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Azadirachta indica leaves extract assisted green synthesis of Ag-TiO_2 for degradation of Methylene blue and Rhodamine B dyes in aqueous medium

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Abstract: Aqueous pollution due to textile industry is an important issue. Photocatalysis is one of the methods used for eradication of dyes from textile industrial effluents. In this study, the synthesis, characterization and evaluation of photo catalytic activity of Ag-TiO_2 is reported. TiO_2 catalysts with 2, 4, 6 and 8% loading of Ag were prepared by green methods using *Azadirachta indica* leaves extract as reducing agent with titanium dioxide and silver nitrate as precursor materials. Prepared catalyst was characterized by advanced techniques and was used as catalyst for degradation of Methylene blue and Rhodamine B dyes. Deposition of Ag greatly enhanced the catalytic efficiency of TiO_2 towards degradation of dyes. Irradiation of catalyst excites electrons from conduction band of catalyst to valence band yielding an electron-hole pair. This electron-hole pair undergoes secondary reactions and produce $OH^•$ radicals. These active radicals take part in degradation of dyes. More than 90% dyes were degraded in 120 min. Photo catalytic degradation of Methylene blue and Rhodamine B followed Eley-Rideal mechanism which states that dye react in fluid phase with adsorbed oxygen.

Keywords: TiO_2; Ag-TiO_2; Methylene blue; Rhodamine B; photo degradation; Eley-Rideal mechanism

1 Introduction

Dyes and pigments are predominantly used in different industries and a reasonable amount of these compounds go to environment through industrial effluents. As these compounds are toxic and carcinogenic in nature, therefore, their impact on the environment is a major concern. Furthermore, these dyes impart color to aqueous body blocking the penetration of sunlight and dissolution of oxygen [1-3]. Thus, a number of physical and chemical techniques such as filtration, precipitation, coagulation, adsorption and oxidation have been pursued for elimination of these toxic compounds. Photocatalytic oxidation, which is one of the viable and developing methods utilized for destruction of toxic pollutants and dyes, has increased much research enthusiasm for late years. The photocatalytic oxidation technique has a number of preferences over traditional techniques, viz less energy requirement, no requirement for sludge disposal and complete degradation of pollutants [4-9]. TiO_2 has been broadly utilized as catalyst for photocatalytic oxidation of a wide scope of pollutants because of its low cost and high stability. However, the photocatalytic activity of TiO_2 has been restrained due two reasons; firstly, the rate of electron–hole pair recombination formed by irradiation is relatively high and secondly, it has wide band gap (about 3.2 eV) [10-14]. These restrictions can be overcome by modification in electronic band structure of TiO_2. This modification has been accomplished by addition of a substance like Ag that decreases the rate of recombination of electron–hole pair [15,16]. Although silver (Ag) is highly effective, however, it cannot be employed as photocatalyst because the recovery of Ag nanoparticles from reaction mixture is difficult. Immobilization of Ag nanoparticles on other substances like TiO_2 is technique to produce an efficient photocatalyst for aqueous phase degradation of pollutants. Immobilization of Ag nanoparticles on TiO_2 prevents the electron-hole pair recombination, thus

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enhancing the photocatalytic activity of TiO_2 [17-19]. Different strategies have been utilized for fabrication of Ag-TiO_2, however, green synthesis has received high consideration in which extract of plants is utilized as stabilizing and reducing agent. A number of plants have been used for green synthesis of nanoparticles [20-27].

In present study, Ag-TiO_2 is fabricated utilizing the aqueous extract of *Azadirachta indica L*, locally called as neem. The prepared Ag-TiO_2 was employed as photocatalyst for degradation of Methylene blue and Rhodamine B dyes.

2 Experimental

2.1 Materials

TiO_2 (Merck), $AgNO_3$ (Alfa Aesar), Methylene blue (Merck), Rhodamine B (commercial grade), *Azadirachta indica* leaves (Botanical garden, University of Agriculture Faisalabad, Pakistan) and distilled water were used in this study.

