



## Kinetic Study for Reduction of Organic Dye using Graphene Oxide Supported Ru-Ag Nanoparticles Catalyst

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The kinetic effect of organic pollutants present in water such as commercial dyes, namely malachite green, rhodamine B, were studied. The kinetic effects of reduction of initial dye concentration using Ru-Ag NPs and substrate were determined. From the  $K_{obs}$  results, the order of rate constant of Ag, Ru and Ru-Ag NPs were studied under pseudo-first order reaction condition. The apparent rate constant for the reduction of rhodamine B and malachite green by using Ru-Ag NPs catalyst,  $k_{obs}$  was initiated to be higher than other mono metallic nanoparticles catalyst. The reason for increased  $k_{obs}$  noticed in Ru-Ag NPs may be attributed due to the size distribution of the Ru-Ag NPs catalyst which is found to be relatively smaller, viz. 10 nm than another catalyst. The result used for calculating the pseudo first order of miscellaneous dye-containing wastewaters. It was also found that the decolourization of the dyes undergoes a fast reaction than the mineralization.

**Keywords:** Graphene oxide, Malachite green, Rhodamine B, Ru-Ag nanoparticles, Kinetic studies, Reduction.

### INTRODUCTION

Textile industries releases enormous quantity of waste water containing high concentration of dyes [1]. The non-biodegradable nature dye baths causes severe environmental troubles [2]. Rhodamine B is one of the predominant xanthene cationic dyes, is generally used in industry as a dye for paper, silk, wool, jute leather, cotton. The xanthene dyes (rose bengal, eosin Y and rhodamine 6G, etc.) are used as fluorescent markers in constitutional nanosized studies, photosensitizers and laser dyes. They have long been familiar to be harmful, to insects (insecticide). They are toxic if consumed by human and animals and cause irritation to the skin, eyes and lung [3,4]. They described the utilization of *Plectranthus amboinicus* leaf extract [5] as reducing agent for the synthesis of AgNPs as a catalysts which shows high antimicrobial activity. The first time synthesis of SnO<sub>2</sub> NPs using *Plectranthus amboinicus* leaf extract as reducing agent were reported here as a reference [5].

In the presence of NaBH<sub>4</sub>, electron transfer occurs due to the catalytic reductive degradation of organic dye molecules by metal nanoparticles (MNPs), which is responsible for reducing speed of the reaction [6-11].

Rhodamine B and malachite green [12] are basic dyes that have become more important in the textile industry due to their more rigid structures than other organic dyes. Their cationic structure is best applied to anionic fabrics which contain negative charges. The dyes are brilliant and most fluorescent among other synthetic dyes. In addition, the chromophore in their structures is known to be carcinogenic. Rhodamine B and malachite green have been extensively used around the world in silk, wool and cotton dyeing industries. Recently, increasing use of these dyes has been linked to increase risks of cancer. A number of methods have been developed in recent years for their degradation and treatment

Photocatalytic effect of organic compounds such as methyl green and rhodamine B in water is noticeable due to the sensitive, biological collision of miscellaneous industrial and agricultural pollutants [13,14]. The photocatalytic activities of homogeneous or heterogeneous reactions depends up on the nature of their reactants and materials (semiconductors). An example of heterogeneous photocatalytic reaction using semiconductor materials TiO<sub>2</sub> and ZnO, observed by photodecomposition of organic pollutant molecules into less harmful compounds [15-19].

Graphene sheets can be synthesized by three major methods, such as mechanical exfoliation, chemical vapour deposition (CVD) onto metal or Si substrates and the chemical, electrochemical, or thermal reduction of graphene oxide. Chemical vapour deposition method is most successful for the mass production of graphene and can be used to fabricate immense areas of graphene while restricting the number of inadequacy [20].

In recent years, many research works focusing on the degradation mechanism of rhodamine B [21-26], most of them are problematic under the mechanism of visible illustration. In this current study, Ru-Ag NPs are used as a catalyst for the reduction of organic dyes namely rhodamine B and malachite green.

## EXPERIMENTAL

Graphite powder (SRL), silver nitrate (SRL), ruthenium trichloride hydrate (SRL), potassium dichromate (SRL), rhodamine B and malachite green (SRL), sodium borohydride (SRL), double distilled water were analytical grade of 99 % purity and used as received.

