



Pt/Al₂O₃ Catalyzed Decolorization of Rhodamine B Dye in Aqueous Medium

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ABSTRACT

In this study 5% Pt supported on alumina (Pt/Al₂O₃) was used as catalyst for decolorization of Rhodamine B dye in aqueous medium in an agitated slurry batch reactor. Influence of different reaction parameters like temperature, time of reaction, speed of agitation, catalyst dose and initial concentration of Rhodamine B dye on decolorization was investigated. About 60-80% decolorization was noted in 120 minutes at temperature 303-323K. 550-908 were observed as turnover frequencies (TOF) for 100-300 ppm solution of Rhodamine B dye. Catalyst was tested for re-usability. It was found that fresh and used catalyst has almost same catalytic performance. The decolorization reaction followed the Langmuir-Hinshelwood type of mechanism, where adsorption of Rhodamine B at surface of catalyst followed Freundlich adsorption isotherm. Curve Expert software was used for kinetic analyses of the experimental data. 15.36 kJmol⁻¹, 20.14 kJmol⁻¹, -5.7 kJmol⁻¹, 34.12 Jmol⁻¹ and -4.59 kJmol⁻¹ were determined as apparent activation energy, true activation energy, enthalpy of adsorption, entropy and Gibbs free energy respectively.

Keywords: Rhodamine B, catalytic decolorization, Langmuir-Hinshelwood mechanism, Freundlich adsorption isotherm, turn over frequency

1. INTRODUCTION

Textile industries produce a huge amount of toxic and non-biodegradable dye effluents. These dye effluents release toxic and potential carcinogenic substances into the aqueous phase which cause severe environmental pollution problems [1]. The disposal of these industrial dye effluents has attracted extensive attention in the field of water pollution prevention and cure. Rhodamine B (RhB), an important representative of xanthene dyes is one of the

organic dyes which is extensively involved in coloring paper, laser dye and textile industry due to its high stability. It is highly water soluble and stable dye and is found as a reddish violet powder. It comes under the trade name of D & C Red Number 19. Its Color Index number is 45170:1. The effluents of these industries causes water pollution with Rhodamine B dye. The existence of this hazardous dye in the waste water causes serious environmental problems

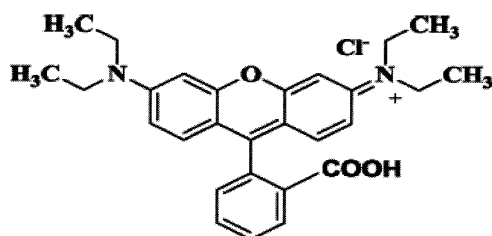
[2, 3]. It causes irritation of the skin, eyes, and respiratory tract in human being and animals. Therefore, the elimination of Rhodamine B dye from aqueous system is considered as one of the important challenges in the recent years using simple and low costs process [4, 5].

Various traditional physical and chemical techniques have been attempted for the removal of dyes/pollutants from wastewater such as physical absorption [6], chemical degradation [7], biological degradation, coagulation by chemical agents [8], and oxidation by Fenton and hypochlorite methods [9]. However, these methods are less attractive due to long time requirement, high operational costs and production of the secondary pollution, since solid wastes would be produced in these processes, which can bring another environmental problem of sludge treatment and disposal. Therefore great attention has been given to different alternatives for the removal of Rhodamine B dye from wastewater.

The wet oxidation (WO) process is one of the most convenient, economically and technologically viable techniques for this purpose [10]. Wet oxidation is the oxidative degradation of dye in aqueous solution by means of oxygen at elevated temperatures (398-593 K) and pressures (0.5-20 MPa). Due to high temperature and pressure, high equipment and operational costs are inevitable, which can be lowered by adding a suitable catalyst either homogenous or heterogeneous type, referred as catalytic wet oxidation (CWO). Several homogeneous catalysts like Co(dimeth-

ylglyoximato)(SO₃)₂³⁻ complex [11], Al(III) phthalocyaninetetrasulfonate³⁻ complex [12] and Co(III) dimethylglyoximate complex [13] exhibit good performances for different waste water treatments, however the metal ions left in the treated water is also a pollutant, which requires additional costly separation process [14]. The problem of this second contamination can be overcome by heterogeneous catalysts and hence this process has gained much attention. Heterogeneous catalytic wet oxidation is more promising process for the waste water treatment, using solid supported/unsupported metals/metal oxides as heterogeneous catalysts; where oxygen, ozone, hydrogen peroxide, or a combination can be used as the oxidative agent [15-17]. Tang et al., [18] have reported TiO₂/C catalyzed degradation of Rhodamine B dye in aqueous medium. About 80% dye was degraded in 60 minutes at 323K. Gan and coworkers [19] have reported almost complete degradation of 5ppm solution of Rhodamine B at 323 K in the presence of silica supported iron catalyst. Similarly Das and Bhattacharyya [20] have employed MnO₂, NiO and ZnO as heterogeneous catalysts for degradation of 1 ppm solution of Rhodamine B dye in aqueous medium.

Heterogeneous wet catalytic process of wastewater has many advantages like easy recovery, regeneration and reuse of the catalyst. Considerable efforts have been devoted to the investigation of Pt-based heterogeneous catalysts to achieve high catalytic performances and utilization efficiencies [21-28].



Molecular structure of Rhodamine B

Searching an environmental friendly chemical process for removal of dyes from aqueous system has been an active topic. In this paper, we have chosen Rhodamine B (Rh B) as a model pollutant for the catalytic decolorization/degradation tests. This paper is, therefore, aimed to evaluate the catalytic efficiency of Pt/Al₂O₃ toward decolorization/degradation of Rhodamine B dye in aqueous medium. Moreover, the influence of various parameters like time, temperature, catalyst dose, speed of agitation, initial concentration of dye on degradation of dye has been examined.

