



## Photocatalytic Degradation Study of Rhodamine-B by Green Synthesized Nano TiO<sub>2</sub>†

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In present investigation, TiO<sub>2</sub> nano particles synthesized by green route using titanium isopropoxide precursor and *Azardica indica* leaf extract were used for the photocatalytic degradation of Rhodamine-B. The green synthesized nano TiO<sub>2</sub> were characterized by X-ray diffraction spectroscopy, particle size distribution, Fourier transform infrared and scanning electron microscopy. Photocatalytic degradation was conducted in batch experiments, wherein the effect of process parameters such as photo catalyst concentration, pH and contact time on dye degradation rate under UV irradiation was studied. The extent of degradation was quantized by measuring the absorbance of samples by UV-visible spectrophotometer. The nano TiO<sub>2</sub> synthesized showed the effective degradation of Rhodamine-B. The degradation kinetics was also studied.

**Keywords:** Photocatalytic degradation, Nano TiO<sub>2</sub>, Green synthesis, Rhodamine-B.

### INTRODUCTION

The treatment of industrial wastewater is a major global concern due to increased level of pollution and scarcity for the pure water. The industries such as textiles, chemicals, mining *etc.* contribute to the greater extent to the water pollution as the wastewater coming from these industries contain heavy metal ions and organic materials such as dyes which causes bad influence to human beings and environment. Dyes in wastewater are the major concern as they are the source for aesthetic pollution and cause perturbations in aquatic life [1]. Many of these dyes are toxic, carcinogenic, mutagenic, or even stable to biological degradation [2]. Wastewater treatment methods such as coagulation, adsorption on activated carbon, ultrafiltration, reverse osmosis, ion exchange and oxidation with peroxide are efficient nevertheless, they do not destruct the pollutant molecule [3]. This gap is filled by the advanced oxidation processes (AOP) which has added advantages of conduction of degradation under ambient conditions and lead to complete mineralization of organic carbon. Photocatalytic degradation is one of the examples of advanced oxidation process, which can oxidize a wide variety of toxic and persistent organic compounds to harmless inorganics such as mineral acids, carbon dioxide and water [4]. The mechanism of the photocatalytic degradation is based on generation of an

electron/hole pair by the light source. In recent year, new nanomaterials are produced in homogeneous and heterogeneous form for the photocatalytic degradation of dye as these materials show a high efficiency and a high surface-to-volume ratio along with high surface energy [5]. Nano TiO<sub>2</sub> semiconductor photocatalysts is the most suggested catalyst owing to its stable, harmless and inexpensive properties. It also activated with ultraviolet (UV) light. TiO<sub>2</sub> has been used for the degradation of different kinds of compounds. Rhodamine-B (RhB) as model compound because it shows a strong absorption band in the visible region of the electromagnetic spectrum (555 nm) and this dye is characterized by having a high stability at different pH values. Rhodamine-B is a dye that belongs to a class of compounds called xanthenes, with m.w. 479.02 g mol<sup>-1</sup> and a formula C<sub>28</sub>H<sub>31</sub>N<sub>2</sub>O<sub>3</sub>Cl. It is stable in aqueous solution, used as a dye in textiles, food, cosmetics and as analytical reagent during the determination of metals in solution, especially alkali and alkaline earth metals but can cause aesthetic pollution in the aquatic environments showing high resistance to biological and chemical degradation [6].

There is a development of experimental processes for the synthesis of nanoparticles of different sizes, shapes and controlled dispersity. With the development of new chemical or physical methods, the concern for environmental contaminations are also increased as the chemical procedures involved

