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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], Makarand Madhao Ghangrekar [7], Anna Kallistova [8], Nikolai Pimenov [8], Muhammad Zahoor [9,*] and Gul Shahzada Khan [10]

[1] Department of Chemistry, University of Malakand, Chakdara KPK 18800, Pakistan; salmajabeen746@gmail.com (S.J.); sufaidkhan1984@gmail.com (M.S.K.)
[2] Department of Chemistry, Shaheed Benazir Bhutto Women University, Peshawar 25000, Pakistan; rznkhattak@yahoo.com
[3] Institute of Chemistry, University of Tartu, 14a Ravila St., 50411 Tartu, Estonia
[4] Institute of Forestry and Rural Engineering, Estonian University of Life Sciences, 5 Kreutzwaldi St., 51014 Tartu, Estonia; Juris.burlakovs@emu.ee
[5] Georges Lamaitre Center for Earth and Climate Research, Earth and Life Institute, Université Catholique de Louvain, B-1348 Louvain, Belgium; sergio.rubin@uclouvain.be
[6] Centro Nacional de Investigaciones Biotecnológicas, CNIB, 429 Cala Cala, Cochabamba 591 4, Bolivia
[7] Department of Civil Engineering, Indian Institute of Technology Kharagpur, Kharagpur 721302, India; ghangrekar@civil.iitkgp.ernet.in
[8] Research Centre of Biotechnology, Winogradsky Institute of Microbiology, Russian Academy of Sciences, Leninsky Prospect, 33, Build. 2, 119071 Moscow, Russia; kallistoanna@mail.ru (A.K.); npimenov@mail.ru (N.P.)
[9] Department of Biochemistry, University of Malakand, Chakdara KPK 18800, Pakistan
[10] Department of Chemistry, College of Science, University of Bahrain, Sakhir 32038, Bahrain; gulskhan79@yahoo.com
* Correspondence: ivar.zekker@ut.ee (I.Z.); mohammadzahoorus@yahoo.com (M.Z.)

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Abstract: The catalytic activity of Pd/ZrO_2 was studied in terms of the degradation of rhodamine-B dye in the presence of hydrogen peroxide. Pd/ZrO_2 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 ΔH, ΔG and ΔS were also calculated. The negative values of ΔH (−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, $ZrOCl_2 \cdot 8H_2O$, 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.

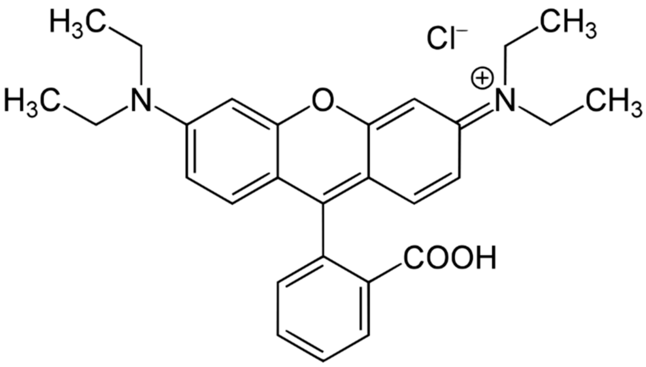


Figure 1. Chemical structure of rhodamine-B.

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

Name of Dye	Rhodamine-B
Molecular Formula	$C_{28}H_{31}ClN_2O_3$
Molecular Weight	364.4 g/mol
Λ_{max}	555 nm
Dye content	97%
Slightly soluble	Acetone and Ethanol
Manufacturing method	4-amino 3 methylebenzenesulfonic acid dia azo and naphtalen-2-ol Coupling

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 $ZrOCl_2 \cdot 8H_2O$ 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/ZrO_2). First of all, aqueous solution of 2 mL of $PdCl_2$ (5.1×10^{-5} M) was added to 10 g of ZrO_2 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.

