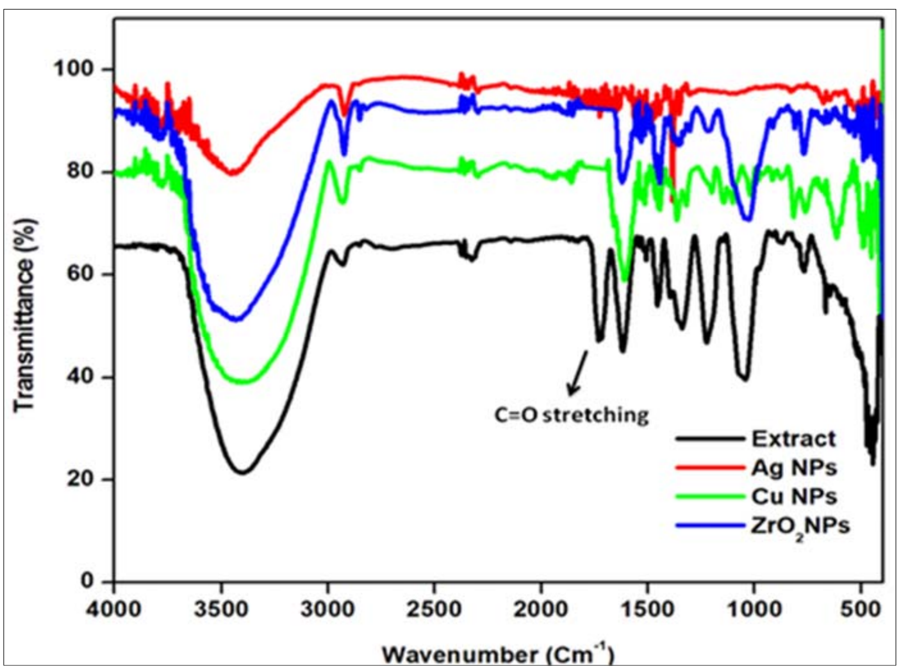


Fig 2: FT-IR spectra of Extract and Metal nanoparticles

The spectrum of Spicy Jatropha flower extract shows band of hydroxyl group at 3396 cm^{-1}, α, β- unsaturated ketone band at 1716 cm^{-1}, olefinic band at 1617 cm^{-1}. Primary and secondary alcohols give a band at 1072 cm^{-1}. The band at 1716 cm^{-1} which belongs to C=O stretching mode completely disappears in all the metal NPs. The shifting of these bands is a clear indication that the coordination of carboxylic acids in the protein of Spicy Jatropha flower extract plays a major role in dispersing, stabilizing and capping of Ag, Cu and ZrO_2 NPS [15-17].