2.2 Synthesis of Ag-TiO_2

First, the dried leaves (20 g) of *Azadirachta indica* were boiled in distilled water for 2 h. Then, after cooling the mixture, the aqueous extract was separated by filtration and was used for synthesis of Ag-TiO_2. For synthesis of Ag-TiO_2, a 50 mL plant extract was added dropwise to a mixture containing a known amount of $AgNO_3$ and TiO_2 under continuous stirring. Afterward, the synthesized Ag-TiO_2 was filtered, washed and dried at 80°C for 12 h. Ag-TiO_2 catalysts with 2, 4, 6 and 8% Ag loading were prepared. The leaves of referred plant contain a variety of phytochemicals including flavonoids and phenolic components which are considered as reducing agent for reduction of Ag^{1+} to Ag [28-32].

2.3 Photocatalytic degradation experiment

The photocatalytic activity of Ag-TiO_2 was demonstrated with two different solutions of Methylene blue (λ_{max}= 660 nm) and Rhodamine B (λ_{max}= 554 nm) in a batch reactor. A 50 mL dye solution was taken in a reactor vessel. Then, a pre-weighed amount of photocatalyst was suspended in dye solution for 30 min in dark. Finally, the reaction mixture was irradiated with UV light. Reaction samples were withdrawn from the reactor after regular time intervals and were analysed using UV–visible spectrophotometer (U-2800, HITACHI, Japan). Equation 1 was used to calculate the degradation efficiency.

$$Degradation\ (\%) = \frac{A_o - A}{A_o} \times 100 \tag{1}$$

where A_o is the initial and A is the final absorbance at λ_{Max} of each dye. Effect of Ag loading, temperature and concentration on degradation of dyes was also investigated.

2.4 Reaction kinetics

The kinetics of present degradation study can be described by pseudo first order kinetics model in terms of Eley–Rideal (E-R) mechanism. This mechanism is described by Eq. 2 which transforms to Eq. 3 and Eq. 4 by considering constant pressure of oxygen and integration respectively.

$$Rate = -\frac{dC}{dt} = k_r O_{2\,(ads)} C \tag{2}$$

$$-\frac{dC}{dt} = kC \tag{3}$$

$$\ln\frac{C_o}{C_t} = kt \tag{4}$$

3 Results and discussion

3.1 Characterization

Phase investigation and crystallinity of synthesized Ag-TiO_2 was performed by XRD measurement with JDX-3532 Japan X-Ray Diffractometer and the results are given in Figure 1. The XRD pattern of TiO_2 is dominated with sharp and well-resolved peaks at 25°, 36°, 48° and 55° which correspond to (1-0-1), (0-0-4), (2-0-0) and (1-0-5) diffraction planes, respectively, of anatase structural phase (JCPDS# 21-1272). In spectrum of Ag-TiO_2, additional peaks at 2θ 38° and 44° can be observed corresponding to face cantered cubic unit cell of Ag [33-37].

Figure 2 shows the scanning electron micrographs of TiO$_2$ and Ag-TiO$_2$ recorded with JSM-5910 Japan Microscope. Micrographs show that particles of TiO$_2$ are spherical, uniform and homogeneous in morphology. Furthermore, it can also be noted that the particles are well dispersed and non-agglomerated. The Ag particles deposited on TiO$_2$ are also well dispersed. Uniformity and smoothness in shape and homogeneous nature of catalyst particles play an important role in reproducible catalytic activities.

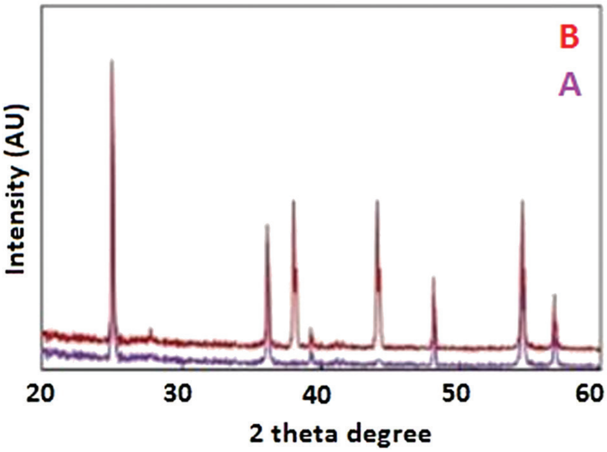

Figure 1: XRD pattern of TiO$_2$ (A) and Ag-TiO$_2$ (B).