2. MATERIALS AND METHODS

2.1 Material

All chemicals used in this work were commercially supplied as analytical grade reagents, and used without further purification. Double distilled water was used throughout the experiments. 35% (w/w) Hydrogen peroxide (Merck), 5% Pt/Al₂O₃ (Acros) and commercial grade Rhodamine B dye were purchased from local market of Faisalabad Pakistan.

2.2 Catalytic Experiment

Batch oxidative decolorization/degradation experiments of Rhodamine B using 5% Pt/Al₂O₃ as catalyst were carried out at three different temperatures (303, 313, 323 K) at pH 2.5. For a typical run, 50 mL Rhodamine B solution of known concentration (100, 200 and 300 ppm) was taken in beaker (100 mL) and the temperature of the reaction mixture was kept constant at a desired value by the help of hot plate. Hydrogen peroxide (1 mL), as an oxidant was added to Rhodamine B solution. The reaction mixture was stirred for 15 minutes to gain constant desired temperature (303, 313 or 323 K). After getting the desired temperature, 1 mL sample was taken to determine any change in the Rhodamine B concentration during the heating period. The dosage of Pt/Al₂O₃, catalyst, was 0.025 g for 50 mL of dye solution. The

reaction mixture was stirred continuously at 500 rpm. The solution samples were collected from the reaction mixture at regular interval of time. Catalyst was separated from withdrawn samples by filtration.

2.3 Analysis of Reaction Mixture

Double beam UV-Visible spectrophotometer (U2800, HITACHI, Japan) was used for analysis of reaction mixture. For this purpose standard solutions of Rhodamine B dye were prepared in distilled water. UV-Visible spectrum of each standard solution was recorded in wavelength range 200-800 nm giving the maximum absorbance at 554 nm, λ_{Max} . Absorbance of solutions at 554 nm was plotted against concentration as given in Figure 1. This plot is called as calibration curve or working curve. This plot was used to find the concentration of Rhodamine B dye in reaction mixture.

2.4 Effect of Hydrogen Peroxide on Decolorization

To investigate the effect of hydrogen peroxide on decolorization/degradation of dye, separate experiments were carried out in presence and absence of hydrogen peroxide. For this purpose 0.025 g of Pt/Al₂O₃ was suspended in 40 mL solution of Rhodamine B dye with 100 ppm as initial concentration. Samples were withdrawn from reactor at various time intervals and were analyzed by UV-Visible spectrophotometer.

2.5 Effect of Catalyst Loading

To find out the optimum catalyst dose, various experiments were carried out with 100 ppm as the initial concentration of Rhodamine B with different catalyst loading in the range of 0.025-0.125g. Temperature was maintained at 303 K in all experiments. Initial amount of hydrogen peroxide (1 mL) as oxidants was also kept constant in all investigation.

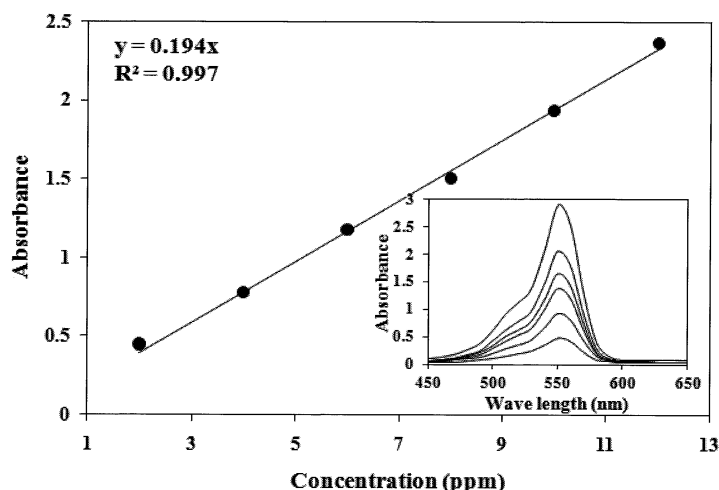


Figure 1. UV-Visible spectra and calibration curve of Rhodamine B dye.

2.6 Time Profile Investigation

The time course study of decolorization of Rhodamine B dye was carried out at 303 K with initial concentration of 100, 200 and 300 ppm. This investigation was carried out by suspending 0.025 g of Pt/Al₂O₃ catalyst in 50 mL solution of Rhodamine B. Hydrogen peroxide (1mL) was added as oxidant and the reaction mixture was stirred continuously at speed of 500 rpm. 1 mL sample was withdrawn from reaction mixture at regular time interval of 15, 30, 45, 60, 75, 90, 105 and 120 minutes. These samples were analyzed by UV-visible spectrophotometer.

2.7 Effect of Temperature

To investigate the effect of temperature on decolorization of Rhodamine B dye, separate experiments were carried out with 100 ppm as the initial concentration of Rhodamine B at temperature 303, 313 and 323 K. These investigations were carried out by suspending 0.025 g of Pt/Al₂O₃ catalyst in 50 mL of 100 ppm solution of Rhodamine B. Hydrogen peroxide (1 mL) was added to reaction mixture and was stirred continuously at 500 rpm. Samples were collected from reaction mixture

at regular intervals of time and were analyzed by UV-Visible spectrophotometer.

