# SOLAR LIGHT ASSISTED DEGRADATION OF RHODAMINE B DYE BY CHEMICALLY SYNTHESIZED SILVER NANOPARTICLES

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*Original scientific paper*
*Received: May 22nd, 2022*
*Accepted: June 25th, 2022*
*HAE-2243*
*https://doi.org/10.33765/thate.13.3.1*

## ABSTRACT

Utilization of dyes and dyestuff is increasing day by day, which affects environmental health and sustainability. Rhodamine B (RhB) is a synthetic xanthene class of dye that has a major application in cosmetic, painting, printing, and textile industries. The toxicity of RhB has been reported in animals, insects as well as humans in parts per billion (ppb) concentration. Exposure to this dye causes skin irritation, nervous system issues, and developmental changes. Therefore, the remediation of the dye is a crucial factor. The aim of this study was solar-assisted photocatalytic degradation of RhB. Synthesis of silver nanoparticles (AgNPs) was carried out with chemical reduction method, and characterization with the X-ray diffraction (XRD). The photocatalytic activity was checked with 1000 mL wastewater in which 10 ppm dye was added. Optimization of physicochemical parameters was performed by one-factor-at-a-time (OFAT) method. Maximum 99.32 % decolourization was observed at 2 g/L catalyst concentration, pH = 6, and 10 ppm dye concentration in 50 min irradiation time at 0.19 mg/L/min rate of decolourization. The initial degradation was confirmed based on chemical oxygen demand (COD) reduction; 89.25 % COD removal at a 0.17 mg/L/min rate was observed. The confirmation of degradation was carried out with UV-visible spectrophotometer and high-performance thin-layer chromatography (HPTLC) analysis. AgNPs were the efficient catalyst for the degradation of RhB. The toxicity study proved that, after degradation of RhB with AgNPs, the degraded products were less toxic than the original ones.

***Keywords***: *decolourization, optimisation, photocatalytic degradation, Rhodamine B (RhB), AgNPs, HPTLC, toxicity*

## INTRODUCTION

The nanotechnology plays a major role in the wastewater treatment. Nanoscience has the combination of nanomaterial and biology which can help to remove pollutants from wastewater. Nanomaterials are building blocks of nanotechnology, ranging in the size from 10 to 100 nm, which have higher surface area for reaction and have attractive shapes [1]. Nanostructures have wide application in different areas, such as electronics, biomedical and material science. Nanostructures are used to improve, purify and preserve quality of soil, water and air in the environment [2]. The synthesis of nanoparticles (NPs) is carried out in two ways: one is bottom-up and the other is top-bottom [3]. Mostly chemically and biologically mediated synthesis of nanoparticles follows the bottom-up method. Different chemical methods have been used for synthesis of NPs, such as sol-gel [4], hydrothermal [5], sonochemical [6], microwave-assisted [7] and vapour deposition [8]. Biologically based synthesis of NPs were carried out with bacteria, fungi and plants [9]. Different metal-based nanostructures and their combined composites, such as iron-magnesium oxides [10], silver-zinc oxides [11], iron-titanium oxides [12], cadmium-based [13], and nickel-based [14] were applied for the purpose of degradation of synthetic pollutants present in wastewater [15]. Photocatalysis is a remarkable method for removal of pollutants from wastewater; catalysts are activated in presence of light and generate free hydroxyl ions that are capable of efficiently oxidizing organic compounds [16]. Many researchers have synthesised metal-based photocatalysts and applied them in removal of organic pollutant. Silver-zinc oxides (Ag/ZnO) were used for degradation of RhB, reactive orange and bisphenol [17]. Zinc oxide (ZnO) based nanostructures were synthesised and applied for RhB degradation [18].

RhB is a xanthene class of dye of a persistent toxic nature that generates harmful free radical ions upon exposure to living bodies. RhB is highly soluble in water, reduces the photosynthetic efficiency of aquatic plants and creates water pollution so that removal from wastewater becomes necessary [19]. This study was based on silver nanoparticles (AgNPs) synthesis and their application in photocatalytic removal of RhB from wastewater. Reported study was based on zinc oxide (ZnO) and titanium oxide ($TiO_2$) nanostructures that are cost-effective but require UV light rather than solar light for activation, while AgNPs activation is possible with solar (visible) light irradiation. This reduces the overall costs of treatment compared to other metal-based nanostructures.

## MATERIALS AND METHODS

### Media, chemicals and reagents

Disodium hydrogen phosphate ($Na_2HPO_4$) and silver nitrate ($AgNO_3$) were of analytical grade. RhB was purchased from dye industry. All experiments were carried out in double distilled water to avoid impurities.