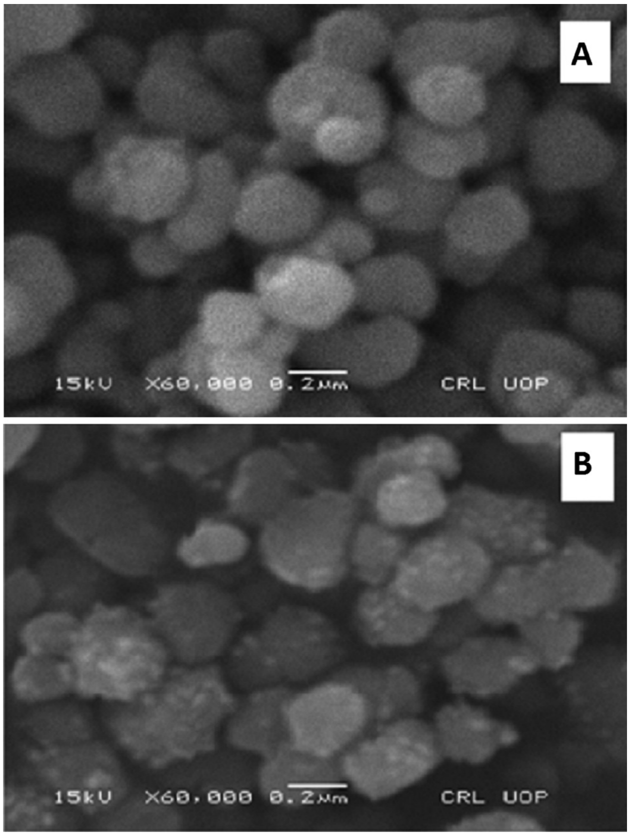

Figure 2: Scanning electron micrographs: (a) TiO$_2$, (b) Ag-TiO$_2$.

The particle size distribution of prepared catalysts measured with Analysette 22 Compact, Germany is given in Figure 3. The particle sizes ranges from 0.001 to 20 µm, however, 85% of the particles have particles size equal to or less than 2µm. The surface area measured with Quanta Chrome, Nova 2200e instrument was found as 58 m^{2}g^1 and 51 m^{2}g^1 for TiO$_2$ and Ag-TiO$_2$ respectively. The decrease in surface area by deposition of Ag on TiO$_2$ might be due to blockage of micropores by Ag nanoparticles.

3.2 Photocatalytic activity

Separate degradation experiments were performed with solutions of Methylene blue and Rhodamine B dye for evaluation of catalytic activity of biosynthesized Ag-TiO$_2$. This investigation was performed by suspending a 0.1 g 6% Ag-TiO$_2$ catalyst in 50 mL of 100 mg/L dye solution at 40°C and the resulting data in terms of C_t/C_o (C_o and C_t represents initial concentration of dye and concentration of dye at different time interval respectively) is given in Figure 4. This data is derived from measurement of absorbance at different time interval at λ_{max} of each dye. The data presented in Figure 4 indicates that fabrication of Ag enhanced the photocatalytic activity of TiO$_2$ for degradation of dyes. Similarly, the effect of Ag loading on photocatalytic activity of TiO$_2$ was also investigated. For this purpose, degradation of Methylene blue dye was studied with 2, 4, 6 and 8% loading of Ag under identical experimental