**UV-visible spectrophotometer:** The UV-visible spectra were measured on Perkin Elmer Lambda-35 instruments with UV Win-lab software. The measurements were carried out in the wavelength range of 200-800 nm under ambient conditions.

The comparative catalytic activity of mono and bimetallic nanoparticles catalysts were examined by conducting the reduction of rhodamine B and malachite green is a model reaction keeping under identical pseudo-first order experimental condition. The reaction was carried out individually in a standard quartz cuvette with 1 cm path length to which 2.5 mL water, 0.25 mL rhodamine B and malachite green (1 mmol), 0.25 mL NaBH<sub>4</sub> (100 mmol) and 5 mg of respective catalyst was added. After mixing the respective solution the corresponding cuvette was placed in a UV-visible spectrometer maintaining the temperature at 27 °C. The occurrence of the reaction was recorded in the range from 200-700 nm. The decreasing trend of characteristic peak was recorded at regular intervals of time (5 min) and the same has been used for the calculation of pseudo first order rate constant. The pseudo first rate constant was calculated using the formula.

$$K_{\text{obs}} = \ln[(A-A_0)/(A-A_t)]/t$$

where, A = absorbance at infinity time, A<sub>0</sub> = initial absorbance, A<sub>t</sub> = absorbance at different time t.

The comparative K<sub>obs</sub> values are calculated for another one bimetallic and three mono metallic nanoparticles catalysts. The observed K<sub>obs</sub> value reveals that the Go-Ru/Ag NPs catalyst is found to be superior catalysts compare to other bimetallic and mono metallic nanoparticles.

Graphite oxide was prepared by the using Hummer method and exfoliated into graphene oxide by sonication in water. These graphene oxide supported mono and bimetallic nanoparticles catalyst were prepared by chemical reduction method. The first catalyst *viz.*, Ru-Ag bimetallic nanoparticles was prepared by taking in a 100 mL round bottom flask, typically, 0.06 mm of ruthenium trichloride hydrate to which potassium tetrachloroargantate was added. Sonicated (5 mg and 30 mL water for 30 min) grapheme oxide was added to the above

mixture and the reaction was stirred for further 2 h at 120 °C. Finally 0.1 M sodium borohydride solution was added to the reaction mixture. The resulting solution was cooled and centrifuged at 2500 rpm. The water and ethanol were used for further purification. The collected product was dried at 70 °C in vacuum oven.

In a similarly manner, by adopting the same quantity of the reagents and experimental procedure the bimetallic and mono metallic nanoparticles catalysts *viz.*, Ru/Ag, Ru and AgNPs were also prepared. The metal precursors for Ru/Ag, Ru and AgNPs were AgNO<sub>3</sub> and RuCl<sub>3</sub>·H<sub>2</sub>O solution. The reduction of Ag<sup>+</sup>/Ru<sup>3+</sup>, Ag<sup>+</sup>/Ru<sup>3+</sup> to Ru/Ag, Ru and AgNPs was noticed through the change of colour.

## RESULTS AND DISCUSSION

It is well known that the research on catalysis is proved to be a essential subject and this achievement in turn can strengthen the economy of the industries. In the last two decades the research interest on development of homogeneous nanoparticles catalyst has expand tremendously owing to its and unexplainable advantages. To synthesis homogeneous mono/bimetallic nanoparticles catalysts, one should need an appropriate template to stabilize/encapsulate the metal nanoparticles. Further in the preparation of homogeneous metal nanoparticles as catalyst, identification of template/stabilizing agent is proved to be a bigger task.

**Kinetic study for the reduction of rhodamine B using graphene oxide supported Ru-Ag NPs catalyst:** In order to realize the effect of [NaBH<sub>4</sub>], [substrate] and [catalyst] in the reduction process of organic dyes, the catalyst *viz.*, Ru-Ag NPs was employed and studied under pseudo-first order reaction condition. The kinetics reduction reaction of the dyes was measured between the absorbance of the product with decreasing trend 544 nm against the time through UV-visible spectrophotometer. From the observed rate constants, it is understood that the [NaBH<sub>4</sub>], [substrate] and [Catalyst] has been largely influenced the k<sub>obs</sub> in the reduction of organic dyes substrate.