### Synthesis of AgNPs nanostructure

The synthesis of AgNPs nanostructures was carried out according to [20]. 10 g/L $Na_2HPO_4$ was prepared and 30 mM of $AgNO_3$ were added directly into solution. The solutions were converted into yellowish ppts form and centrifuged at 10000 x g for 10 min. Ppts were taken in evaporating bowl and dried in oven at 80 °C. The AgNPs powder was further characterised.

### Characterisation of AgNPs nanostructure

*X-ray diffraction (XRD)*

XRD was performed according to [20]. XRD was performed with Bruker diffractometer using $K_\alpha$ radiation in 2Θ range. The diffraction was monitored with a UV-visible spectrophotometer.

### Photocatalytic efficiency of AgNPs nanostructure on Rhodamine B dye

Photocatalytic efficiency was checked in 1000 mL wastewater with a dye concentration of 10 ppm. The wastewater was prepared according to [21]. RhB was added in simulated mineral media at a concentration of 10 ppm. The simulated mineral media consisted of (mg/L): $NH_4CI$: 200, $K_2HPO_4$: 250, NaCl: 1000, $Na_2CO_3$, 1500, $NaHCO_3$: 1000, starch: 200, glucose: 100 and 10 mL/L of a trace element solution containing (mg/L) $CaCl_2 \cdot 2H_20$: 3000, $MgSO_4 \cdot 7H_20$: 3000, $FeSO_4 \cdot 7H_20$: 5000, $ZnSO_4 \cdot 7H_2O$: 100, $H_3BO_3$, 100, $CuSO_4 \cdot 5H_2O$: 50, $MnCl_2$: 0.05, $CoCl_2$: 0.05 and $(NH_4)_6MO_7O_{24} \cdot 4H_2O$: 0.05. The final pH of the influent was adjusted to 7.0. 1 g/L catalyst was added to check catalytic efficiency. The flask was kept under solar light radiation with magnetic stirring. Samples were taken at 10-minute intervals. Separation of NPs was done by centrifugation at 10000 x g for 10 min. The supernatant was taken and subjected to decolourization assay. Decolourization assay was performed in UV visible spectrophotometer (Thermo Scientific) at 554 nm. The percentage of decolourization was calculated using the following formula:

$$\text{Dec. (\%)} = \frac{\text{Initial absorbance - Final absorbance}}{\text{Initial absorbance}} \times 100 \quad (1)$$

## Effect of physical parameters on dye degradation

Effects of different physical parameters on RhB decolourization were checked with the one-factor-at-time (OFAT) method. Radiation source is important for catalyst activation; solar light and UV light were selected to check the effect on RhB decolourization. Concentration of RhB played a vital role in decolourization. A concentration of 0.5 to 3 g/L was considered to check the decolourization. A concentration of 5 to 25 mg/L was selected to check the effectiveness of catalyst. Irradiation time plays a role in the photocatalytic reaction. The visible light and UV light were used for 10 to 50 min to react with RhB and decolourize it.

## Analytical techniques for RhB removal

*COD reduction*

COD reduction was performed according to standard protocol [22]. COD reduction was analysed by dichromate closed reflux method. A system with a total volume of 7 mL, which consisted of 2.5 mL of effluent, 1.5 mL of potassium chromate digestion solution and 3.5 mL of acid reagent, was used and digested for 2 h in COD digester (Patel scientific instruments Pvt. Ltd.).

*High-performance thin-layer chromatography (HPTLC)*

Degradation study was carried out according to [23] with HPTLC. The sample was applied to a silica gel plate (HPTLC Silica gel 60 F254, Merck, Germany) using a sample applicator with a micro syringe and spraying with nitrogen gas (Linomat V, CAMAG, Switzerland). A mixture of butanol : acetic acid : water (4 : 1 : 5 v/v) was used as a solvent system to resolve metabolites on thin layer chromatography (TLC) plate. The system was developed in pre-equilibrated twin trough chamber and scanned by TLC scanner (CAMAG TLC scanner 4, Switzerland) at 366 nm.