3. RESULTS AND DISCUSSIONS

3.1 Analysis of Reaction Mixture

Straight line equation of calibration curve (given in Figure 1) was used to determine the concentration of reaction mixture samples taken at various interval of time. Equation 1 was used to determine the percent decolorization of Rhodamine B dye.

$$\% \text{ Decolorization} = \frac{(RhB)_0 - (RhB)_t}{(RhB)_0} \times 100 \quad (1)$$

Where (RhB)₀ and (RhB)_t represent initial concentration and concentration of Rhodamine B after regular interval of time respectively.

3.2 Effect of Hydrogen Peroxide on Decolorization

Figure 2 depicts the comparison of decolorization of Rhodamine B in presence and absence of hydrogen peroxide. It can be noted that about 9% decolorization was achieved in 20 minutes which was increased to 11% after 120 minutes. Decolorization in the absence of hydrogen peroxide is due to

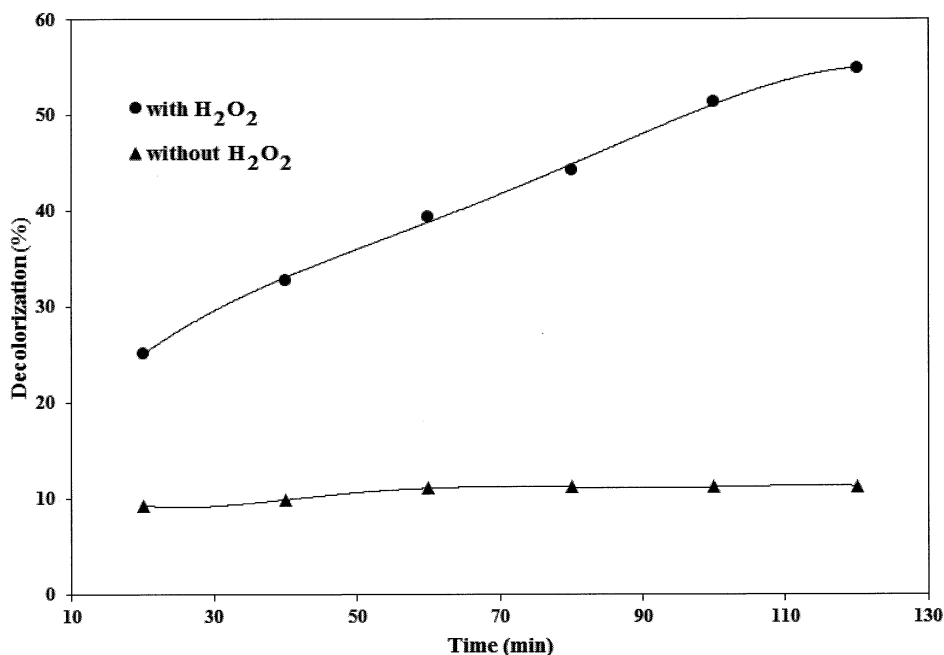


Figure 2. Effect of hydrogen peroxide on decolorization of Rhodamine B dye. Reaction Conditions: Rhodamine B 100 ppm (40 mL), Temperature 303K, Catalyst 0.025g, Agitation 500 rpm.

dissolved oxygen in water. In the presence of hydrogen peroxide, 25% decolorization was achieved in 20 minutes which increased to 55% after 120 minutes. It can be concluded that hydrogen peroxide acts as an efficient oxidant in this investigation and therefore it was used in all subsequent experiments. Hydrogen peroxide decomposes to oxygen and water. Oxygen is used in decolorization/degradation of Rhodamine B dye. Catalytic reaction in absence of hydrogen peroxide is due to dissolved oxygen in water.

3.3 Effect of Catalyst Loading

It was observed that degradation of Rhodamine B initially increases with increase in catalyst loading from 0.025-0.05g and then decreases with further increase in catalyst loading from 0.05-0.125 g of catalyst as given in Figure 3a. With high dose of catalyst, the reaction mixture could not be homogenized properly at given speed of agitation. Therefore

the decolorization decreased with rise in catalyst loading. Reaction can be homogenized by increasing the speed of agitation; however at high speed of agitation, splashing of the reaction mixture was observed. This also resulted in decrease of decolorization of the dye. The Figure 3a shows that decolorization increases up to 0.05 g of the catalyst; hence 0.05 g of catalyst seems to be the optimum catalyst dose. However this can't be taken as optimum catalyst dose. Though decolorization of dye increased with rise in catalyst loading; however the decolorization per gram of catalyst per minute decreased with increase in catalyst loading as depicted in Figure 3b. Therefore 0.02 g of catalyst can be taken as optimum catalyst load as maximum decolorization per gram of catalyst per minutes was achieved using 0.025 g of catalyst (Figure 3b) [14, 29, 30].