**Effect of [substrate]:** The substrate concentration varied from 0.8 to 1.4 mm at constant temperature 27 °C and the experiments were performed by maintaining the other parameters as constant. The rate constants are calculated from the plot 2 + log (A-A<sub>t</sub>) *vs.* time and the calculated values are given in Fig. 1. The observed rate constants are decreased invariably on increasing the dyes are given in Table-1 (Fig. 2). The decreasing trend of rate constant is due to lesser availability of BH<sub>4</sub><sup>-</sup> in aqueous phase and thus minimizing the formation of product.

**Effect of [NaBH<sub>4</sub>]:** The effect of concentration of NaBH<sub>4</sub> for reduction of rhodamine B was studied in the range from 60 to 110 mm keeping the other parameters as constants. From the plot of 2 + log (A-A<sub>t</sub>) *vs.* time, the pseudo-first order rate

TABLE-1

[Rh-B] (mm)	[NaBH <sub>4</sub> ] (mm)	[Catalyst] (mg)	K <sub>obs</sub> × 10 <sup>-3</sup> (s <sup>-1</sup> )
0.8	100	5	2.6940
1.0	100	5	1.6680
1.2	100	5	1.3615
1.4	100	5	1.2343

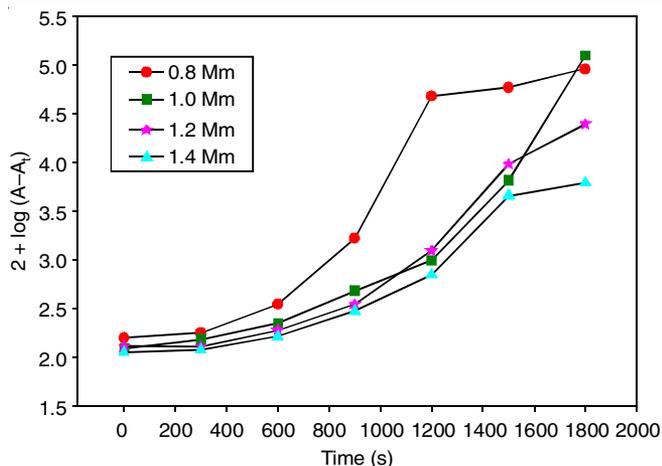


Fig. 1. Plot of  $2 + \log (A-A_0)$  vs. time

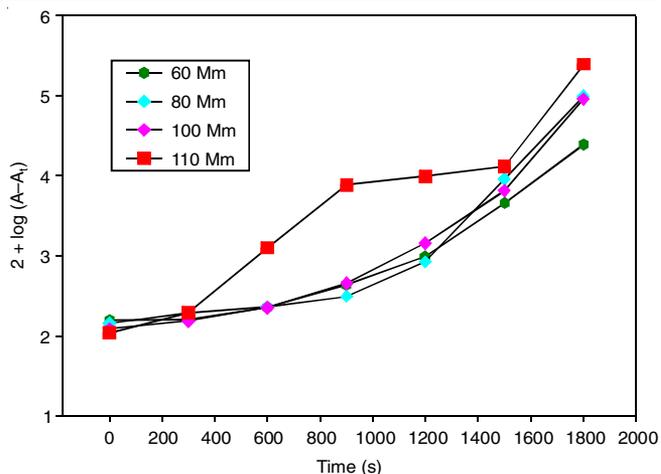


Fig. 3. Plot of  $2 + \log (A-A_0)$  vs. time

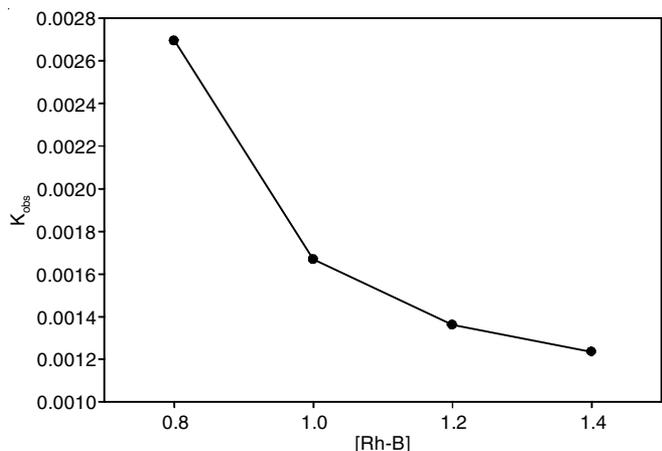


Fig. 2.  $K_{obs}$  vs. [Rh-B]

