Palladium-Supported Zirconia-Based Catalytic Degradation of Rhodamine-B Dye from Wastewater

Salma Jabeen 1, Muhammad Sufaid Khan 1 ⊗, Rozina Khattak 2, Ivar Zekker 3,*; Juris Burlakovs 4 ⊗, Sergio S. dC Rubin 5,6,7, Makaran Madhao Ghangrekar 7, Anna Kallistova 8, Nikolai Pimenov 8, Muhammad Zahoor 9,10 and Gul Shahzada Khan 10

Abstract: The catalytic activity of Pd/ZrO2 was studied in terms of the degradation of rhodamine-B dye in the presence of hydrogen peroxide. Pd/ZrO2 was prepared by impregnation method, calcined at 750 °C and characterized by XRD, SEM and EDX. The catalyst showed good catalytic activity for dye degradation at 333 K, using 0.05 g of the catalyst during 5 h. The reaction kinetics followed the pseudo-first order kinetics. The Freundlich, Langmuir and Temkin isotherms were applied to the data and the best fit was obtained with Freundlich isotherm. Thermodynamic parameters, like ∆H, ∆G and ∆S were also calculated. The negative values of ∆H (~291.406 KJ/mol) and Gibbs free energy (ΔG) showed the exothermic and spontaneous nature of the process. The positive ΔS (0.04832 KJ/mol K) value showed suitable affinity of catalyst for dye degradation. The catalyst was very stable, active and was easily separated from the reaction mixture by filtration. It can be concluded from the results that the prepared catalyst could be effectively used in dyes degradation/removal from water subjected to further validation and use for various dyes.

Keywords: dye; heterogeneous catalyst; rhodamine-B; thermodynamics

1. Introduction

Water pollution caused by the hazardous organic pollutants is an ever increasing problem, because many manufacturing sectors such as leather, textile, pharmaceutical, cosmetics, paint and ink industries are using organic dyes. Some part of the used dyes is discarded as pollutant into water bodies, whose recovery is of utmost importance as they are toxic to aquatic life and negatively affect the photosynthesis of aquatic plants. Mostly, the dyes are not effectively removed from water by the conventional methods of sewage handling and needs advanced technologies [1–4].
Rhodamine B (RB), is mostly used in dying of leather, silk, cotton, wool and paper, and its residues are discharged into environment and if untreated these residues can affect skin, respiratory system, eyes and gastrointestinal tract [5]. Some dyes are non-biodegradable showing resistance to chemical, photochemical and biochemical degradations [6]. Previously, flocculation, adsorption, coagulation, biological and chemical degradation, ion exchange and precipitation methods have been utilized for the removal of dyes from aqueous media [7–10]. These methods are limited due to the production of secondary pollutants, high cost, and lengthy processing time. Moreover, the dyes have complex structures and resistance to heat and chemicals, resulting in poor thermal degradation [11,12]. Thus, an alternative method, which is less expensive and environmental friendly, is needed for the removal of dyes from dye-loaded effluents. The catalytic wet oxidation (CWO) process, which consumes molecular oxygen and requires less energy is in use for a long time, as it is eco-friendly, scientifically feasible, and cost-effective [13–15]. Both-homogenous and heterogeneous catalysts (metal oxides and supported metal oxides containing, respectively) have been utilized for CWO. However, the heterogeneous catalysts have received considerable attention due to their easy recovery, re-usability, and simple separation [16,17]. Among, heterogeneous catalysts, palladium (Pd)-based catalysts have shown a high activity for total organic carbon (TOC) and removal of other components present in dyes [18]. Thus, due to a high activity, cost-effectiveness, and ease of operation, the Pd-based heterogeneous catalysts can be a better alternative for the removal of dyes from wastewater.

In this study, a Pd based Pd/ZrO$_2$ was prepared using impregnation method, calcined at 750 °C and characterized by different techniques like XRD, SEM, EDX etc. and was used as catalyst for the degradation rhodamine B.