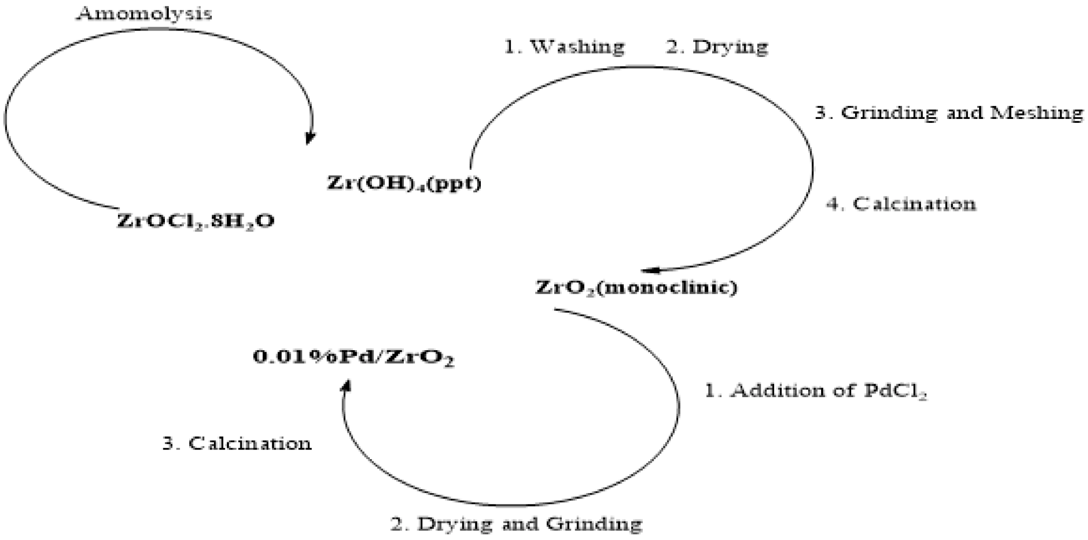


Figure 2. Preparation of catalyst Pd/ZrO_2.

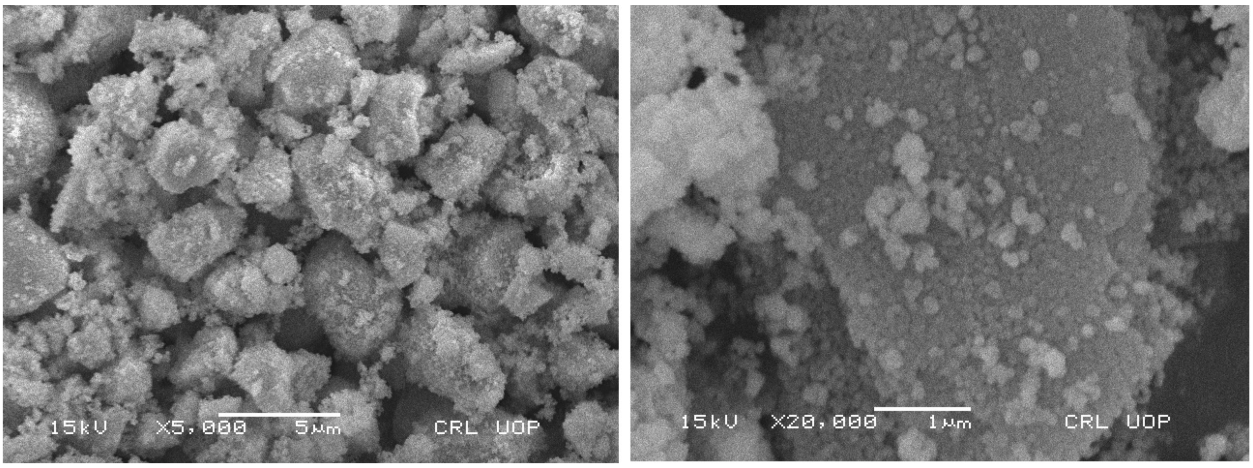
2.4. Catalytic Degradation of Rhodamine-B Dye