6.3 XRD spectra of synthesized Metal nanoparticles

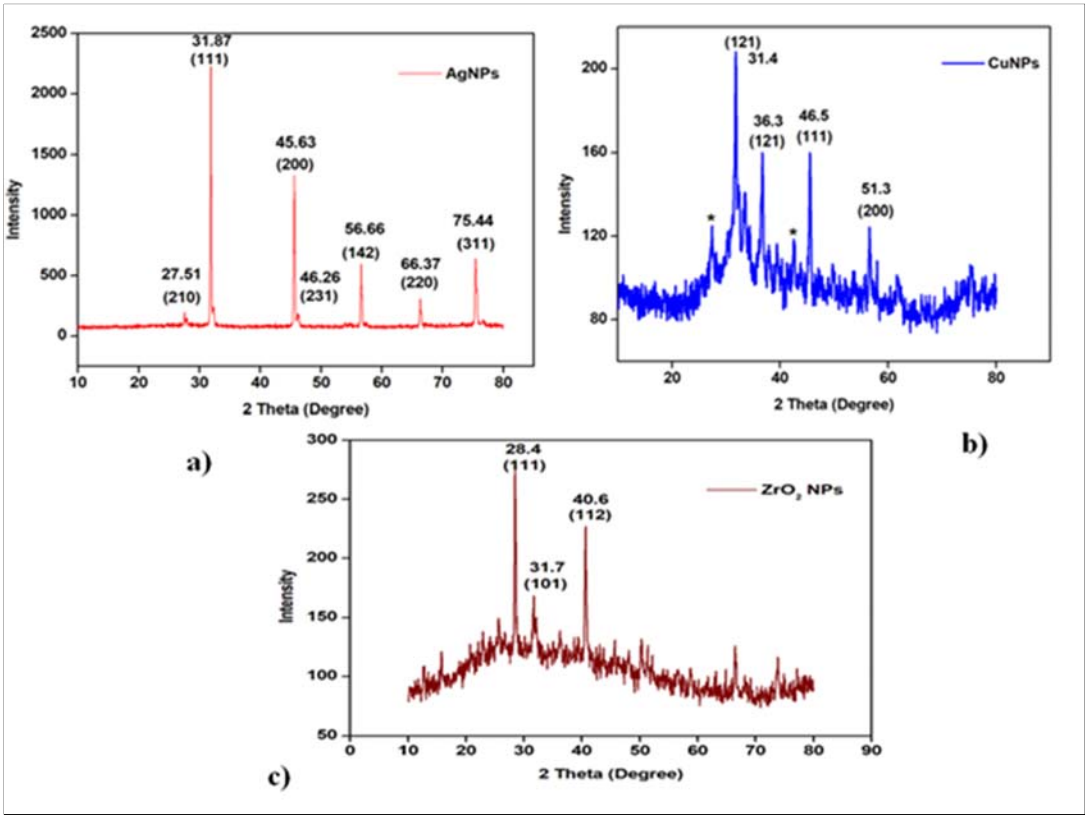


Fig 3: XRD spectrum of a) AgNPs b) CuNPs and C) ZrO_2NPs

Fig. 3 showed the XRD spectrum of Ag, Cu and ZrO_2 nanoparticles. The diffraction peaks observed are sharp and they fall in nanometer range. The face-centered cubic structure of Ag and CuNPs has good agreement with International Center of Diffraction Data card (JCPDS, file No. 04-0783) [18] and (JCPDS-03-1005)[19] respectively. The Monoclinic structure of ZrO_2NPs has good agreement with JCPDS-37-1484 [20]. The particle size of the synthesized nanoparticles was calculated using Debye Scherrer formula. The average crystalline size of the Ag, Cu and ZrO_2 nanoparticles was 10-40 nm.

7. Catalytic Study

7.1 Malachite Green (MG)

The synthesized metal nanoparticle was used as catalyst for the reduction of MG by $NaBH_4$. The rate of degradation of colour of MG using $NaBH_4$ was monitored in the presence/absence of MNPs using UV-Vis spectrophotometer, which is shown in fig 4.

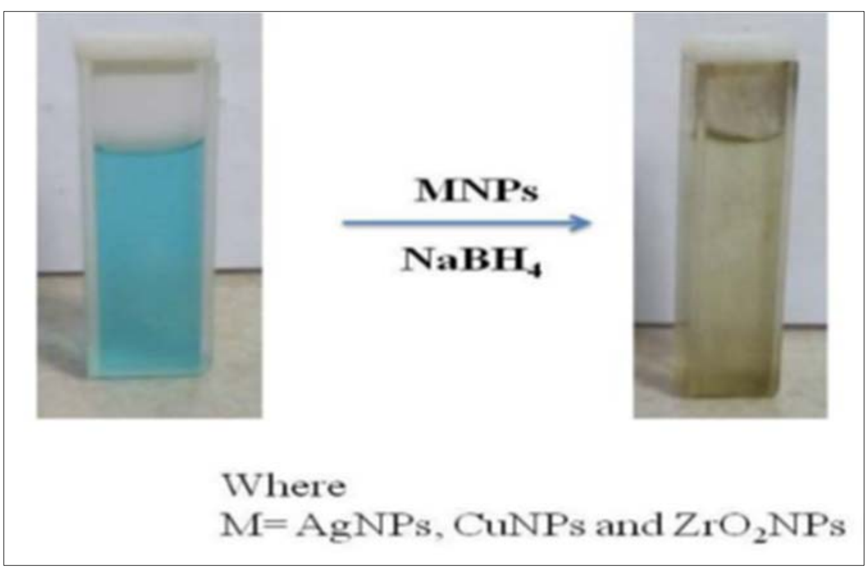


Fig 4: Photo picture of the vial solution for the reduction of malachite green by $NaBH_4$ in the presence of synthesized metal nanoparticle