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in the synthesis of nanomaterials generate a large amount of hazardous by-products. Thus, there is need for “green chemistry” that includes a clean, non-toxic and environmental friendly method of nanoparticle synthesis [7]. The plant-mediated biosynthesis of nanoparticles is advantageous over chemical and physical methods because it is cost-effective and environment-friendly method, where it is not necessary to use high pressure, energy. TiO<sub>2</sub> nanoparticles are synthesized using *Lactobacillus* sp. and *Sachharomyces cerevise* possessed antibacterial and antifungal properties [8]. Use of plant extracts for nanoparticle synthesis can be advantageous over biological processes because it eliminates the elaborate process of maintaining cell cultures and can also be suitably scaled up for large-scale nanoparticle synthesis [9]. Recently, green TiO<sub>2</sub> nanoparticles have been synthesized using plant extracts like *Nyctanthes arbor-trists*, *Catharanthusroseus*, *Jatropha curcas* L and *Annonasquamosa* [10-13]. There are several studies available for degradation of Rhodamine-B where in TiO<sub>2</sub> films [14-17], sand supported TiO<sub>2</sub> [18], aqueous suspension of TiO<sub>2</sub>, TiO<sub>2</sub>-coated silica and TiO<sub>2</sub> coated silicone sealant [19-21] are used. The objective of present study is to investigate the effect of operating parameters on the photocatalytic degradation of Rhodamine-B by green synthesized nano TiO<sub>2</sub>.

## EXPERIMENTAL

Analytical grade titanium isopropoxide and ethanol were procured from Spectrochem Pvt. Ltd. Mumbai, India for synthesis of nano TiO<sub>2</sub>. The healthy leaves of neem were collected from RVCE campus, Bangalore, Karnataka, India. Rhodamine-B dye was obtained from S.D. Fine Chemicals, Bangalore. UV source was obtained using a Phillips 12 w mercury vapour lamp capable of producing a minimum wavelength of 253 nm.

**Green synthesis of nano TiO<sub>2</sub>:** The collected neem leaves were gently washed to remove dust. Leaves were shade dried at room temperature for about 15 days under dust free condition. Dried leaves were cut into fine pieces, grinded and sieved to get the finest powder. Dried leaves (3 g) were mixed with 50 mL of ethanol and extracted under reflux condition at 50 °C. After 5 h, the ethanolic leaf extract was obtained by filtering the mixture through Whatmann No. 1 filter paper and either directly used in the synthesis of titanium dioxide nanoparticles or stored at 4 °C for further experiments.

For the synthesis of titanium dioxide nanoparticles, the Erlenmeyer flask containing 0.4 M of titanium tetraisopropoxide in ethanolic leaf extract was reacted under stirring at 50 °C. After 4 h of continuous stirring, the formed titanium dioxide nanoparticles was acquired by centrifugation at 10000 rpm for 15 min. Then the centrifuged particles were washed with ethanol and again subjected to centrifugation at 5000 rpm for 10 min. Separated titanium dioxide nanoparticles were dried and grinded to calcinate at 500 °C in muffle furnace for about 3 h. The calcined titanium dioxide nanopowder was used for further analytical techniques.

**Photocatalytic experiments:** Dye solution of 10 ppm was used throughout the experiment. Solutions were prepared by dissolving the desired amount of compound in distilled water. The photocatalytic degradation was carried out under UV

sources, visible light and no light conditions. The degradation was carried out in a batch reactor with a magnetic stirrer. In all cases during the photolysis experiments, the slurry composed of the dye solution and catalyst was placed in the reactor and stirred magnetically with simultaneous exposure to UV light. The samples were withdrawn at periodic intervals from the reactor and centrifuged to assess the extent of decolourization and degradation. The kinetics of the photocatalytic degradation is changed by varying the levels of catalyst loading. The kinetics of the degradation reaction is slow and attains equilibrium without completely degrading the dye. To obtain the 100 % degradation at a faster rate, higher loadings of catalyst is required. Hence the dyes were degraded at various catalyst loadings and tested for their efficiency.

**Effect of catalyst loading on degradation of the dyes:** 100 mL of the Rhodamine-B was taken in a 500 mL beaker and 25 mg of TiO<sub>2</sub> was added to it. It was then kept in the UV light source. An initial sample was collected at zero time and its concentration found. Next the samples were taken at uniform intervals of 30 min. The concentration of the samples was found and its effectiveness was found. The catalyst loading of 25, 50, 75, 100, 150 and 200 mg was studied.