2. Material and Methods
2.1. Chemicals

All the reagents used were of analytical grade with high purity (99%) and were used without a further purification. Triple-distilled water was used in the synthesis procedure of the catalyst. Hydrogen peroxide, rhodamine-B, ZrOCl$_2$·8H$_2$O, and PdCl$_2$ were used in the present work and purchased from Sigma-Aldrich (Munich, Germany). The chemical structure of the selected dye is presented in Figure 1 and its properties are given in Table 1.

![Figure 1. Chemical structure of rhodamine-B.](image)

Table 1. Physiochemical properties of rhodamine-B [19].

| Name of Dye                      | Rhodamine-B                                                                 |
|---------------------------------|-----------------------------------------------------------------------------|
| Molecular Formula               | C$_{28}$H$_{31}$ClN$_2$O$_3$                                                |
| Molecular Weight                | 364.4 g/mol                                                                 |
| $\lambda_{\text{max}}$          | 555 nm                                                                     |
| Dye content                     | Acetone and Ethanol                                                         |
| Slightly soluble                | 4-amino 3 methylebenzenesulfonic acid dia azo and naphtalen-2-ol Coupling   |
| Manufacturing method            |                                                                             |
2.2. Instrumentation

UV-Visible spectrophotometer (UV-1800 ENG. SOFT) is used to determine the dye concentration in liquid samples. The scanning electron microscopy (SEM) was carried out using JSM5910 (manufacturer: JEOL, Tokyo, Japan) to visualize surface morphology of prepared catalyst [SEM properties were: energy: 30 kV, magnification (max): 300,000× and resolving power (max): 2.3 nm]. X-ray diffraction (XRD) was carried out by X-ray diffractometer (model: JDX-3532, JEOL, Tokyo, Japan) in order to determine size of the particles with measuring parameters: voltage: 20–40 kV, current: 2.5–30 mA, X-rays: CuKα (λ = 0.154 nm), 2 theta range: 0 to 160°. Energy dispersive X-ray (EDX) analysis was carried out using INCA200 (Oxford Instruments, Buckingham, UK). The BET surface area was analyzed by pore size and surface area analyzer (model: NOVA2200e, Quantachrome, Boynton Beach, FL, USA).

2.3. Catalyst Preparation

2.3.1. Support Preparation

For the palladium catalyst, the monoclinic zirconia was used as a supporting material. About 0.25 M aqueous solution of ZrOCl₂·8H₂O was titrated against ammonia and Zr(OH)₄ white dense precipitate were formed, which were then washed after attaining Cl⁻ free and neutral sample in modified Soxhlet apparatus. The prepared precipitate was dried overnight at 110 °C in an oven (WiseVen, Hanoi City, Vietnam) and then it was homogenized. The sample was grinded and meshed (passed through 170 and 200 µm US standard mesh sieves). At 750 °C the meshed sample was calcined in the program controlled furnace at 0.5 °C/min temperature for 3 h.

2.3.2. Palladium Loading on Support Material

The incipient wetness technique was used for the preparation of the catalyst (0.01 wt.% Pd/ZrO₂). First of all, aqueous solution of 2 mL of PdCl₂ (5.1 × 10⁻⁵ M) was added to 10 g of ZrO₂ to prepare a paste. The paste of the sample was then dried overnight in an oven at 110 °C. After this, the sample was crushed and meshed (passed via 170 and 200 µm US standard mesh sieves) and then calcined at 750 °C in the furnace at 0.5 °C/min for 3 h. The overall scheme of synthesis is presented in Figure 2.

![Figure 2. Preparation of catalyst Pd/ZrO₂.](image_url)

2.4. Catalytic Degradation of Rhodamine-B Dye

The dyes standard solutions were prepared in distilled water. Working dye solutions (rhodamine-B 15 mg/L) of 10 mL and catalyst quantity (0.020 g) were mixed together
at 303 K. About 1 mL hydrogen peroxide was added to the mixture of reaction and the agitation speed was 500 rpm. The undegraded amount of dye was determined at 555 nm using UV-Visible spectrometer. The effect of time, catalyst dose and temperature on the selected dye degradation were also evaluated.