3.4 Time Profile Investigation

It was found that absorbance of Rhodamine

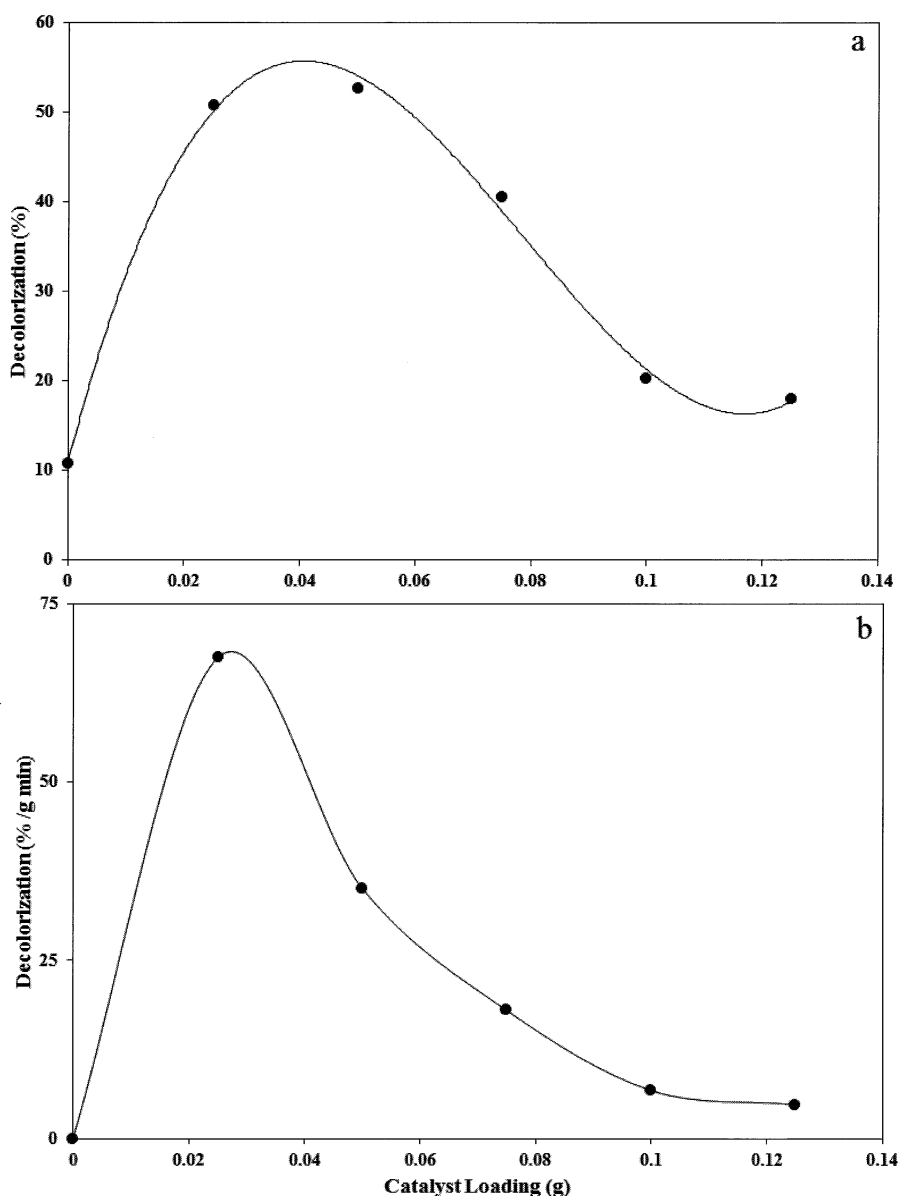


Figure 3. Effect of catalyst loading on decolorization of Rhodamine B dye.

Reaction Conditions: Rhodamine B 100 ppm (50 mL) Temperature 303K, Agitation 500 rpm, Hydrogen peroxide 1 mL.

B at 554 nm decreases with reaction time which indicates that decolorization of Rhodamine B dye increases with time. Previously prepared calibration curve (Figure 1) was used for determination of concentration of reaction mixture after various time intervals. It was noted that approximately 31.2% of 100 ppm

Rhodamine B dye degraded within first 15 minutes and gradually the degradation increased to 61% after 120 minutes of reaction time. The degradation was 25.4% of 200 ppm dye within 15 minutes of reaction time and for a longer reaction time of 120 minutes, 48.5% of dye was degraded. Finally, for 300 ppm of Rhodamine

B dye, the degradation was only 17.3% in the first 15 minutes and gradually degradation increased to 41.4% after 120 minutes of reaction time as given in Figure 4. Catalytic efficiency of a catalyst can be explored in term of Turn over frequency (TOF), which is the number of moles of substrate reacted per mole of the catalyst per hour. In present investigation 550, 891 and 908 were noted as TOF with 100, 200 and 300 ppm solution of Rhodamine B respectively. These TOF values are sufficiently high which indicate that the present catalytic decolorization is an efficient process. As rate of reaction is proportional to the concentration of reactant, therefore degradation of dye must increase with concentration of dye; however it can be noted from Figure 4 that conversion/decolorization decreases with increase in concentration of dye. Actually it is the amount of dye degraded increases with concentration as given in Table 1.

3.5 Effect of Temperature

The results of time profile investigation at different temperatures revealed that conversion/decolorization of Rhodamine B increases with temperature. It was noted that approximately 31.2% of 100 ppm Rhodamine B dye degraded/decolorized in 15 minutes at 303 K and gradually degradation/decolorization increased to 34.5% at 313 K and 36.5% at 323 K. Similarly 61.3% dye was decolorized in 120 minutes of reaction time at 303 K which was increased to 69.9% at 313 K and 80.9% at 323 K respectively. These results are given in Figure 5. TOF also increased from 550 to 640 with increase in temperature from 303 to 313 K.

3.6 Effect of Mass Transfer

The decolorization of Rhodamine B dye in present investigation using $\text{Pt}/\text{Al}_2\text{O}_3$ as a catalyst is a typical slurry-phase reaction having reactants in liquid phase and catalyst in solid