**Effect of irradiation time on degradation of the dyes:** The effect of irradiation time on the rate of photocatalytic degradation of Rhodamine-B was studied after selecting the optimum dosage of the photocatalyst. The irradiation time varied from 5 to 240 min with intervals of 30 min. 100 mL of the dye solution containing optimum amounts of the photocatalyst was exposed to UV light at room temperature. After every 30 min, a small aliquot of the sample was withdrawn, centrifuged and the UV-visible spectra were recorded for each sample.

**Effect of pH on the degradation of the dyes:** The mother solutions of varying pH are first prepared and then the photocatalyst reaction takes place. pH of 5, 7, 9, 10, 11 and 13 was considered for study. The pH was then measured using a pH meter. 100 mL of its mother solution is taken in a beaker and 150 mg of TiO<sub>2</sub> is added and kept in the UV source.

**Detection method:** The present work involves synthesis and application of synthesized nano TiO<sub>2</sub> particles for dye degradation. The synthesized nano TiO<sub>2</sub> particles have to be characterized and are to be tested for dye degradation feasibility.

**Characterization of the photocatalyst:** Crystal phase identification of titanium dioxide nanoparticles were characterized by powder X-ray diffraction using a Panalytical X Pert PRO Diffractometer with K<sub>α</sub> radiation ( $\lambda = 1.5406 \text{ \AA}$ ). Titanium dioxide nanoparticles was loaded on a 0.4 mm Kapton capillary tube, sealed at both ends under N<sub>2</sub> in a glove box and mounted on standard goniometer heads to determine the grain size and phase. A beam of 21 keV (wavelength = 0.5904 Å) was used. The beam size was 3 mm (h) × 1 mm (r). Mythen strip detector was used to collect the data for 5 min. The particle size and morphology of the titanium dioxide nanoparticles were examined using Scanning electron microscopic observations. SEM measurements were performed on a JEOL JSM 6390 instrument operated at an accelerating voltage at 15 kv. Fourier transform infrared (FTIR) spectra of the samples were measured using Perkin Elmer spectrum one instrument in the

diffuse reflectance mode at a resolution of 4 cm<sup>-1</sup> in KBr pellets. Powder samples for the FTIR were prepared similar to powder diffraction measurements. The FTIR spectra of synthesized TiO<sub>2</sub> nanoparticles taken were analyzed, which discussed for the possible functional groups for the formation of nanoparticles. Almost all particulate materials in contact with a liquid acquire an electronic charge on their surfaces. Zeta potential is an important and useful indicator of this charge, which can be used to predict and control the stability of colloidal suspensions.

**Photocatalytic degradation studies:** A systronics UV-visible spectrophotometer was used for measuring changes in absorbance and thus the concentration at different time intervals at 555 nm. The concentrations of the solution was found at various times of intervals and tabulated. From the concentration of the samples, the % degradation of the dyes for various time intervals was obtained. The equation for finding the % degradation is given by eqn. 1:

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

A graph of % degradation vs. time was then plotted and the results were observed.

## RESULTS AND DISCUSSION

The formation of titanium dioxide nanoparticles as well as their morphological dimensions in the SEM study demonstrated that the average size was from 15 to 100 nm with inter-particle distance (Fig. 1).