3. Results and Discussion

3.1. Characterization of the Catalyst

The SEM of the prepared catalyst is given in Figure 3, where palladium supported on zirconia, in which active metal palladium is uniformly scattered on the zirconia surface.

![Figure 3. SEM images of Pd/ZrO$_2$ at different magnifications of: (a) 5000×, (b) 20,000×.](image)

The EDX spectrum reveals that the catalyst consisted only of palladium and zirconium dioxide, which are presented in Figure 4. The elemental composition of the catalyst is also shown in the EDX spectra in the Figure 4.

![Figure 4. EDX spectrum of Pd/ZrO$_2$ composite.](image)

The palladium zirconia X-ray diffraction pattern is shown in Figure 5, which indicates the crystalline structure of catalyst. Major peaks of monoclinic zirconia were observed at 2θ values of 28.7° and 31.9°. The broad peaks representing zirconia, while some minor peaks
Figure 5. XRD pattern of Pd/ZrO$_2$.

3.2. Effect of Time on Degradation

The time-effect on % degradation of dye was checked at different time intervals, e.g., 60, 120, 180, 240, and 300 min at 303 K temperature. At 1 mL hydrogen peroxide addition to 10 mL solution of dye, the degradation of rhodamine-B increased with time. Its UV-visible spectra are given in Figure 6 and the maximum degradation (Figure 7) of dye was achieved after 5 h, which was considered as optimal reaction time.

Figure 6. UV-visible spectra of RB degradation by Pd/ZrO$_2$. 

3.3. Effect of Temperature on Degradation of Dye

The effect of temperature on RB degradation by Pd/ZrO$_2$ catalyst was explored at different temperatures like 303, 313, 323, and 333 K at 5 h. The catalyst amount chosen was 0.020 g and dye solution applied was 10 mL (15 mg/L) during the experiments. The increase in temperature increased the % degradation of dye and the optimum temperature was found to be 333 K, as depicted in Figure 8.

3.4. Effect of Catalyst Amount on the Degradation of Dye

The catalyst surface provides reaction sites for the degradation. The effect of the amount of catalyst was investigated in the range of 0.01–0.1 g. It is clear from Figure 9 that the % degradation of dye increased up to catalyst quantity of 0.05 g and beyond this quantity degradation efficiency decreased because of the surface saturation. The optimum catalyst was thus taken as 0.05 g, which was used in the subsequent experiments.
3.5. Thermodynamic Study of Rhodamine-B Dye Degradation

Parameters of thermodynamics were calculated to evaluate the free energy change and sorption spontaneity. The Gibbs free energy change ($\Delta G$), enthalpy changes ($\Delta H$) and entropy change ($\Delta S$) were calculated using the following Equations (1)–(3):

$$K_D = \frac{q_e}{C_e}$$  

(1)

$$\Delta G = -RT\ln K_D$$  

(2)

$$\ln K_D = \frac{\Delta G^0}{RT} + \frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$$  

(3)

where, $K_D$ = distribution constant, $C_e$ = equilibrium concentration, $q_e$ = the amount of RB dye present at equilibrium.

By plotting $\ln K_D$ verses $1/T$ (K$^{-1}$), the slope and intercept values obtained (Figure 10) were used for $\Delta H$ and $\Delta S$ calculation, respectively, which are given in Table 2.
Table 2. Calculated parameters of thermodynamics for RB dye degradation.

| Temperature (K) | ∆H° (kJ/mol) | ∆S° (kJ/mol) | ∆G° (kJ/mol) |
|-----------------|--------------|--------------|--------------|
| 303 K           | -29,140.6    | 48.32        | -14,434.7    |
| 313 K           | -14,434.7    | -14,104.4    | -13,588.2    |
| 323 K           | -14,104.4    | -13,588.2    | -12,984.6    |
| 333 K           | -13,588.2    | -12,984.6    | -12,580.1    |

At different temperatures, i.e., 303, 313, 323 and 333 K, the values thermodynamic parameters like ∆G, ∆H and ∆S (Table 2). The value of ∆H is negative, showing that the interaction of sorption is exothermic in nature. The ∆G negative values shows that the sorption process is feasible and spontaneous. The ∆G value at low temperature are high indicating that degradation capacity of catalyst at low temperatures is high. The positive value of ∆S showed the increase in affinity of catalyst for dye degradation and randomness increasing during sorption, which also confirmed the spontaneous nature of the sorption [21].