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

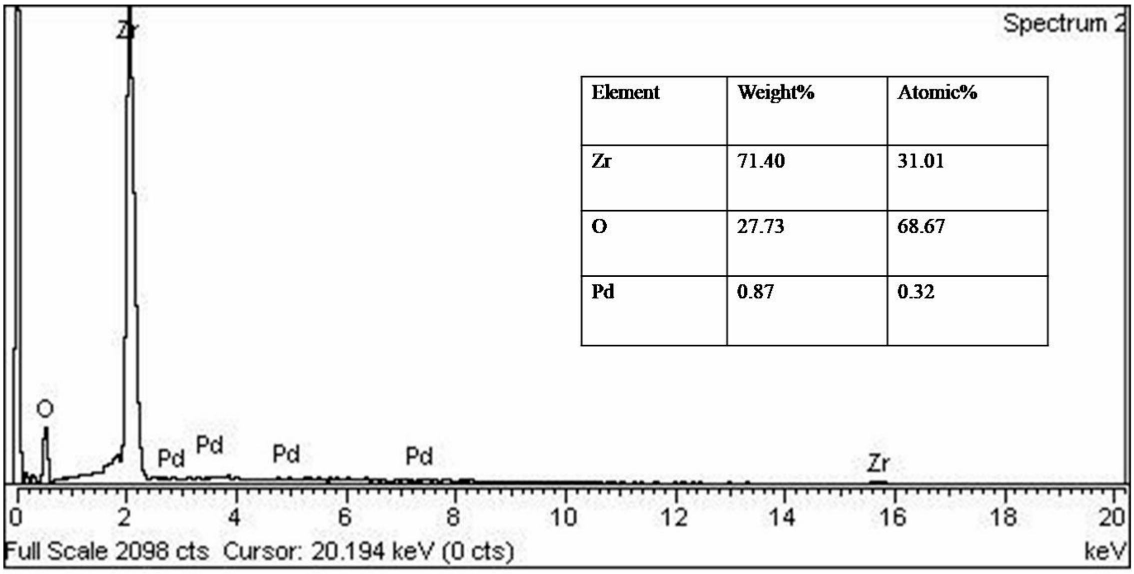
The SEM of the prepared catalyst is given in Figure 3, where palladium supported on zirconia, in which active metal palladium is uniformly scattered on the zirconia surface.



(**a**) (**b**)

Figure 3. SEM images of Pd/ZrO_2 at different magnifications of: (**a**) 5000×, (**b**) 20,000×.

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.



Element	Weight%	Atomic%
Zr	71.40	31.01
O	27.73	68.67
Pd	0.87	0.32

Figure 4. EDX spectrum of Pd/ZrO_2 composite.

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 were assigned to Pd. The palladium peaks are not prominent as their concentration in sample is low (0.001% w/w). Similar results have been reported in previous studies as well [20].