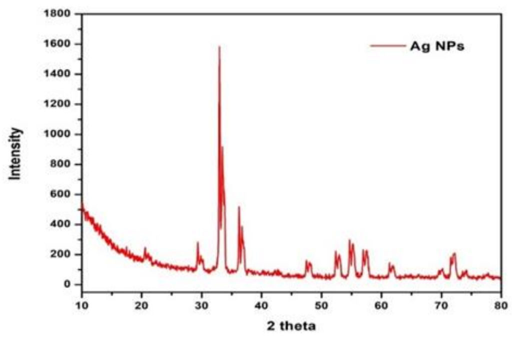
## Toxicity study

The toxicity study was carried out according to [24]. The toxicity of RhB and the treated effluent was compared with distilled water. The study was performed on *Triticum aestivum* seeds. Ten healthy seeds of *Triticum aestivum* were grown in 100 kg soil. The control (RhB), the treated effluent and the distilled water were applied in each container. All sets were performed in triplicates. After 15 days of germination, the length of the root and plumule was observed.

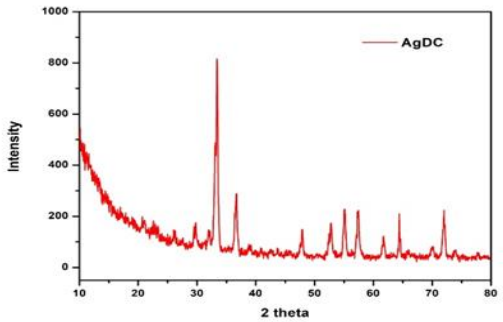
# RESULTS AND DISCUSSION

## Characterisation of AgNPs nanostructure

Results of XRD were compared with standard AgNPs. The 2ϴ angle of the sample and the standard were completely similar, which confirms that it is an AgNPs nanostructure. Figure 1a shows AgNPs characteristics before treatment and 1b after treatment. The results are in accordance with [20].




a)




b)

Figure 1. XRD analysis of AgNPs nanostructure: a) before treatment, b) after treatment

## Photocatalytic effect on the removal of Rhodamine B

Photocatalytic reaction was carried out with activation of AgNPs in presence of light. A RhB removal of 99.32 % was observed with a dye concentration of 10 ppm and a catalyst concentration of 2 g/L at pH = 6 and 50 min of solar light irradiation.

*Mechanism of photocatalysis*

In the presence of solar light, the AgNPs were activated and generated $h^+$ and $e^-$ which were responsible for further generation of free radicals. Free radicals react with RhB and convert it into mineralised products (equations 2 - 4). After the treatment, the presence of Ag was found by using XRD analysis. The mechanism of degradation with AgNPs is described in Figure 2.

$$hv + AgNPs \rightarrow h^+ + e^- + AgNPs \qquad (2)$$

$$AgNPs + O_2 \rightarrow O_2 \qquad (3)$$

$$h^+ + RhB \rightarrow CO_2 + H_2O \qquad (4)$$

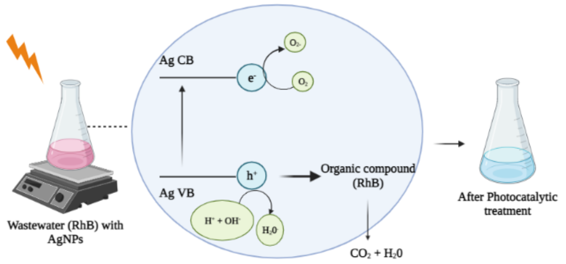



Figure 2. Mechanism of RhB degradation with AgNPs

## Effect of physical parameters on Rhodamine B removal

Effects of physical parameters on RhB decolourization, such as catalyst concentration, dye concentration, pH and radiation time, were studied. The results showed that an increased concentration of the catalyst results in an increase in active site for reaction. The reaction occurred on the surface of nanostructure, which increased RhB decolourization [25]. A maximum decolourization of 96.52 % was observed at a rate of 0.05 mg/L/min with a catalyst concentration of 2 g/L (Figure 3). Similar results were found with same catalyst in 75 min irradiation time [20]. Effective catalyst concentration was able to decolourize 99.87, 99.32 and 83.68 % at RhB concentrations of 5, 10 and 15 mg/L, respectively (Figure 4). Similarly, 100 mM of RhB was degraded 40 % in presence of UV illumination by using ZnO as photo catalyst [26]. In another study, 95 % degradation was obtained under UV light at irradiation time of 3 h using ZnO composite catalyst [18]. The pH plays a vital role in degradation study, as atmospheric pressure affects surface charge of the photo catalyst [27]. The effect of pH in range of 3 to 8 on RhB decolourization was studied (Figure 5). A maximum RhB decolourization of 99.32 % was observed at 0.1 mg/L/min rate. Thus, maximum decolourization was observed at slightly acidic pH. Similarly, nickel oxide based RhB degradation of 80.33 % was observed at pH = 10 [28]. Radiation time also plays a role in dye decolourization, as wavelength is responsible for activation and generation of radicals. A maximum decolourization of 99.32 % was observed at a reaction rate of 0.05 mg/L/min under visible solar light irradiation (Figure 6). Accordingly, 95 % decolourization was observed at 70 min of UV irradiation using ZnO as a nanocatalyst [29].