3.6. Kinetic Study of Rhodamine-B Degradation

The kinetics parameters were calculated using pseudo 1st and pseudo 2nd order models at 303 K. From the plots of resulting values as shown in the Figure 11, the kinetics parameters were also calculated, which are presented in Table 3.

Table 3. Calculated values for kinetic study.

| Time (min) | C_0 | C_e | q_i | q_e | q_i - q_e | Log(q_i - q_e) |
|------------|-----|-----|-----|-----|-----------|----------------|
| 30         | 15  | 15  | 1.92| 15  | 13.08     | 1.92           |
| 60         | 15  | 15  | 2.3 | 15  | 12.70     | 2.3            |
| 120        | 15  | 15  | 3.23| 15  | 11.77     | 3.23           |
| 180        | 15  | 15  | 5.59| 15  | 9.41      | 5.59           |
| 240        | 15  | 15  | 8.89| 15  | 6.11      | 8.89           |
| 300        | 15  | 15  | 9.28| 15  | 5.72      | 9.28           |

The pseudo first order equation can be given as:

\[
\log(q_i - q_t) = \log q_e - \frac{K_1 t}{2.303}
\]
where \( q_e \) is the catalyst amount (mg/g) at equilibrium, \( q_t \) is the catalyst amount (mg/g) at any given time (min), and \( K_1 \) is the pseudo 1st order reaction rate constant for sorption (min\(^{-1}\)).

The pseudo-second-order equation can be expressed as:

\[
\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 q_e^2}
\]

where \( q_e \) is the catalyst amount (mg/g) at equilibrium, \( q_t \) is the catalyst amount (mg/g) at a given time (min), and \( K_2 \) is the pseudo 2nd order reaction rate constant for sorption (g/mg \times min).

From the linear plot, the time \((t)\) versus \(\log(q_e-q_t)\), the rate constant for 1st order kinetic \((K_1)\) was determined, whereas the \(q_e\) and \(q_t\) are the amount of dye adsorbed (mg/g) at equilibrium and time \(t\), respectively (Figure 11a). Similarly, for 2nd order kinetic \((K_2)\) rate constant was calculated from the linear plot of time vs. \(t/q_t\) (Figure 11b). The kinetic constants are presented in Table 4 along with \(R^2\) values.

### Table 4. Calculated values of \(R^2\) and rate constant for kinetics models.

| Models                  | \(R^2\) Value | Rate Constant         |
|-------------------------|---------------|-----------------------|
| Pseudo-first-order      | 0.968         | \(K_1 = 0.004606\) (min\(^{-1}\)) |
| Pseudo-second-order     | 0.947         | \(K_2 = 0.0236\) (g/mg \times min) |

The pseudo first order \((R^2 = 0.968)\) regression coefficients value was comparatively higher than that of the pseudo-second order \((R^2 = 0.947)\) model.

#### 3.7. Isotherm Study of Rhodamine-B Degradation

The relationship with the adsorbed amount of dye and the solution’s concentration was checked with the Langmuir, Freundlich and Temkin isotherm models. Linear regression value was used to determine the best fit among the isotherms.

#### 3.7.1. Freundlich Isotherm

On heterogeneous surface this isotherm is used to explain the adsorption and the data frequently fit to the given equation:

\[
q_e = K_F C_e^{1/n}
\]

The Freundlich isotherm in logarithmic form can be given:

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]

The \(q_e\) is the amount of dye adsorbed per gram of the adsorbent at equilibrium (mg/g) and \(C_e\) is the equilibrium concentration of adsorbate (mg/L). The \(1/n\) is the sorption intensity (g/L), which is attained from the slope of the plot given in Figure 12. \(K_F\) is Freundlich constant obtained from intercept of the Figure 12.