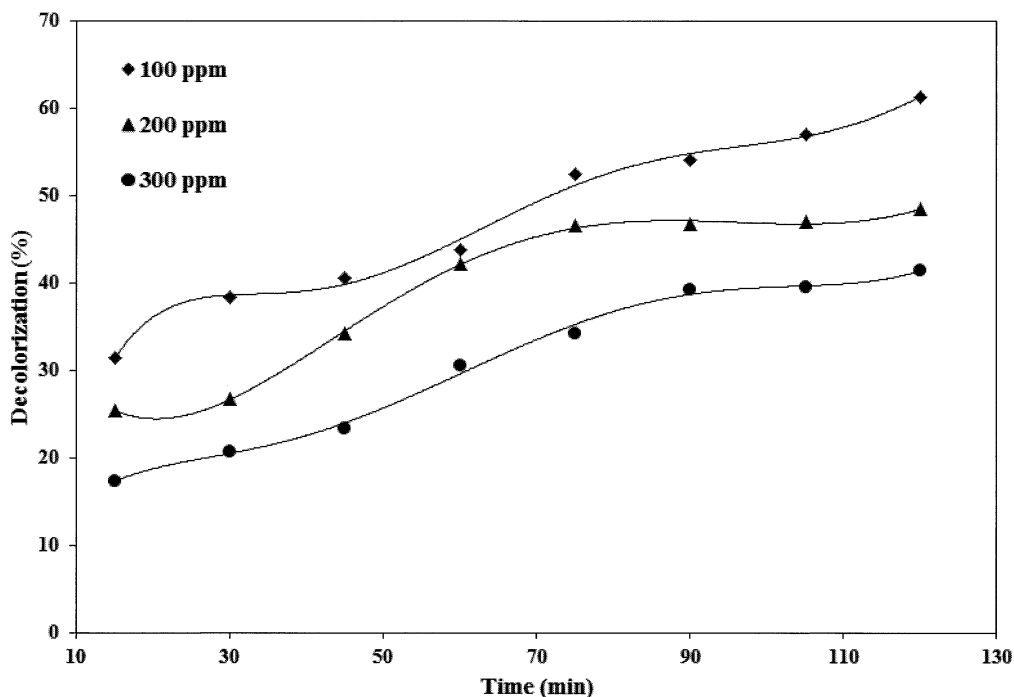


Figure 4. Effect of concentration of dye on decolorization of Rhodamine B dye. Reaction Conditions: Catalyst 0.025 g, Temperature 303K, Agitation 500 rpm, Hydrogen peroxide 1 mL.

Table 1. Comparison of decolorization of Rhodamine B with different initial concentrations.

| Time (min) | 100 ppm | | 200 ppm | | 300 ppm | |
|------------|----------------|------------------------|----------------|------------------------|----------------|------------------------|
| | Conversion (%) | Amount converted (ppm) | Conversion (%) | Amount converted (ppm) | Conversion (%) | Amount converted (ppm) |
| 15 | 31.4 | 31.4 | 25.4 | 50.8 | 17.3 | 51.8 |
| 30 | 38.4 | 38.4 | 26.8 | 53.6 | 20.7 | 62.1 |
| 45 | 40.6 | 40.6 | 34.2 | 68.5 | 23.4 | 70.2 |
| 60 | 43.8 | 43.8 | 42.2 | 84.3 | 30.5 | 91.8 |
| 75 | 52.5 | 52.5 | 46.6 | 93.2 | 34.3 | 103.0 |
| 90 | 54.1 | 54.1 | 46.7 | 93.5 | 39.2 | 117.9 |
| 105 | 57.1 | 57.1 | 46.9 | 94.0 | 39.5 | 118.5 |
| 120 | 61.4 | 61.4 | 48.5 | 97.0 | 41.4 | 124.3 |

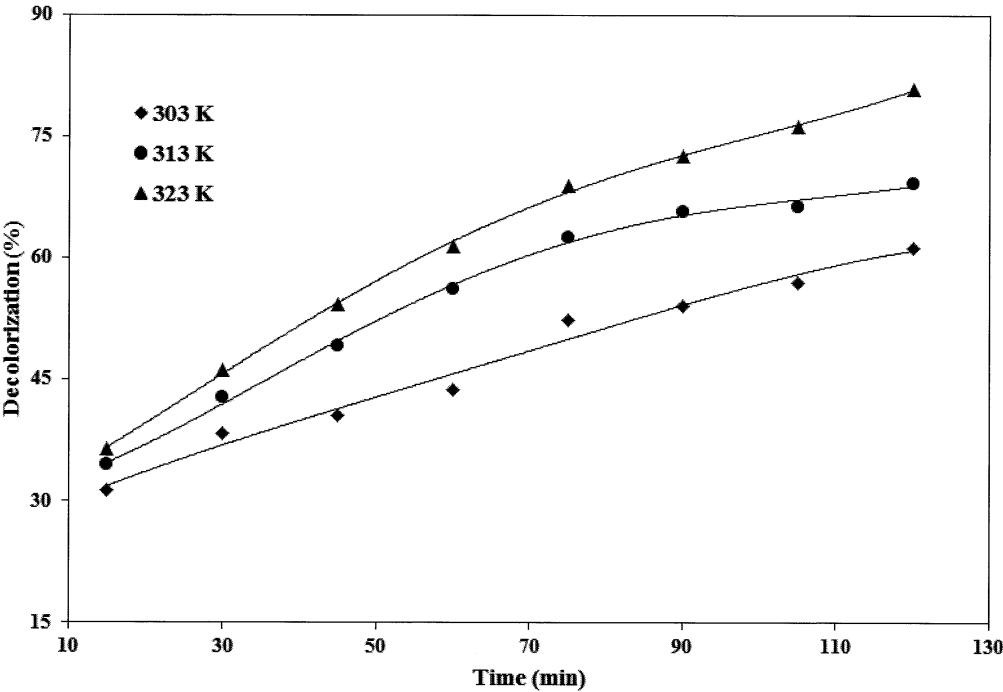


Figure 5. Effect of temperature on decolorization of Rhodamine B dye.
Reaction Conditions: Rhodamine B 100 ppm (50 mL) Catalyst 0.025 g, Agitation 500 rpm, Hydrogen peroxide 1 mL.

phase. It is generally assumed that surface catalyzed reactions occur by reaction between reactants adsorbed at the surface of catalyst. The surface catalyzed reaction can be broken down into following basic five steps. Any one of these step can be rate determining step [31].