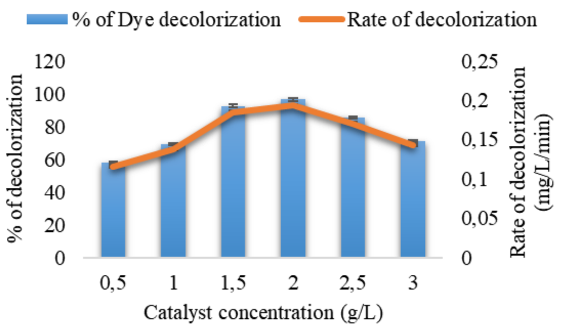



Figure 3. Effect of catalyst concentration on RhB decolourization

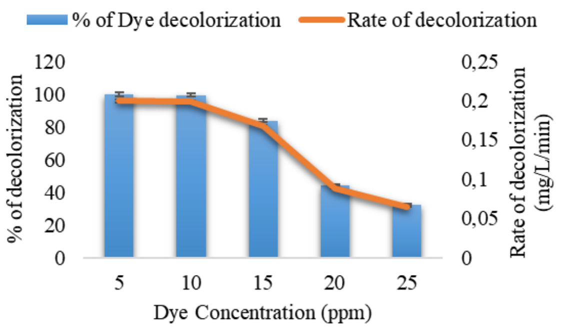



Figure 4. Effect of dye concentration on RhB decolourization

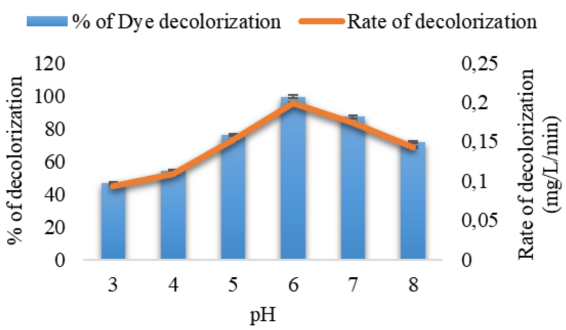



Figure 5. Effect of pH on RhB decolourization

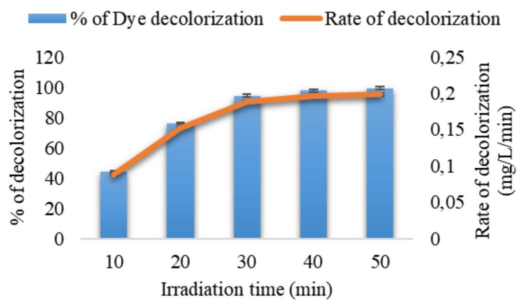



Figure 6. Effect of irradiation time on RhB decolourization

## Analytical techniques for RhB removal

After treatment with AgNPs, samples were centrifuged at 10000 x g for 10 min. The supernatant was taken for further analytical analysis.

*COD analysis*

Unknown samples were measured with standard COD graph. The percentage of COD reduction was calculated according to standard formula. Maximum COD reduction of 89.25 % was observed at the rate of 74.97 mg/L/min (Figure 7).

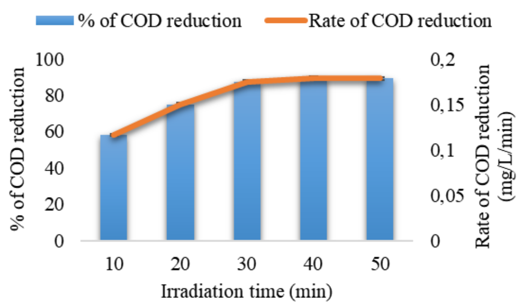



Figure 7. Effect of irradiation time on COD reduction

*HPTLC analysis*

HPTLC analysis showed different peaks with 0.56 and 0.58 retention factor ($R_f$) at a reaction time of 30 min. After that, this peak was removed at 50 min reaction time. The area unit (AU) was also decreased with irradiation time. The complete removal of peak of RhB at 50 min reaction indicates complete mineralisation of RhB from wastewater. The HPTLC graph is shown in Figure 8.