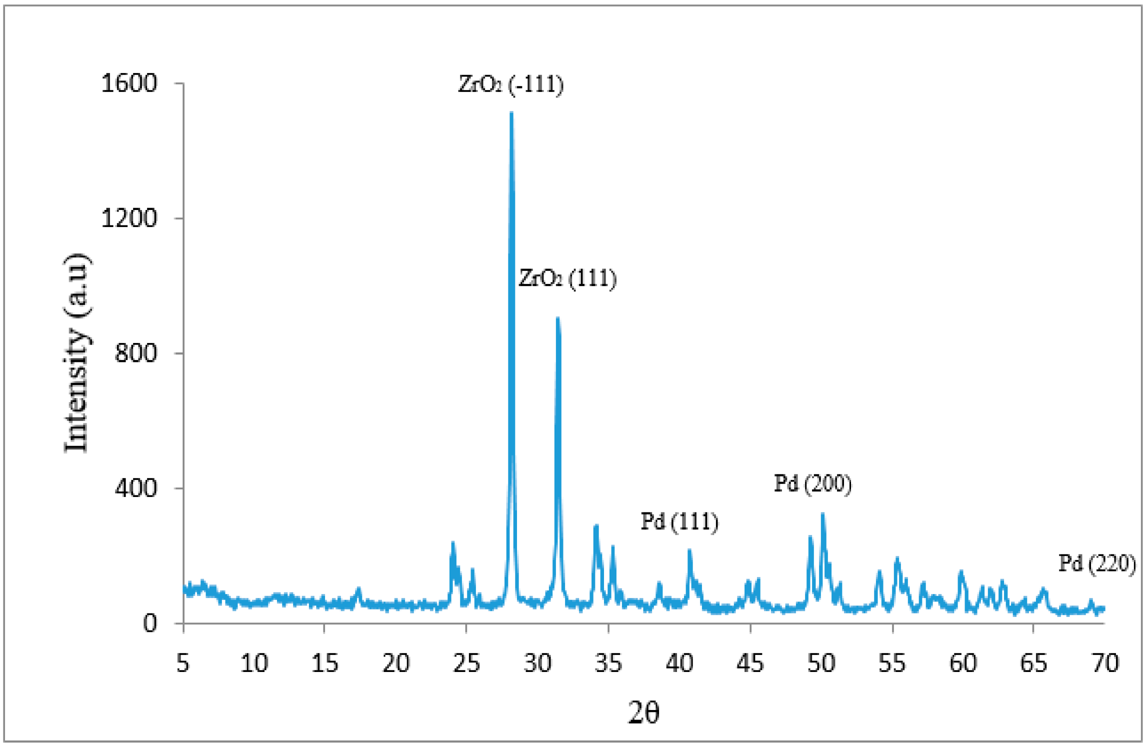


Figure 5. XRD pattern of Pd/ZrO$_2$.

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.

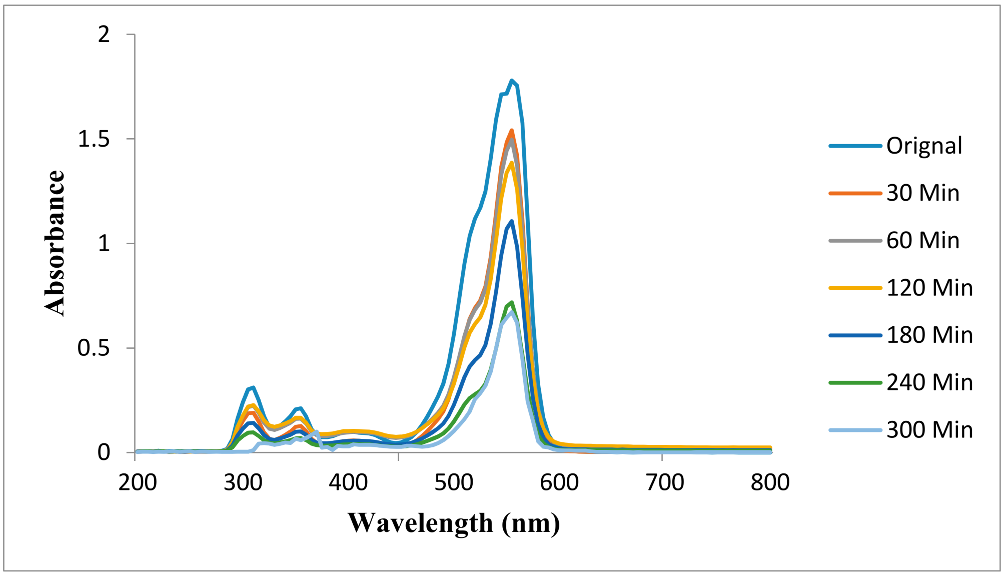


Figure 6. UV-visible spectra of RB degradation by Pd/ZrO$_2$.