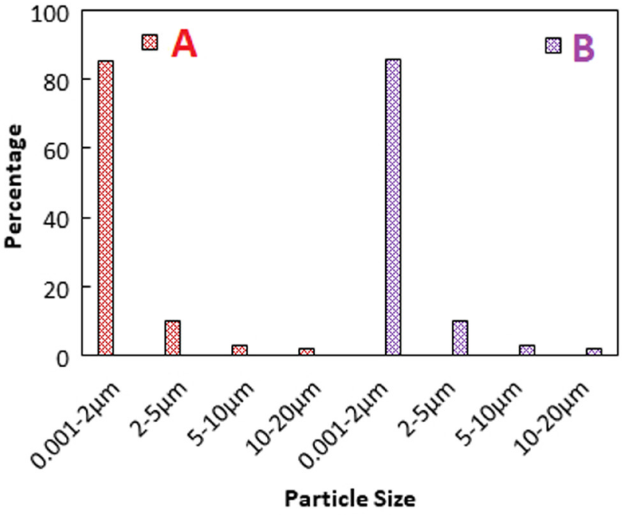

Figure 3: Particle size distribution of the catalysts particles: (A) TiO$_2$, (B) Ag-TiO$_2$.

conditions. It was found that 65, 84, 97 and 78% of dye degraded after 120 min of reaction with 2, 4, 6 and 8% Ag-TiO$_2$ as catalyst respectively. Higher concentration of Ag block the active center of TiO$_2$, therefore, the photocatalytic activity decreased at higher Ag loading. Hence, 6% loading of Ag was considered as optimum loading [38,39]. It is proposed that heterogeneous photocatalytic degradation reaction takes place through the creation of positive hole (h^+_{VB}) in valence band and photo excited electron (e^-_{CB}) in the conduction band of catalyst by irradiation. These positive holes and photo excited electrons produce OH$^\bullet$ radicals by a series of secondary reactions. These OH$^\bullet$ radicals are highly reactive species which attack on dye molecules and produce degradation products. The positive hole reacts with water molecule and produces OH$^\bullet$ radical and H$^+$. Similarly, superoxide anion is formed by reaction of electron with oxygen which produces OH$^\bullet$ radical by a series of further reaction. The proposed mechanism was confirmed by performing the degradation experiments with Methylene blue dye in absence of irradiation. The results showed that degradation efficiency [30] in absence of light was much lower in comparison to degradation efficiency under irradiation (97%). In another experiment, the degradation efficiency was observed as 48% in the presence of isopropyl alcohol, OH$^\bullet$ radical scavenger [40]. These results support the proposed mechanism. The proposed mechanism can be summarized as follows:

$$Catalyst + Irradiation \rightarrow h^+_{VB} + e^-_{CB} \tag{5}$$

$$h^+_{VB} + H_2O \rightarrow OH^{\cdot} + H^+ \tag{6}$$

$$e^-_{CB} + O_2 \rightarrow O_2^- \tag{7}$$

$$H^+ + O_2^- \rightarrow HO_2 \tag{8}$$

$$HO_2 \rightarrow H_2O_2 + O_2 \tag{9}$$

$$H_2O_2 \rightarrow OH^{\cdot} \tag{10}$$

$$OH^{\cdot} + Dye\ molecules \rightarrow Degradation\ products \tag{11}$$

The deposition of Ag reinforces the catalytic activities of TiO$_2$ because the Ag nanoparticles prevent the recombination of positive holes and photo excited electrons [36,37,41,42].

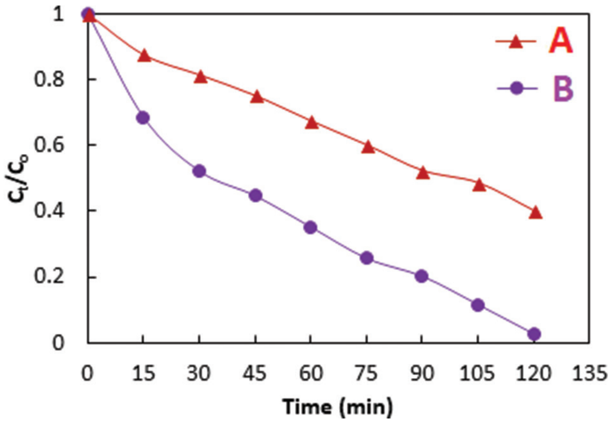

Figure 4a: Photo degradation of Methylene blue dye catalyzed by TiO$_2$ (A) and Ag-TiO$_2$ (B) in aqueous medium.