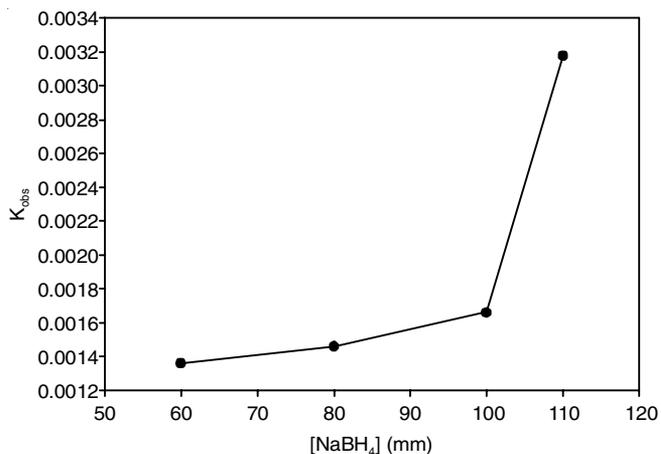


Fig. 4.  $K_{obs}$  vs. [NaBH4]

constants were evaluated and the corresponding plots were depicted in Fig. 3. The observed rate constants increased with the increase in the concentration of NaBH<sub>4</sub> and presented in Table-2 and the plots are depicted in Fig. 4. On increasing the [NaBH<sub>4</sub>], the adsorption of BH<sub>4</sub><sup>-</sup> ions onto the nanoparticles surfaces also parallelly increases, as a result, the relay of electrons from BH<sub>4</sub><sup>-</sup> (donor) to the rhodamine B (receptor) increases. It is worth to state that under the fixed concentration of NaBH<sub>4</sub> the reduced product *viz.*, organic dyes remains non-oxidized, since the liberated hydrogen eliminates the air hence prevents the oxidation. In addition to this the evolved hydrogen bubbles from the catalyst surface helps in mixing of the solution and thus offering the favourable conditions to increase the reaction rates.

**Effect of catalysts:** Similarly, in the case of change in the concentration of the catalyst, the  $k_{obs}$  were found to increases with respect to the concentration of catalyst irrespective of organic dyes used. The effect of graphene oxide-Ru-Ag NPs

was performed by varying the concentration of the catalyst from 3 to 8 mg which is shown in Fig. 5, keeping the other parameters constant. The plot derived from observed rate constant against the amount of catalyst was shown in Table-3. From this plot, it has been understood that the amount of catalyst and the rate constant are parallel to each other are given in Fig. 6. It has been obviously known fact, that at higher concentration of the catalyst, the active sites of nanoparticles is also high that enhances the rate constant.

TABLE-2

[Rh-B] (mm)	[NaBH <sub>4</sub> ] (mm)	[Catalyst] (mg)	$K_{obs} \times 10^{-3} (s^{-1})$
1.0	60	5	1.36140
1.0	80	5	1.46140
1.0	100	5	1.66179
1.0	110	5	3.17710

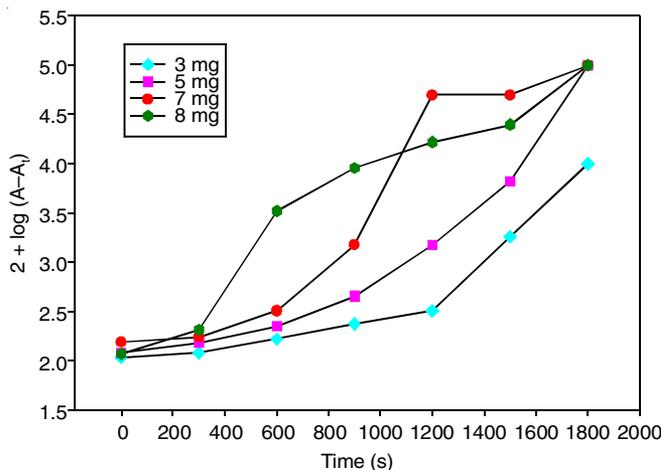


Fig. 5. Plot of  $2 + \log (A-A_0)$  vs. time

TABLE-3

[Rh-B] (mm)	[NaBH <sub>4</sub> ] (mm)	[Catalyst] (mg)	$K_{obs} \times 10^{-3} (s^{-1})$
1.0	100	3	1.0686
1.0	100	5	1.6815
1.0	100	7	2.3915
1.0	100	8	3.5000