1. Transport of reactants to the catalyst
2. Adsorption of reactants at catalyst surface
3. Reaction between adsorbed reactants on surface of catalyst
4. Desorption of the products from catalyst
5. Transport of products away from the catalyst

Steps 2, 3 and 4 are chemical in nature. These steps jointly are regarded as catalytic reaction. If any of these steps is slow step i.e rate determining step, the reaction is said to be taking place in kinetic controlled region. Step 1 and 5, on the other hand are physical process which involve no chemical change.

When either of these is slower, the reaction is said to be diffusion control or rate is said to be diffusion limited [29, 30]. The dependence of rate (conversion) of reaction on speed of agitation shows the existence of mass transfer limitation. To investigate the effect of speed of agitation on decolorization in present investigation, the decolorization of Rhodamine B dye was studied at various speed of agitation in the range of 100-600 rpm at 300 K using 0.025 g catalyst and 100 ppm as initial concentration for 30 minutes. Effect of agitation on reaction is shown in Figure 6, which shows that initially decolorization increases with agitation speed, showing a mass transfer regime from 200 to 500 rpm. The later part of the graph shows that the increase in agitation speed above 500-600 rpm has no effect on the decolorization. This is the region where reaction is most probably free from the external mass transfer limitations i.e. reaction is taking place in kinetic controlled regime. This is the region of our interest and all

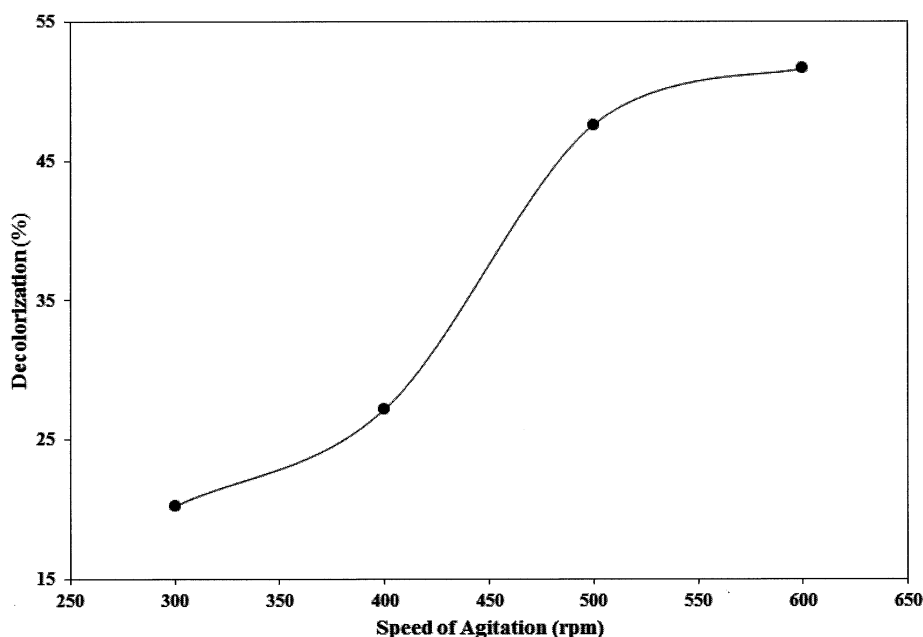


Figure 6. Effect of agitation on decolorization of Rhodamine B dye.

Reaction Conditions: Rhodamine B 100 ppm (50 mL) Temperature 303K, Catalyst 0.025 g, Hydrogen peroxide 1 mL.

the subsequent experiments were performed at 500 rpm. A PTFE coated stirrer bar was used for stirring [14, 29, 30].

3.7 Reaction Kinetics

The rates of surface catalyzed reactions are complex, because adsorption of the reactants on the surface of the catalyst, reactions between the adsorbed reactants and desorption of the products take place simultaneously. Quasi-equilibrium and quasi-steady state hypotheses can be used to simplify the reaction. The kinetics of the degradation of Rhodamine B dye in present case can be expressed as power rate law [32, 33].

$$\text{Rate} = k[\text{RhB}]^m[\text{H}_2\text{O}_2]^n \quad (2)$$

Where k is rate constant and m and n are the reaction orders with respect to Rhodamine B dye and hydrogen peroxide, respectively. In present investigation hydrogen peroxide is in excess as compared to Rhodamine B, so it

can be taken as constant. Equation 2 can be transformed to equation 3.

$$\text{Rate} = k[\text{RhB}]^m \quad (3)$$

On rearrangement and integration, we get

$$\ln \frac{[\text{RhB}]_0}{[\text{RhB}]_t} = kt \quad (4)$$

Where $[\text{RhB}]_0$ and $[\text{RhB}]_t$ represent initial concentration and concentration of Rhodamine B at time t respectively. Equation 4 is a straight line equation slope of which is rate constant of the reaction. Although this representation has limited utility; however it can be used to obtain a preliminary dependency of rate of reaction on concentration of Rhodamine B. Equation 4 was applied to time profile data at various temperatures as given in Figure 7. From the slope of these plots, rate constant were determined which are listed in Table 2.