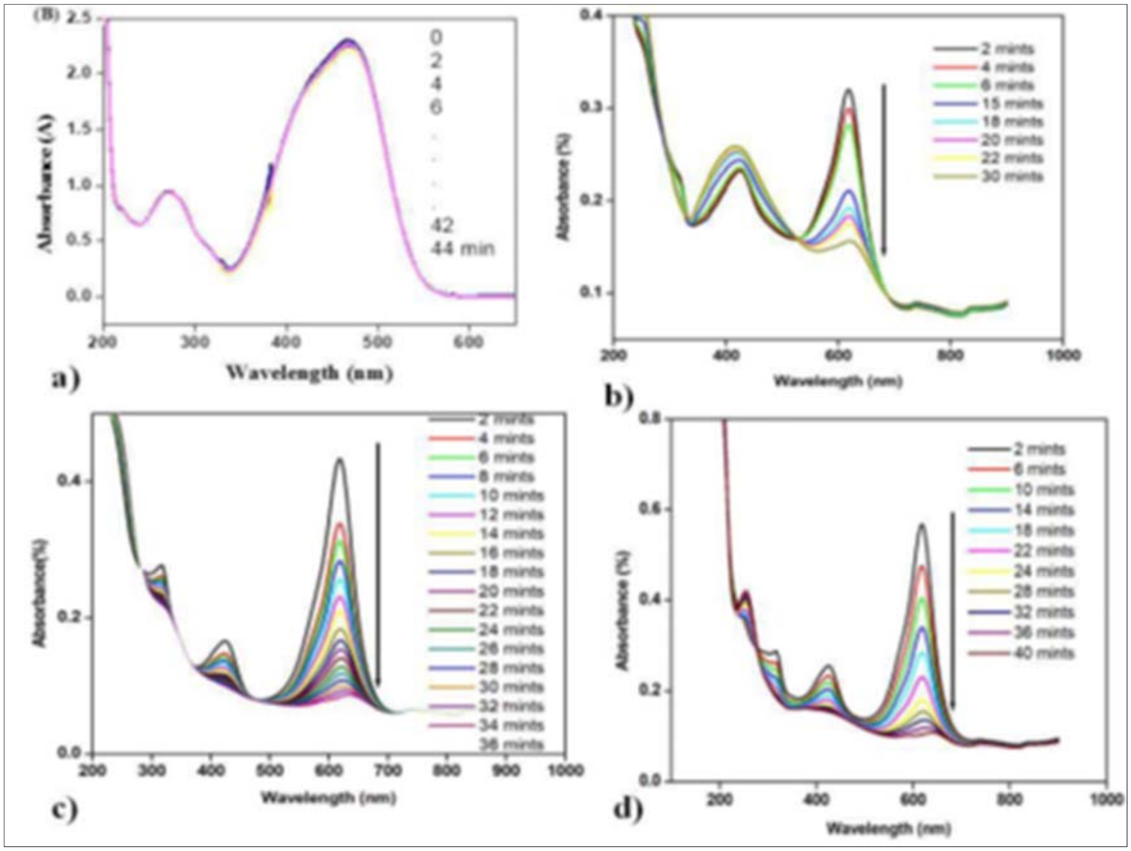


Fig 5: Time-dependent UV-visible spectra for the catalytic reduction a) the absence of catalyst (MNPs); b) in the presence of AgNPs; c) in the presence of CuNPs; d) in the presence of ZrO_2NPs