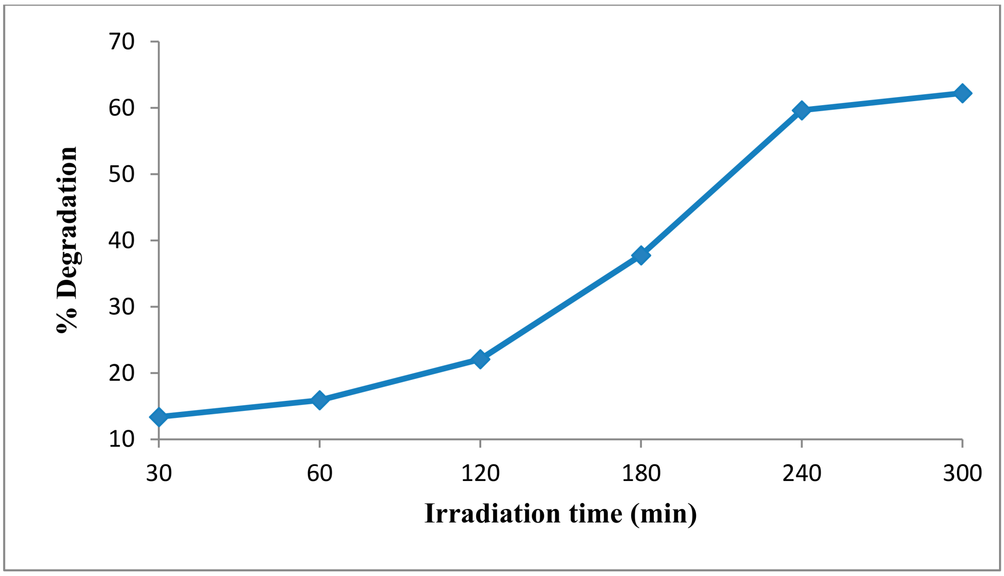


Figure 7. Time profile study for % degradation of RB catalyzed by Pd/ZrO_2.

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.

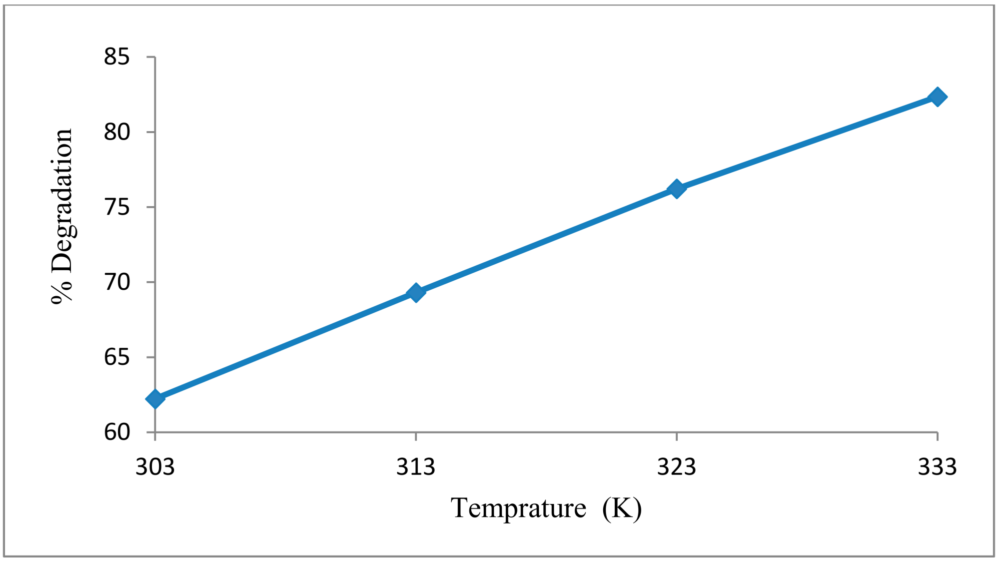


Figure 8. Effect of temperature for % dye degradation by Pd/ZrO_2.

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.