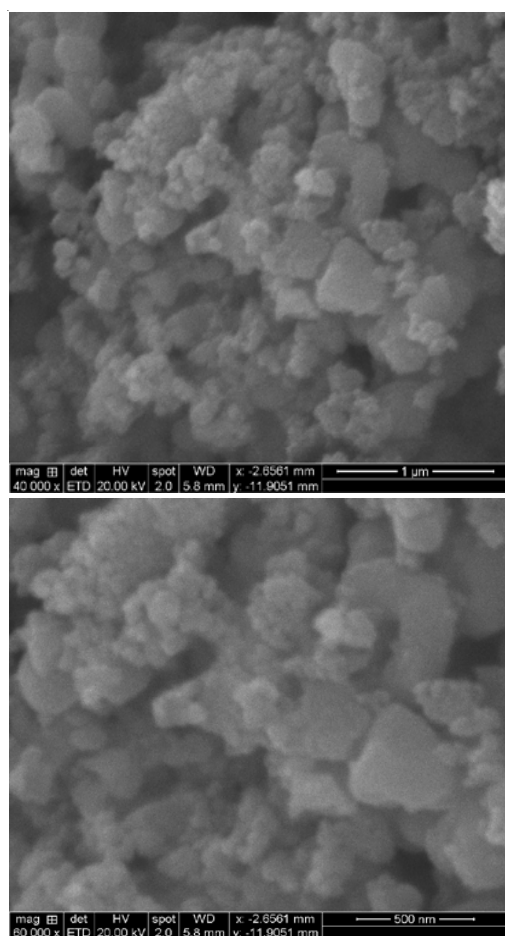


Fig. 1. SEM micrographs of TiO<sub>2</sub> nanoparticle

**XRD analysis:** The powdered sample was used by a Cu-X ray diffractometer for confirming the presence of TiO<sub>2</sub> and analyse the structure. The graph showed main peaks corresponding to 2θ values of 25.23°, 37.99°, 47.90°, 54.58° and 62.48° in the multi-plot shown in Fig. 2. The location of the peaks was compared to literature values (JCPDS Data, Ref. code-00-021-1272) and the presence of titanium dioxide anatase particles was confirmed. The XRD of dried and powdered titanium dioxide nanoparticles is shown in Fig. 2. The average size of the particles was calculated using Debye-Scherrer's formula shown in eqn. 2.

$$d = \frac{k \times \lambda}{\text{FWHM} \times \cos(\theta)} \quad (2)$$

where: d = average size of the particles, in metres, k = a constant which usually ranges from 0.85 to 1. The optimum value is 0.89, λ = is the wavelength used for analysis, for Cu it is 1.541 Å. FWHM = Full width of half maximum, in radians; θ = is the half angle of the peak.

The average diameter of the titanium dioxide particles was calculated to be 20 nm.

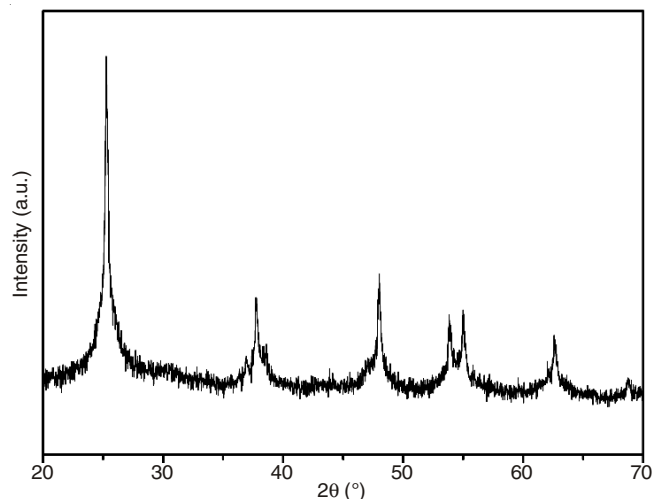


Fig. 2. XRD pattern of TiO<sub>2</sub> synthesized using neem leaf extract

**Particle size distribution:** The particle size distribution was determined by Zetatrac NPA-152 Microtrac. Histograms, from the nanotracer analyzer, representing particle size distribution of the synthesized TiO<sub>2</sub> are shown in Fig. 3. Approximately 90 % of the particles are within 100 nm.