As stated earlier that degradation of Rhodamine catalyzed by Pt catalyst in present

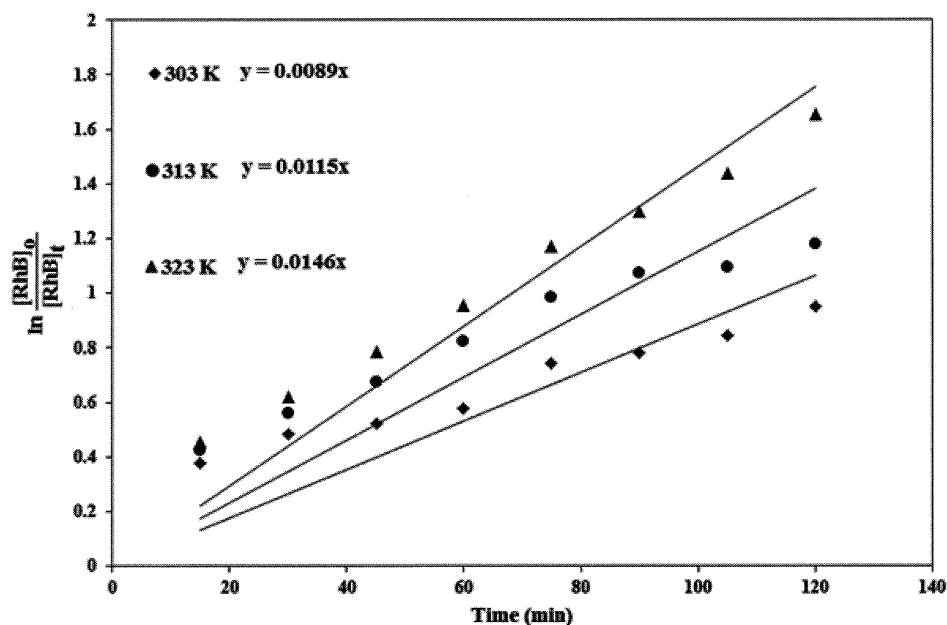


Figure 7. Application of 1st order kinetic expression (equation 4) to time profile data at various temperatures.

Table 2. 1st order rate constants determined by application of 1st order expression (equation 4) to time profile data at various temperatures.

| T (K) | k (min ⁻¹) |
|-------|------------------------|
| 303 | 0.0089 |
| 313 | 0.0115 |
| 323 | 0.0146 |

investigation is heterogeneous (surface) reaction. Langmuir-Hinshelwood kinetic model can be used to describe the surface catalyzed reaction. According to this model it is assumed that the reaction between Rhodamine B and hydrogen peroxide is taking place at the surface of catalyst particles. Recently this model has been described for the reaction involving liquid, although it was initially developed to describe the reaction involving the gaseous reactants [15, 17, 29, 34].

According to Langmuir-Hinshelwood (L-H) theory, first the reactants diffuse to the catalyst surface and get adsorbed. On the surface of catalyst, the adsorbed reactants commence the catalytic reaction and generate a number of products. Finally the products desorbs from the surface. This whole process can be summarized in the following steps [35].

1. $RhB + \theta \rightarrow \theta_{RhB}$
Adsorption of Rhodamine B
2. $H_2O_2 + \theta \rightarrow \theta_{H_2O_2}$
Adsorption of hydrogen peroxide
3. $\theta_{RhB} + \theta_{H_2O_2} \rightarrow \theta_P$
Catalytic surface reaction
4. $\theta_P \rightarrow P$
Desorption of products

Where θ represent the surface sites.

According to Langmuir-Hinshelwood kinetic theory, the rate of reaction is proportional to the fraction of the surface covered by substrate, θ ,

$$Rate = k\theta_{RhB}\theta_{H_2O_2} \quad (5)$$

Where k , θ_{RhB} and $\theta_{H_2O_2}$ represents rate constant, surface covered by Rhodamine B and

hydrogen per oxide respectively. As in present investigation, hydrogen peroxide is in excess, so its concentration assumes to be constant. Therefore equation 5 transforms to

$$Rate = k_r\theta_{RhB} \quad (6)$$

Adsorption of Rhodamine B on the surface of catalyst may take place either according to Langmuir, Temkin or Freundlich adsorption isotherm. Considering the Langmuir adsorption isotherm, the rate expression can be written as

$$Rate = k_r \frac{K_{RhB}[RhB]}{1 + K_{RhB}[RhB] + K_{H_2O_2}[H_2O_2] + K_P[P]} \quad (7)$$

K_{RhB} , $K_{H_2O_2}$ and K_P represent adsorption coefficient for Rhodamine B, hydrogen peroxide and products respectively.

Adsorption/desorption processes are fast enough to be assumed at equilibrium [35]. This assumption helps to simplify the above expression as

$$Rate = k_r \frac{K_{RhB}[RhB]}{1 + K_{RhB}[RhB]} \quad (8)$$

$$Rate = \frac{a[RhB]}{1 + b[RhB]} \quad (9)$$

Considering Temkin adsorption isotherm, equation 6 can be transformed to

$$Rate = k_r(K_1 \ln K_2[RhB]) \quad (10)$$

Where K_1 and K_2 are constants related to heat of adsorption, which decreases linearly with surface coverage.

Similarly considering Freundlich adsorption isotherm, rate of reaction is given by

$$Rate = k_r K_{RhB}[RhB]^{1/n} \quad (11)$$

K and n are empirical constants, which depend on several factors. K can be defined as the adsorption or distribution coefficient and

represent the Rhodamine B adsorbed on the surface of catalyst. The slope, $1/n$, which range between 0 and 1 for favorable adsorption on surface, is a measure of surface heterogeneity. The surface is considered more heterogeneous as its value gets closer to zero. A value of $1/n$ above one is indicative of cooperative adsorption, while $1/n$ below one indicates normal Langmuir adsorption isotherm [34, 36–39].