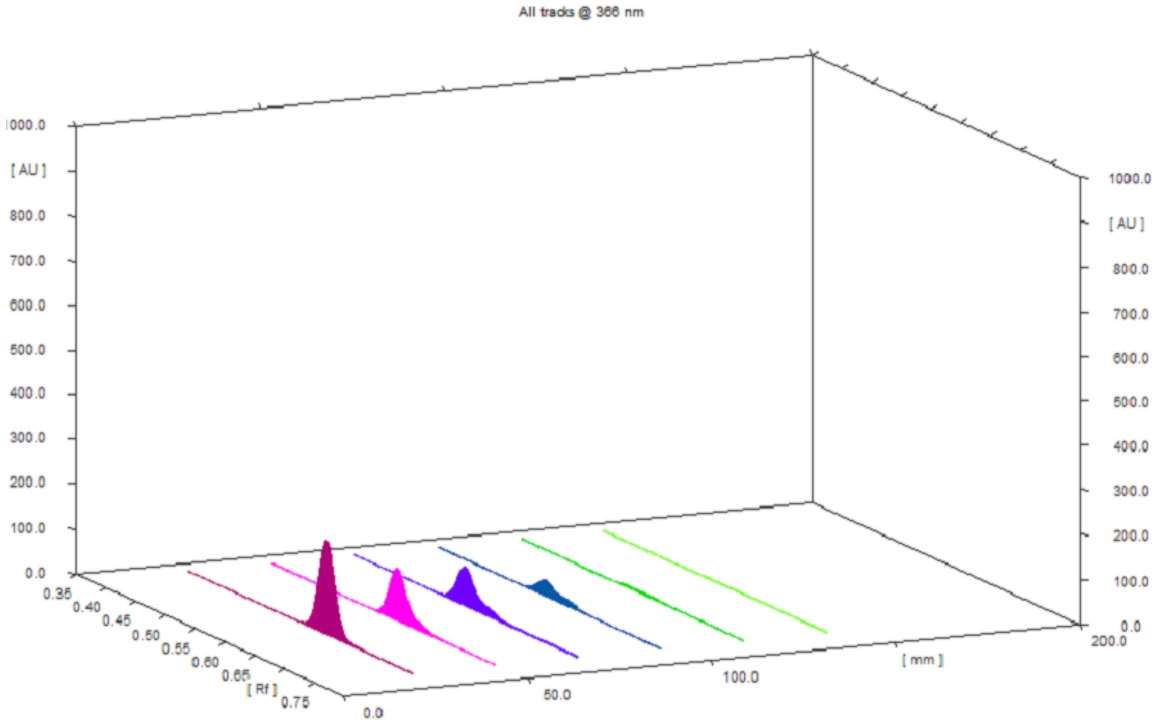



Figure 8. 3D graphic display of HPTLC analysis

## Toxicity study

The toxicity study confirmed that RhB was more toxic to the *Triticum aestivum* than the metabolites. The growth of *Triticum aestivum* was reduced in wastewater containing RhB due to toxicity of RhB. The treated effluent and distilled water show the similar growth of *Triticum aestivum.* Similar results were observed in [30]. The growth was enhanced in the treated effluent because the micronutrients and macronutrients required for growth were found in the treated effluent [31]. The germination percentage, radicle and plumule length are given in Table 1.

Table 1. Toxicity effect of RhB and treated effluent on *Triticum aestivum*

| | Distilled water | RhB (Control) | After AgNPs treatment |
|---|---|---|---|
| % Germination | 100 | 50 | 100 |
| Plumule length | 14.86 ± 0.15 | 7.33 ± 0.76 | 14.7 ± 0.26 |
| Radicle length | 11.6 ± 0.96 | 3.86 ± 0.9 | 9.93 ± 0.70 |

## CONCLUSION

Rhodamine B is a synthetic xanthene class of dye and has toxic properties. Nanoparticles-assisted degradation is an efficient method to remove toxic nature of RhB. AgNPs is an efficient catalyst for photocatalytic degradation. In the presence of solar light, the activated AgNPs is responsible for degradation of RhB. In optimization study, a maximum of 99.32 % decolourization was observed at a catalyst concentration of 2 g/L, pH = 6, a dye concentration of 10 ppm in 50 min irradiation time at a decolourization rate of 0.19 mg/L/min. The degradation was confirmed with COD reduction, UV-visible spectrophotometer and HPTLC analysis. Characterisation of AgNPs was performed with XRD. The toxicity analysis confirmed the lower toxicity of the RhB metabolites than original. It can be concluded that the RhB degradation using solar-assisted AgNPs is efficient for wastewater treatment. The AgNPs is an effective catalyst, less toxic, cost-effective and environmentally friendly.

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