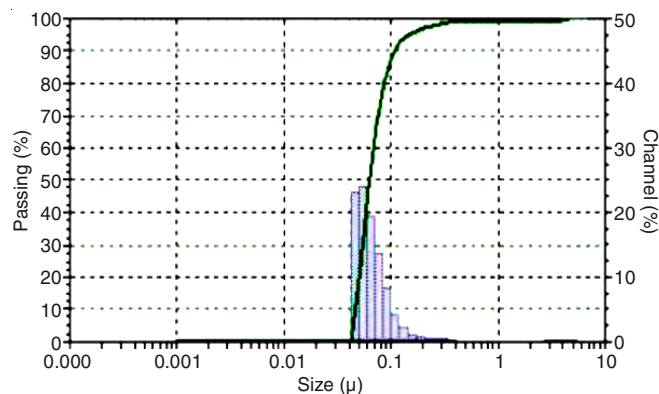


Fig. 3. Particle size distribution of synthesized TiO<sub>2</sub> nanoparticles

**FTIR:** FTIR spectroscopy was conducted to identify the biomolecules responsible for capping of the bioreduced TiO<sub>2</sub> nanoparticles synthesized using plant extract. Fig. 4 shows the synthesized TiO<sub>2</sub> nanoparticles using neem leaves extract. Where the absorption peaks were located at 714 (Ti–O–O bond), 1076 (C–N stretch aliphatic amines 1172 (C–O stretching vibrations in alcoholic groups), 1642 (N–H bend bond) and 3426 (O–H stretching due to alcoholic group).

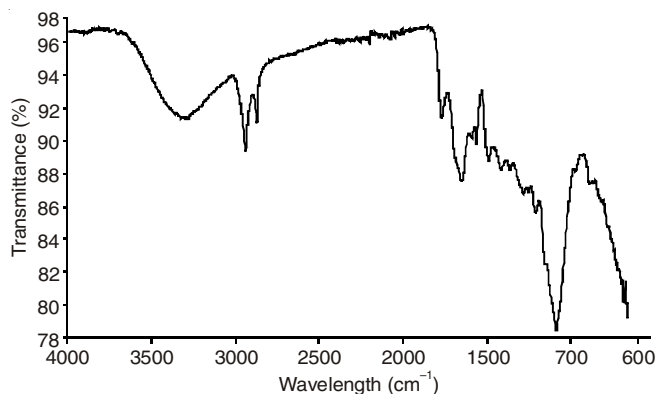


Fig. 4. FTIR spectra of the TiO<sub>2</sub>-nanoparticles

**Photocatalytic degradation:** The photocatalytic reaction is conducted in various light conditions *i.e.* without light, with UV source and using visible source. There was no much degradation of dyes in darkness. From the Fig. 5 it is clear that Rhodamine-B can be degraded best using UV light. Hence it can be said that Rhodamine-B requires high energy light source for proper UV light to degrade it because the energy of the light in the visible region is not enough to cause degradation.

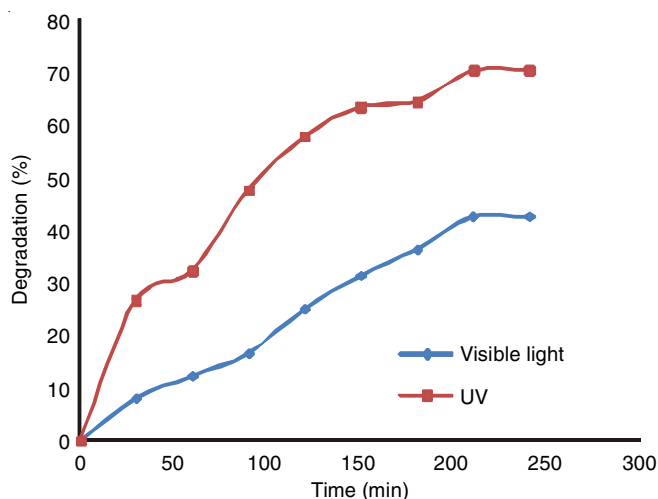


Fig. 5. Effect of light source on photodegradation of Rhodamine-B with 150 mg of TiO<sub>2</sub>

**Effect of catalyst loading on degradation of dyes:** The degradation of Rhodamine-B increases with increase in catalyst loading. From Fig. 6, it is clear that Rhodamine-B degradation increases until the amount of catalyst reaches to 150 mg.