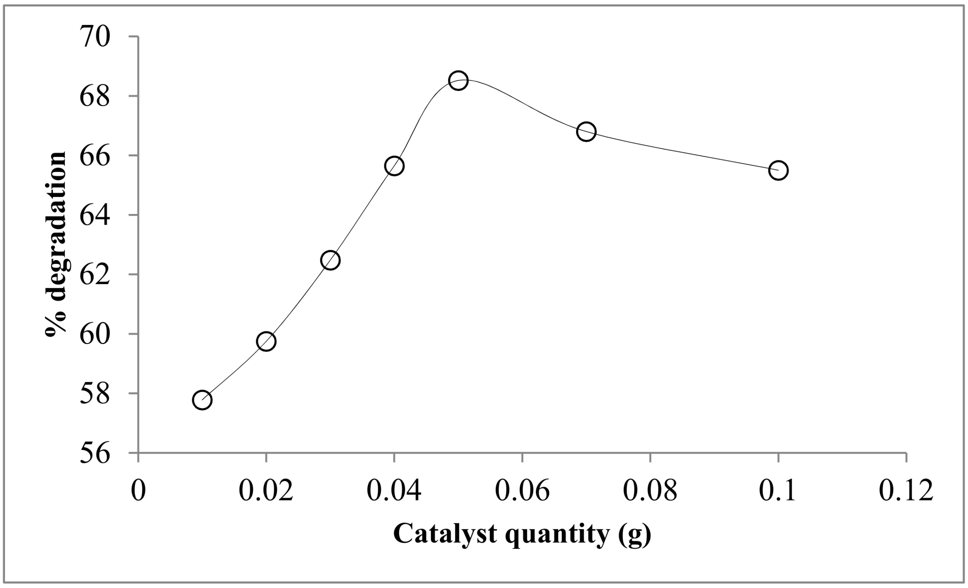


Figure 9. Catalyst loading effect on % degradation of selected dye over Pd/ZrO_2.

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 (ΔG), enthalpy changes (ΔH) and entropy change (ΔS) were calculated using the following Equations (1)–(3):

$$K_D = \frac{q_e}{C_e} \tag{1}$$

$$\Delta \mathrm{G} = -\mathrm{RT}\ln K_D \tag{2}$$

$$\ln K_D = \frac{\Delta \mathrm{G}^0}{RT} = \frac{\Delta \mathrm{H}^0}{RT} + \frac{\Delta \mathrm{S}^0}{R} \tag{3}$$

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

By plotting lnK_D verses 1/T (K^{-1}), the slope and intercept values obtained (Figure 10) were used for ΔH and ΔS calculation, respectively, which are given in Table 2.

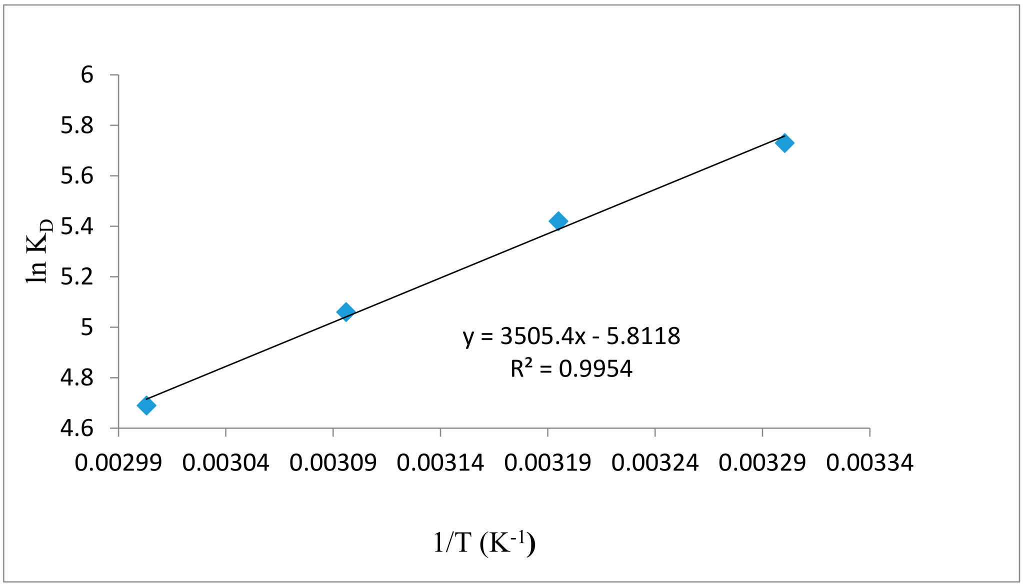


Figure 10. Thermodynamic study for RB dye degradation.