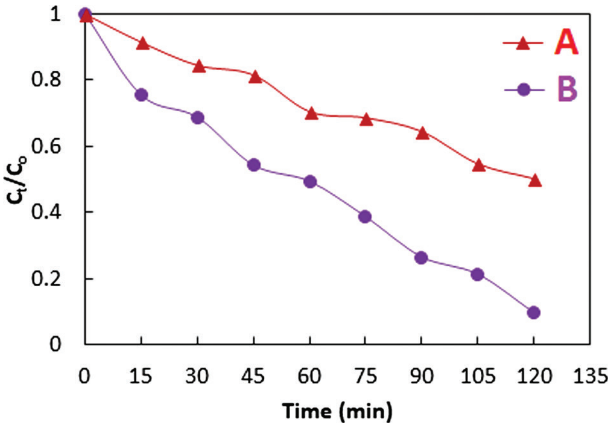

Figure 4b: Photo degradation of Rhodamine B dye catalyzed by TiO$_2$ (A) and Ag-TiO$_2$ (B) in aqueous medium.

3.3 Effect of temperature

Generally, temperature affects the rate of reactions, therefore, we explored the temperature dependence of present catalytic system. For this purpose, separate catalytic experiments were performed with 50 mL of 100 mg/L dye solution over 0.1 g of 6% Ag-TiO$_2$ at 30, 40 and 50°C. The results are given in Figure 5. It can be noted that temperature does not affect significantly the rate of reaction in present study. It is due the fact that photochemical reactions are generally less temperature dependent [4,5]. The experimental data at different temperatures was analysed according to pseudo first order kinetics equation (Eq. 4) and results are given in Figure 6. The slop of straight lines gives the rate constants which are given in Table 1. The activation energy determined

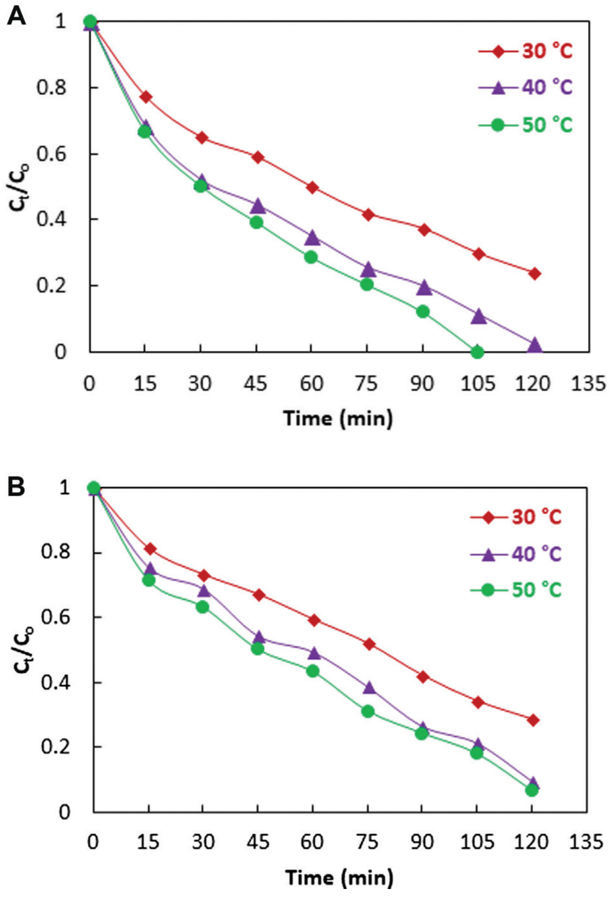

Figure 5: Ag-TiO$_2$ catalyzed photo degradation of (a) Methylene blue dye and (b) Rhodamine B dye, both at various temperatures.

by application of Arrhenius equation to rate constants at various temperature was found to be 27.1 and 20.4 kJ/mol for photo degradation of Methylene blue and Rhodamine B dye respectively.