At this point, the increase in the degradation decreases. From literature, it is identified that as the quantity of adding catalyst is increased it reaches some saturation at one point and there will be no increase further degradation. 150 mg of TiO<sub>2</sub> was used as the optimum value.

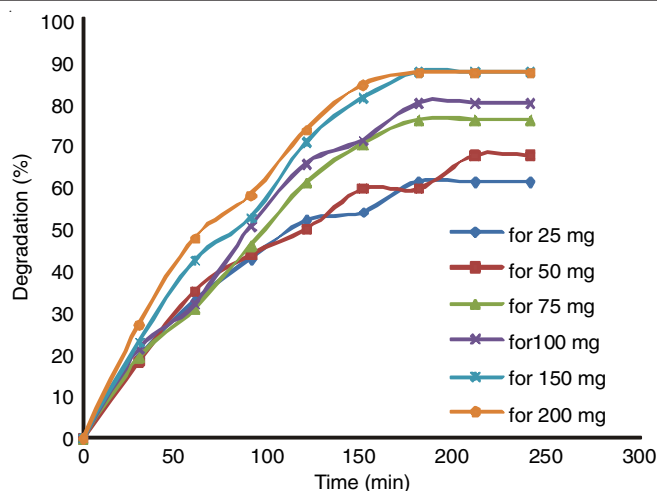


Fig. 6. Combined effect of catalyst loading on degradation of Rhodamine-B

**Effect of irradiation time on degradation of dyes:** It was observed that maximum degradation of the dye occurred in 200–240 min of irradiation. Beyond 240 min, the degradation was found to be negligible (Fig. 7). From the results obtained it can be concluded that the photocatalytic approach promotes the decline of chromophore peaks in the dye molecule in 240 min reflecting that the de-ethylation of Rhodamine-B is the main reaction occurring at the surface.

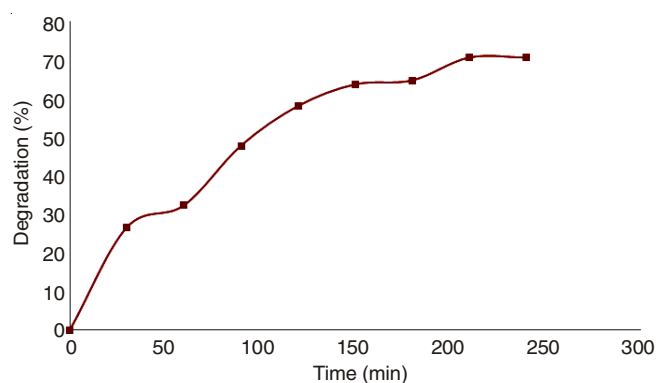


Fig. 7. Effect of irradiation time on photodegradation of Rhodamine-B with 150 mg of TiO<sub>2</sub>

**Effect of pH on degradation of dyes:** At low pH the degradation is lower than neutral, as the pH increased, there is an increase in the degradation upto pH 10 (Fig. 8). The degradation decreases as the pH increased to 11 and its less at pH 13. As pH becomes acidic, the acid reacts with TiO<sub>2</sub> catalyst, decomposing it and forming respective salts. Hence as pH becomes acidic, rate of degradation increases and efficiency decreases. When the pH becomes basic, the hydroxide ions make dyes to degrade up to a certain pH level. After this pH level the hydroxide ions react with TiO<sub>2</sub> forming titanium hydroxide.

**Kinetic studies:** The modified Langmuir-Hinshelwood's reaction kinetics model for heterogeneous reaction systems consisting of a solid and liquid phase reaction was found to match the requirements (Fig. 9). It has also been proposed in literature that the Langmuir-Hinshelwood's modified model is followed by kinetics of photodegradation reaction. According to the model, the reaction occurs in a pseudo first order reaction. The modified model is given by the eqn. 3:

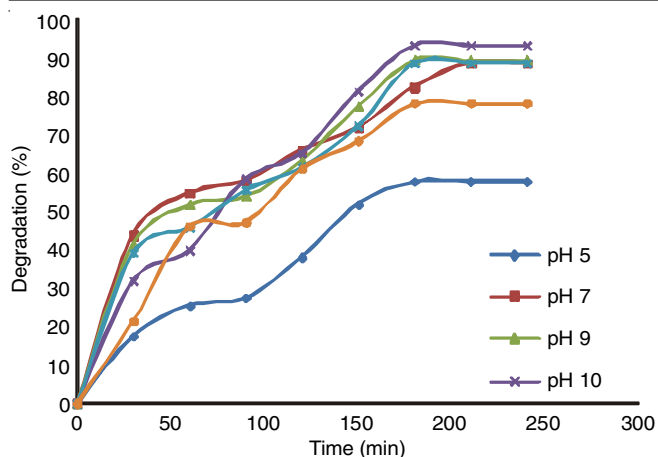


Fig. 8. Effect of pH on the degradation of Rhodamine-B with catalyst loading of 150 mg

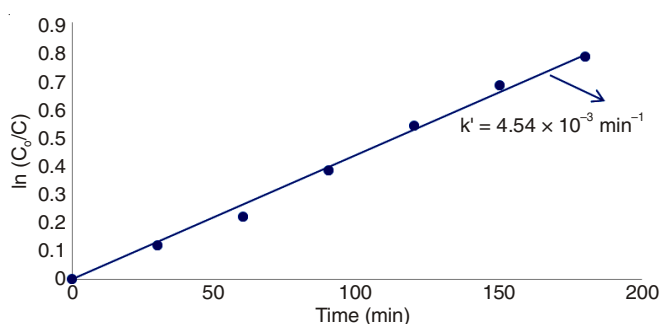


Fig. 9. Kinetics of degradation of Rhodamine-B using 150 mg of TiO<sub>2</sub> for a 10 ppm solution (modified Langmuir-Hinshelwood model)

$$\text{Rate of reaction } -\frac{dc}{dt} = \frac{krkeC}{1+KeC} \quad (3)$$

Eqn. 3 is called first order differential equation and the solution is obtained by integrating the differential equation, thus the solution for the above equation is given by eqn. 4:

$$t = \frac{1}{krke} \ln \frac{C_0}{C} + \frac{1}{kr} (C_0 - C) \quad (4)$$

Here the concentrations of the dyes are very small as these are in ppm ranges. Hence, the second term on the right hand side of the above equation is neglected. The reduced form is given by eqn. 5:

$$t = \frac{1}{krke} \ln \frac{C_0}{C} \quad (5)$$

Eqn. 6 is obtained from rearranging eqn. 5:

$$\ln \frac{C_0}{C} = t kr ke \quad (6)$$

Eqn. 7 was obtained by substituting  $kr ke = k'$  in eqn. 6. We get:

$$\ln \frac{C_0}{C} = tk' \quad (7)$$

where  $k'$  is the overall rate constant of the reaction and can be found by finding the slope of the line drawn between time vs.  $\ln(C_0/C)$ .

The degradation of both the dyes gives degradation data of both the dyes with their respective catalyst loadings, 150

mg of TiO<sub>2</sub> for 100 mL and 10 ppm solution of Rhodamine-B. The kinetic data was plotted with time is the abscissa and  $\ln(C_0/C)$  in the ordinate. From the graph obtained, it is clear that both the dyes follow the Langmuir-Hinshelwood model of kinetics with a pseudo-first order rate of reaction for Rhodamine-B is  $4.54 \times 10^{-3} \text{ min}^{-1}$ .

## Conclusion

Nano TiO<sub>2</sub> was synthesized by green route by neem leaves which give promising results in photocatalytic degradation of Rhodamine-B in the presence of UV light. With increase in the amount of catalyst, the degradation rate also increased. When the loading reaches certain point, the increase in the degradation decreases and reaches saturation. Optimum pH to be maintained was found to be 10. The system follows the Langmuir Hinshelwood modified model for Heterogeneous reaction between a solid and liquid phase. The overall rate constant of the degradation for Rhodamine-B is found to be  $4.54 \times 10^{-3} \text{ min}^{-1}$ .

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