#### 3.7.2. Langmuir Isotherm

This isotherm is used to give the information about the monolayer formation on the homogeneous surface and it can be given by the below equation:

\[
q_e = \frac{K_L C_e}{1 + a L C_e}
\]
In linearized form the equation can be given as:

\[
\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{aL C_e}{K_L}
\]  

(9)

where the \( C_e \) is the concentration at equilibrium (mg/L), \( q_e \) is the adsorbed amount (mg/g), \( K_L \) and \( aL \) are the constants of Langmuir isotherm, which show the maximum sorption ability (mg/g) and strength for bonding, respectively. The theoretical monolayer capacity (\( Q_0 \)) is numerically equal to \( K_L / aL \). Langmuir adsorption isotherm was plotted with \( C_e / q_e \) against \( C_e \) and a line with correlation coefficient of 0.9726 (\( R^2 \)) was attained (Figure 13).

Figure 12. Freundlich Isothermal study.

3.7.3. Temkin Isotherm

This isotherm is used to determine the interaction of catalyst with the dye in degradation process. The following equation represents this model:

\[
q_e = \frac{RT}{b} \ln AC_e
\]  

(10)
This equation in linear form can be given as:

\[ q_e = B \ln A + B \ln C_e \]  

(11)

where \( B = RT/b \), \( R \) is gas constant (8.314 J/mol K), \( b \) is the Temkin constant, which is related to the heat of adsorption (J/mol), \( A \) is the Temkin isotherm constant (L/g), and \( T \) is the absolute temperature in Kelvin. The graph was plotted \( q_e \) versus \( \ln C_e \) and a linear curve was obtained with the slope \( B \) and intercept \( B \ln A \) (Figure 14). The numerical values of the isotherm models used are given in Table 5.

![Figure 14. Temkin isothermal plot.](image)

**Table 5. Calculated parameters for isothermal models.**

| Sample No | Models               | Parameters | Values          |
|-----------|----------------------|------------|-----------------|
| 1         | Freundlich isotherm  | \( K_F \)  | \( 3 \times 10^{85} \) |
|           |                      | \( N \)    | -0.002          |
|           |                      | \( R^2 \)  | 1               |
|           |                      | \( k_L \) (mg/g) | 0             |
|           |                      | \( Q_0 \) (mg/g) | 0             |
| 2         | Langmuir isotherm    | \( a_L \)  | 0               |
|           |                      | \( R^2 \)  | 0.972           |
|           |                      | \( \Lambda_T \) | 0             |
| 3         | Temkin isotherm      | \( b_T \)  | 0               |
|           |                      | \( R^2 \)  | 0.969           |

Based on the values of \( R^2 \), it was concluded that best fit of isotherm data could be obtained with Freundlich model.

4. Conclusions

The Pd/ZrO\(_2\) catalyst was prepared, characterized and used for the catalytic degradation of Rhodamine-B dye. The optimal conditions for Rhodamine-B dye degradation were: 0.050 g catalyst amount, reaction time 5 h, temperature 333 K for 10 mL dye solution (15 mg/L) and agitation rate of 500 rpm. The reaction followed pseudo first kinetics and best fit of isotherm data was obtained with Freundlich model. The \( \Delta H \), \( \Delta G \) and \( \Delta S \) were calculated and the negative values of \( \Delta H \) (−291.406 KJ/mol) showed the exothermic nature of the process while from negative values of Gibbs free energy (\( \Delta G \)) at different temperatures the spontaneous nature of the process was inferred. The positive value of
ΔS (0.04832 KJ/mol) also indicates the spontaneous nature of process. From the results it can be concluded that the prepared catalyst could be effectively used in dyes degradation subjected to further validation and use against other dyes.

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