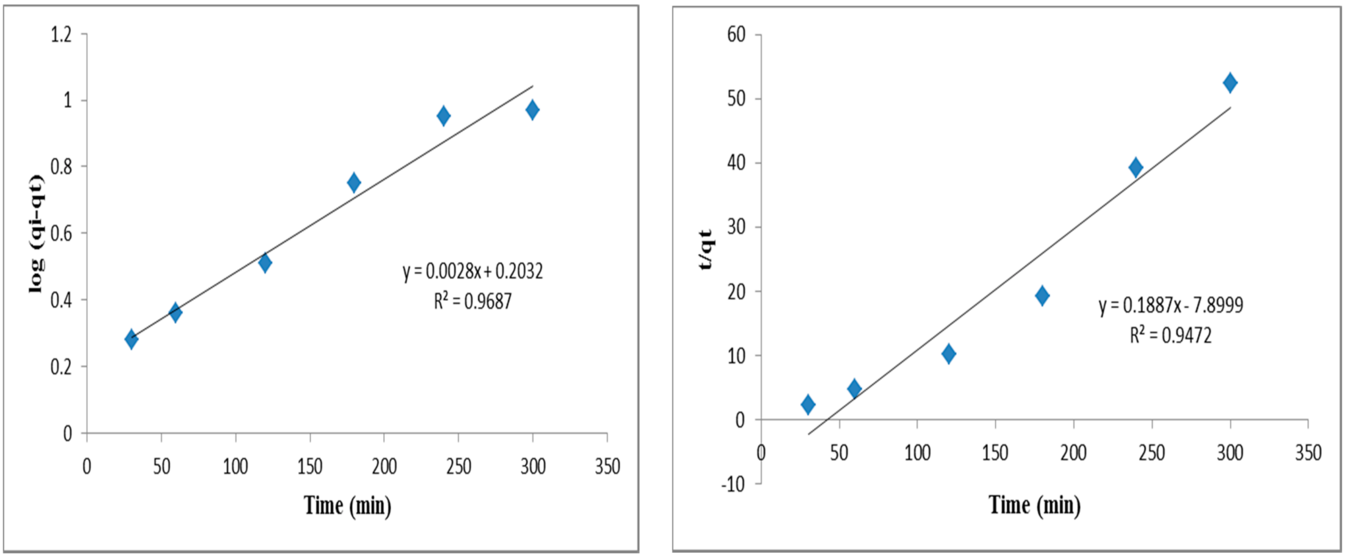
Table 2. Calculated parameters of thermodynamics for RB dye degradation.

ΔH° (kJ/mol)	ΔS° (kJ/mol)	ΔG° (kJ/mol)			
		303 K	**313 K**	**323 K**	**333 K**
−29,140.6	48.32	−14,434.7	−14,104.4	−13,588.2	−12,984.6

At different temperatures, i.e., 303, 313, 323 and 333 K, the values thermodynamic parameters like ΔG, ΔH and ΔS (Table 2). The value of ΔH is negative, showing that the interaction of sorption is exothermic in nature. The ΔG negative values shows that the sorption process is feasible and spontaneous. The ΔG value at low temperature are high indicating that degradation capacity of catalyst at low temperatures is high. The positive value of ΔS 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.



(**a**) (**b**)

Figure 11. (**a**) Pseudo 1st order kinetics model; (**b**) pseudo 2nd order kinetics model.

Table 3. Calculated values for kinetic study.

Time (min)	C_i	C_e	q_i	q_t	q_i-q_t	Log(q_i-q_t)
30	15	1.92	15	13.08	1.92	0.28
60	15	2.3	15	12.70	2.3	0.36
120	15	3.23	15	11.77	3.23	0.51
180	15	5.59	15	9.41	5.59	0.75
240	15	8.89	15	6.11	8.89	0.95
300	15	9.28	15	5.72	9.28	0.97

The pseudo first order equation can be given as:

$$\log(q_i - q_t) = logq_e - \frac{K_1 t}{2.303} \tag{4}$$

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:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 q_e^2} \tag{5}$$

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 × 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 × 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:

$$q_e = K_F C_e^{1/\mathrm{n}} \tag{6}$$

The Freundlich isotherm in logarithmic form can be given:

$$\log q_e = \log K_F + \frac{1}{\mathrm{n}} \log C_e \tag{7}$$

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:

$$q_e = \frac{\mathrm{K_l} C_e}{1 + aLC_e} \tag{8}$$

In linearized form the equation can be given as:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{aLC_e}{K_L} \quad (9)$$

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_o) 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).