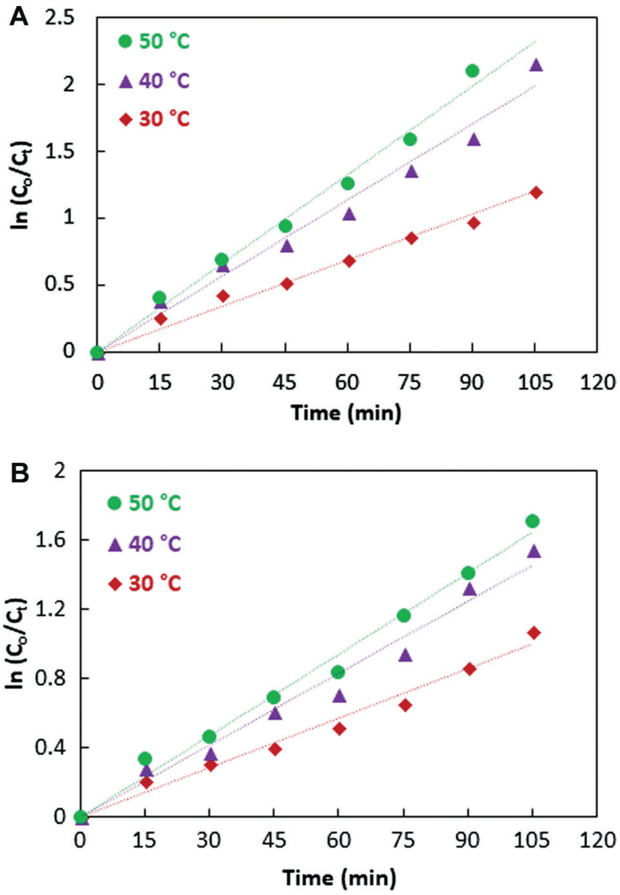

Figure 6: Kinetics of Ag-TiO$_2$ catalyzed photo degradation of (a) Methylene blue dye and (b) Rhodamine B dye, both at various temperatures.

Table 1: Rate constants of Ag-TiO$_2$ catalyzed photo degradation of Methylene blue and Rhodamine B dye at various temperatures.

T (°C)	Methylene blue		Rhodamine B	
	k (per min)	R^2	k (per min)	R^2
30	0.0141	0.984	0.0095	0.0981
40	0.0189	0.979	0.0139	0.976
50	0.0221	0.991	0.0157	0.991

3.4 Effect of initial concentration of dye

To investigate the effect of initial concentration of dye on rate of reaction, separate experiments were performed with 100, 200 and 300 mg/L as initial concentration of dyes. Photocatalytic degradation experiments for Methylene blue and Rhodamine B dye were performed at 40°C with 6% Ag-TiO$_2$ catalyst. It was found that 97, 79 and 60% of Methylene blue dye degraded with 100, 200 and 300 mg/L as initial concentration after 120 min of reaction respectively. Similarly, 90, 74 and 58% Rhodamine B dye degraded after 120 min of reaction with 100, 200 and 300 mg/L as initial concentration respectively. The experimental data with various initial concentration of dyes was analysed according to first order kinetic equation (Eq. 4) and the results are given in Figure 7. The rate constants determined from the slops of straight lines in Figure 7 are given in Table 2. The data listed in Table 2 shows that rate constants decreases with increase in initial concentration of dye.

It can be noted that increase in concentration causes a decrease in degradation efficiency, which is due to two reasons. Frist, the concentrated solution becomes more intense in colour which results in hindrance to penetration of radiations to the catalyst surface. Secondly, as other experimental conditions are same, so the ratio of number of $OH^•$ radicals to number of molecules of dye decreases with increase in concentration, hence, the rate of reaction decreases with increase in initial concentration of dye [4,5,36,37,43,44].