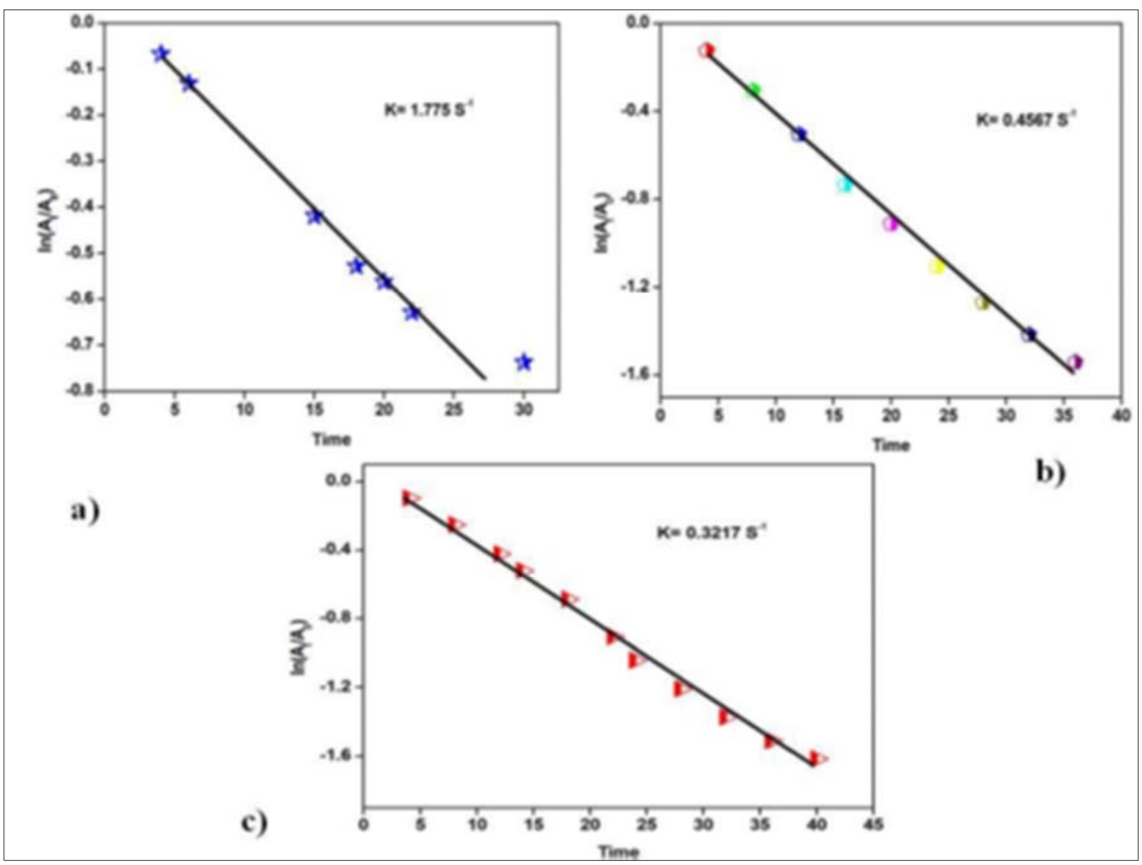


Fig 6: Degradation kinetics of MG a) AgNPs b) CuNPs c) ZrO_2NPs

The experiment showed that the MG in aqueous solution was successfully degraded using the bio-synthesized metal nanoparticles as a catalyst under the visible light irradiation at room temperature. The UV–Vis absorption spectra of MG (Fig. 5) showed a gradual decrease in λ_{max} due to the catalytic reduction by $NaBH_4$ in the presence of synthesized metal nanoparticles.

A hypsochromic shift has occurred in the absorption maximum of the degraded solution at different time interval. After irradiation under the visible light for 30 minutes for AgNPs (fig. 5b), 36 minutes for CuNPs (fig.5c) and 40 minutes for ZrO_2NPs (fig.5d), the absorption peak shifted from 618 to 610 nm. However, during irradiation, the intensity of the maximum peak (at 617 nm) reduces, while the other two peaks at 424 and 319 nm vanish. At the same time, an intense peak appears at 246 nm. The process of destruction of the conjugated structure is apparent in the UV-visible spectra of MG under visible irradiation. The rate of degradation of dye was estimated by studying the reduction kinetics, which showed pseudo-first order rate. Kinetics can be described as in $(A_t/A_0) = -kt$, where k is the apparent first-order rate constant (Sec^{-1}), t is the reaction time. At and A0 are the absorption of dyes at time t and 0 respectively, The induction time, a linear correlation between ln (A_t/A_0) and the reaction times was observed, which indicated that the degradation is a pseudo-first order reaction.

The kinetic studies revealed that the degradation process of MG dye followed pseudo-first order kinetics model with rate constant of AgNPs is 1.775 S^{-1}, CuNPs is 0.4567 $S^{-1}$and ZrO_2NPs is 0.3217 S^{-1}[21].

Table 1: Comparison of rate constant (k) for the catalyzed reduction using different catalysts (Ag, Cu and ZrO_2 nanoparticles) with uncatalyzed reduction

S. No	Concentration of catalyst	Concentration of MG	Concentration of $NaBH_4$	Temperature (ºC)	Rate constant
1.	50µL of 0.01% Ag	50µ L of 5×10^{-3} M	50µ L of 0.5%	32	1.775
2.	50µL of 0.01 % Cu	50µL of 5×10^{-3} M	50µ L of 0.5%	32	0.4567
3.	50µL of 0.01 % ZrO_2	50µ L of 5×10^{-3} M	50µ L of 0.5%	32	0.3217
4.	Without catalyst	50µL of 5×10^{-3} M	50µ L of 0.5%	32	Very small

8. Conclusion

We have described the green aqueous synthesis of Ag, Cu and ZrO_2 metal nanoparticles having an average diameter of 40 nm using the Spicy Jatropha flower extract at room temperature. These metal nanoparticles have been used for the catalytic degradation of malachite green in the presence of $NaBH_4$ and comparison has been made to show their different catalytic activity by measuring the rate constant (k). Silver nanoparticles act as a much better catalyst as compared to copper and zirconium dioxide nanoparticles. Sodium borohydride being such a strong reducing agent is not able to reduce malachite green in the absence of catalyst, indicating the catalytic efficacy of metal nanoparticles.

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