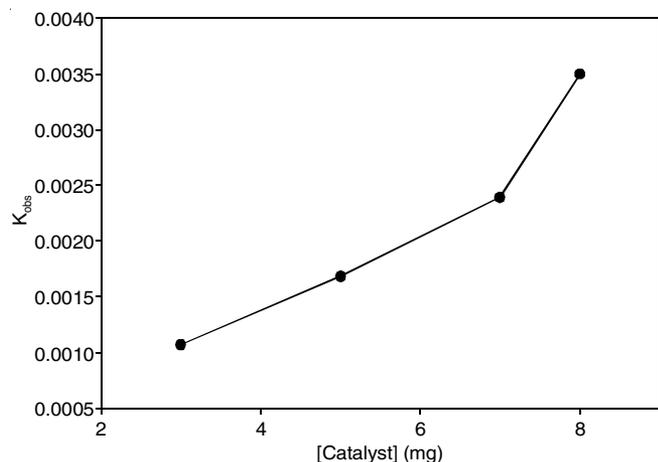
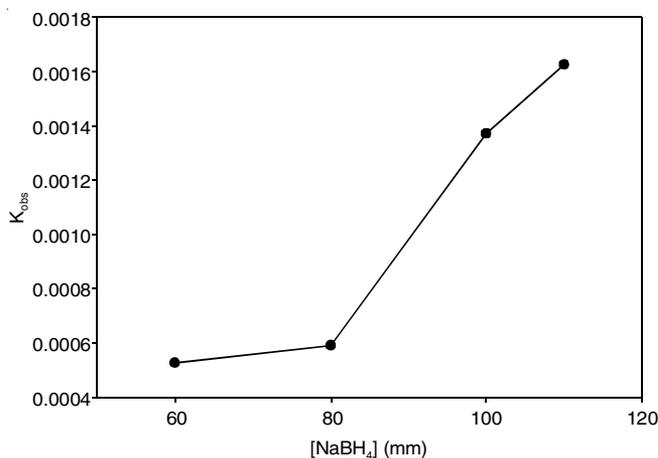
Fig. 6.  $K_{obs}$  vs. [catalyst]

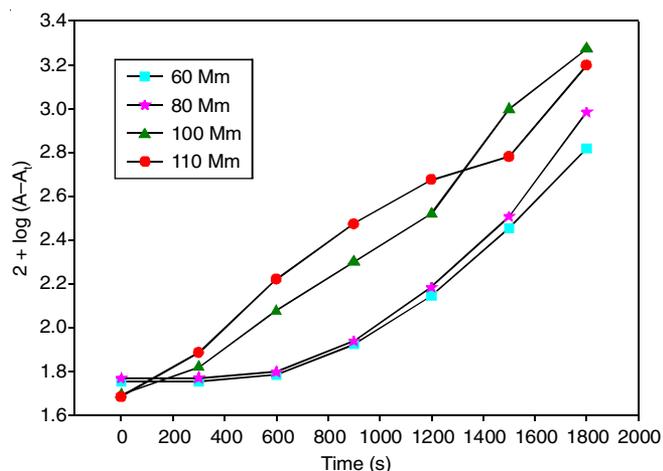
TABLE-4

[MG] (mm)	[NaBH <sub>4</sub> ] (mm)	[Catalyst] (mg)	$K_{obs} \times 10^{-3} (s^{-1})$
1.0	60	5	0.5257
1.0	80	5	0.5900
1.0	100	5	1.3714
1.0	110	5	1.6257

Fig. 8.  $K_{obs}$  vs. [NaBH<sub>4</sub>]

### Kinetic study for the reduction of malachite green using graphene oxide supported Ru-Ag NPs catalyst

**Effect of [NaBH<sub>4</sub>]:** The reduction of malachite green was studied by varying the concentration of NaBH<sub>4</sub> in the range from 60 to 110 mm by keeping the other parameters as constants. From the plot,  $2 + \log (A-A_t)$  vs. time, the pseudo-first order rate constants were evaluated and presented in Fig. 7. The observed rate constants increased with the increase in the concentration of NaBH<sub>4</sub> as shown in Table-4 and the corresponding plots was depicted in Fig. 8. As the concentration of NaBH<sub>4</sub> raises, the adsorption of BH<sub>4</sub><sup>-</sup> ions into the nanoparticle surfaces also increases, as a result, the relay of electrons from BH<sub>4</sub><sup>-</sup> (donor) to the malachite green (receptor) increases. It is worth to state that under the fixed concentration of NaBH<sub>4</sub> the reduced product *viz.*, organic dyes remains non-oxidized, since the liberated hydrogen eliminates the air hence prevents the oxidation.