Time profile data at various temperatures was subjected to kinetic analysis according to Langmuir, Temkin and Freundlich models by linear and non-linear least square method. For non-linear least square method Curve Expert 1.4 software was used. Rate of the reaction was calculated by applying third order polynomial to the time profile data, using Curve Expert software. Freundlich model (equation 11) was found to be applicable to the data. Figure 8 shows the applicability of Freundlich model by non-linear least square method using Curve expert software, from which apparent rate constants, k_{App} and $1/n$ at different temperatures

were determined. The values of rate constants, adsorption co-efficient and $1/n$ are listed in Table 3. It is evident from Table 3 that rate constant of decolorization of Rhodamine B increases with temperature. The value of $1/n$ is less than one, showing the heterogeneous nature of the catalyst surface. Activation energy was calculated by applying Arrhenius equation to rate constants at various temperatures. Rate constants determined by Langmuir–Hinshelwood theory, using Freundlich model (equation 11) listed in Table 3 are true rate constants (true

Table 3. Kinetics parameters determined by application of Freundlich adsorption isotherm (equation 11) to time profile data at various temperatures.

| T (K) | K_r (min^{-1}) | K_{RhB} (Lmol^{-1}) | $1/n$ | R^2 |
|-------|-----------------------------|----------------------------------|-------|-------|
| 303 | 0.451 | 0.143 | 0.555 | 0.91 |
| 313 | 0.609 | 0.137 | 0.675 | 0.95 |
| 323 | 0.712 | 0.124 | 0.757 | 0.99 |

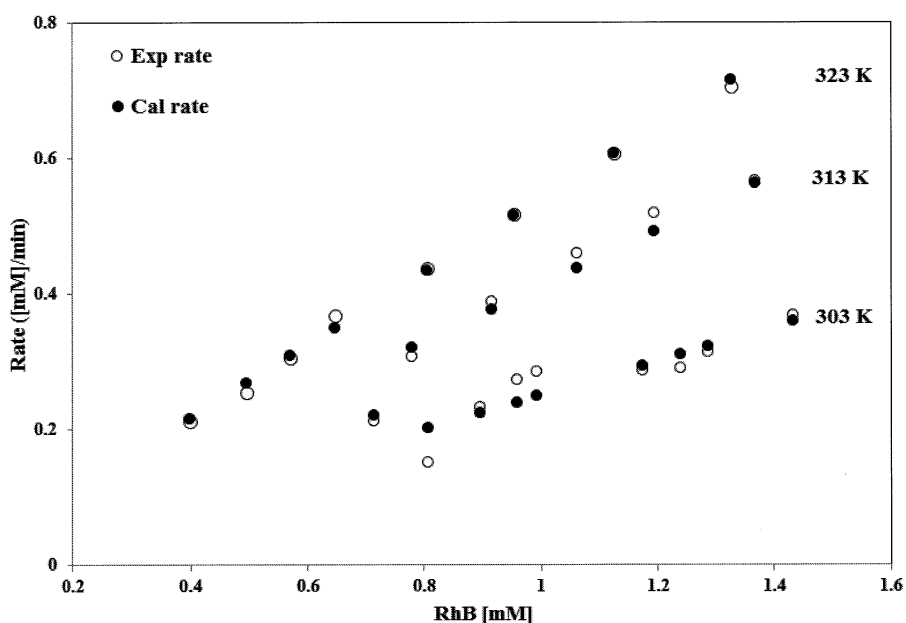


Figure 8. Application of Freundlich adsorption isotherm (equation 11) to time profile by non-linear least square method using Curve Expert software.

in the sense that contributions of adsorption equilibrium constant of Rhodamine B have been excluded); energy calculated using these rate constants is true activation energy, E_T , which was found as $15.36 \text{ kJ mol}^{-1}$. Similarly, rate constants calculated by 1st order expression (equation 4) are apparent rate constants; listed in Table 2, and hence activation energy is apparent activation energy, E_A , which was found as $20.14 \text{ kJ mol}^{-1}$. Enthalpy (ΔH), entropy (ΔS) and Gibb's energy (ΔG) of adsorption for Rhodamine B were determined by applying vant's Hoff isochore (equation 12) to the adsorption constants of Rhodamine B, K_{RhB} , at various temperatures listed in Table 3 and were found as -5.7 kJ mol^{-1} , 35.14 J mol^{-1} and $-4.59 \text{ kJ mol}^{-1}$, respectively.

$$\frac{d \ln K_{RhB}}{dT} = \frac{\Delta H}{RT^2} \quad (12)$$

4. CONCLUSIONS

On the basis of results of present studies, it can be concluded that;

1. Pt/ Al_2O_3 can be used as an effective catalyst for oxidative decolorization of Rhodamine B dye in aqueous medium.
2. The catalytic decolorization of Rhodamine B is more effective in presence of hydrogen peroxide as compared to open to atmosphere.
3. Reaction system is heterogeneous in nature where catalyst can be easily separated from reaction mixture.
4. Catalytic reaction takes place according to Langmuir-Hinshelwood (L-H) mechanism. According to this mechanism reaction proceed in two steps. In first step both reactants adsorb at the surface of catalyst followed by reaction between the adsorbed reactants in second step.
5. Adsorption of Rhodamine B at the surface of catalyst follows the Freundlich adsorption model.

6. 20.14 and $15.36 \text{ kJ mol}^{-1}$ were determined as apparent activation energy and true activation energy respectively.
7. -5.7 kJ mol^{-1} , 35.14 J mol^{-1} and $-4.59 \text{ kJ mol}^{-1}$ were determined as Enthalpy (ΔH), entropy (ΔS) and Gibb's energy (ΔG) respectively.

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