3.5 Effect of pH

pH of reaction mixture is also an experimental parameter that affects the photo degradation efficiency of dyes. The surface charge of titania changes with variation of solution pH and changes the catalytic activity of TiO_2 particles. The surface of TiO_2 becomes positive and negative in acidic and alkaline condition respectively. As both Methylene blue and Rhodamine B dyes are cationic dyes therefore, the alkaline condition favors the adsorption of these dyes on TiO_2 surface. Furthermore, the $OH^•$ radicals are easier to be generated in alkaline solution due to oxidation of OH ions, thus, the degradation efficiency increases with pH [2,45-50]. Therefore, both Methylene blue and Rhodamine B dyes have shown to degrade more at pH 10. Other researchers have also reported similar trends [36,37,51,52].

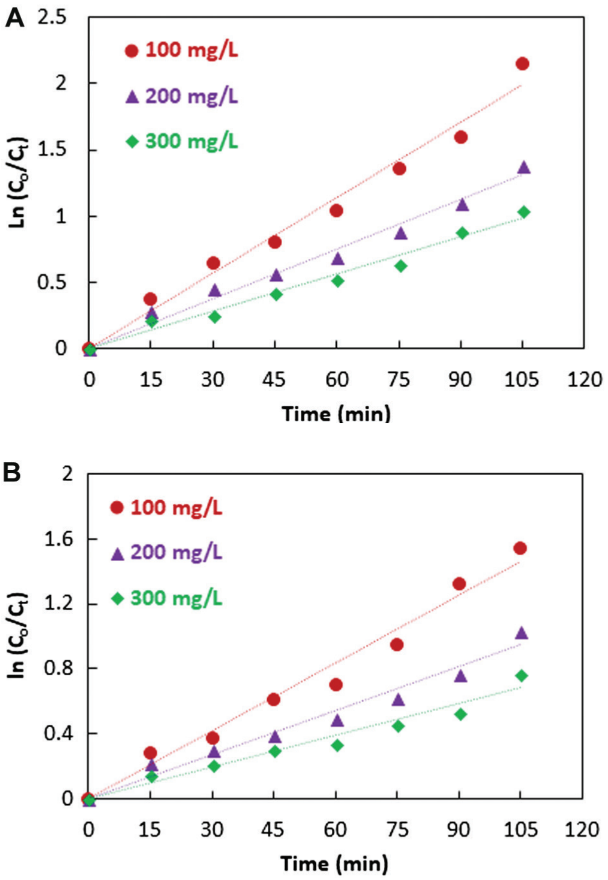

Figure 7: Kinetics of Ag-TiO_2 catalyzed photo degradation of (a) Methylene blue dye and (b) Rhodamine B dye, both with various initial concentrations.

Table 2: Rate constants of Ag-TiO_2 catalyzed photo degradation of Methylene blue and Rhodamine B dye with various initial concentrations of dyes.

Conc. (mg/L)	Methylene blue		Rhodamine B	
	k (per min)	R^2	k (per min)	R^2
100	0.0189	0.979	0.0139	0.976
200	0.0125	0.979	0.0091	0.969
300	0.0095	0.981	0.0068	0.959

4 Conclusions

Ag-TiO_2 was successfully fabricated by environmentally friendly and low cost green method using *Azadirachta indica* leaves extract as reducing agent and titanium dioxide and silver nitrate as precursor materials. The photo catalytic activities of prepared particles were evaluated by degrading Methylene blue and Rhodamine B dyes under UV irradiation. The 6% Ag-TiO_2 exhibited the best catalytic activity for degradation of Methylene blue and Rhodamine B dyes. More than 90% dyes were degraded in 120 min. It was found that there was no loss in catalytic efficiency of prepared Ag-TiO_2 catalyst after recycling it for two times. Photocatalytic degradation of Methylene blue and Rhodamine B followed Eley-Rideal mechanism which states that dye react in fluid phase with adsorbed oxygen.

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