Fig. 7. Plot of  $2 + \log (A-A_t)$  vs. time

**Effect of [catalysts]:** Similarly, in the case of change in the concentration of the catalyst, the  $k_{obs}$  were found to increase with respect to the concentration of catalyst irrespective of organic dyes used. The effect of GO-Ru-Ag NPs, was performed by varying the concentration of the catalyst from 2 to 7 mg which is shown in Fig. 9, keeping the other parameters constant. The plot derived from observed rate constant against the amount of catalyst was shown in Table-5. From this plot, it has been understood that the amount of catalyst and the rate constant are parallel to each other as given in Fig. 10. It has been obviously known fact, that at higher concentration of the

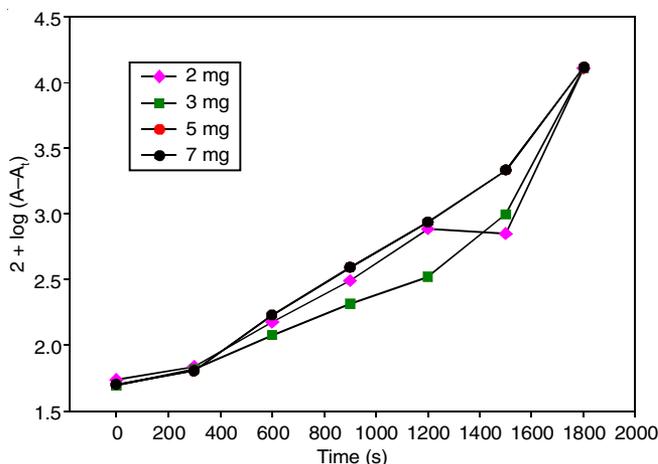
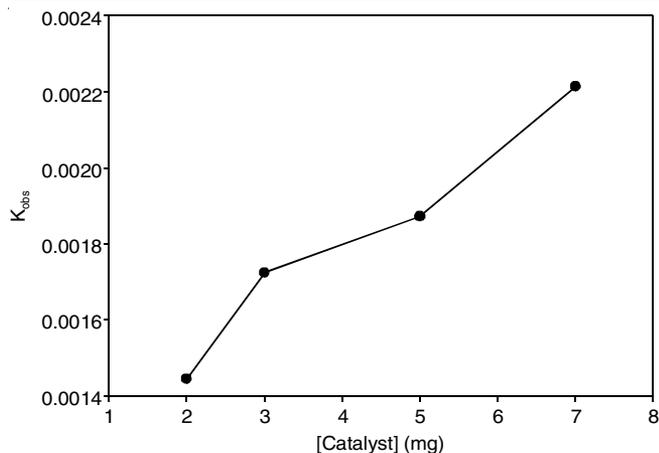
Fig. 9. Plot of  $2 + \log (A-A_t)$  vs. time

TABLE-5

[MG] (mm)	[NaBH <sub>4</sub> ] (mm)	[Catalyst] (mg)	$K_{obs} \times 10^{-3} (s^{-1})$
1.0	100	2	1.4440
1.0	100	3	1.7243
1.0	100	5	1.8728
1.0	100	7	2.2143

Fig. 10.  $K_{obs}$  vs. [catalyst]

catalyst, the active sites of nanoparticles is also high that enhances the rate constant.

### Conclusion

The discolouration of rhodamine B and malachite green is also a pseudo first order with respect to rhodamine B, malachite green and sodium borohydride. The discolouration increases with temperature, the observed rate constants increased with the increase in the concentration of  $\text{NaBH}_4$ . Kinetic study for the reduction of organic dye using graphene oxide supported Ru-Ag NPs catalyst single step process, economic viability; effective and rapid production of nanoparticles could be used to biomedical and environmental applications.

### CONFLICT OF INTEREST

The author declare that there is no conflict of interests regarding the publication of this article.

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