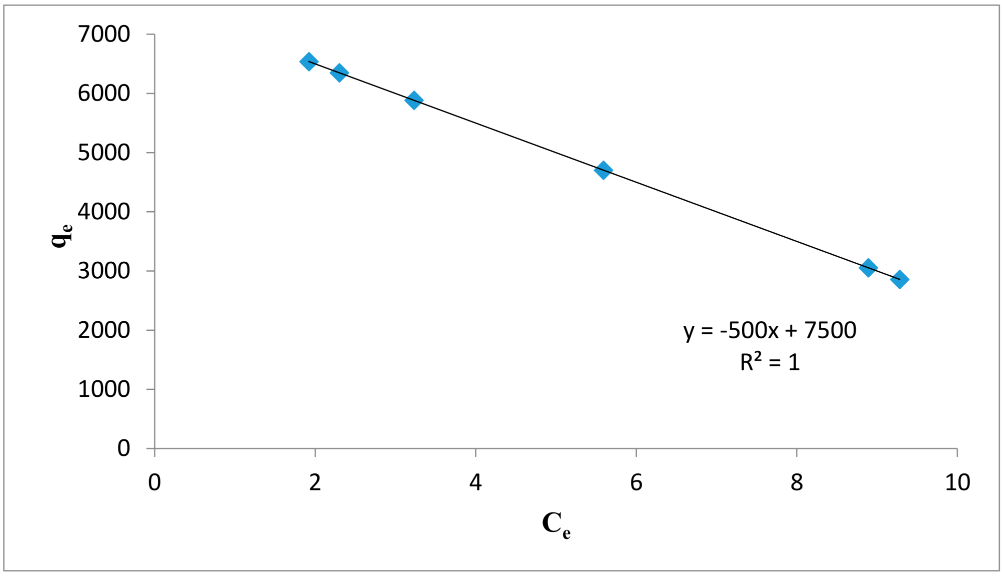


Figure 12. Freundlich Isothermal study.

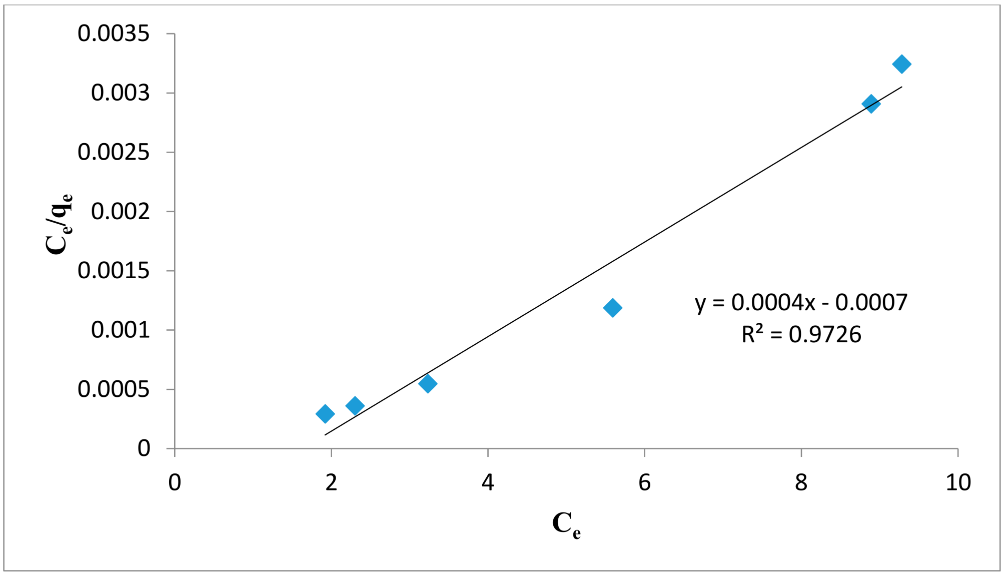


Figure 13. Langmuir isothermal plot.

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:

$$q_e = \frac{RT}{b} lnAC_e \quad (10)$$

This equation in linear form can be given as:

$$q_e = BlnA + BlnC_e \tag{11}$$

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 lnC_e and a linear curve was obtained with the slope B and intercept B lnA (Figure 14). The numerical values of the isotherm models used are given in Table 5.

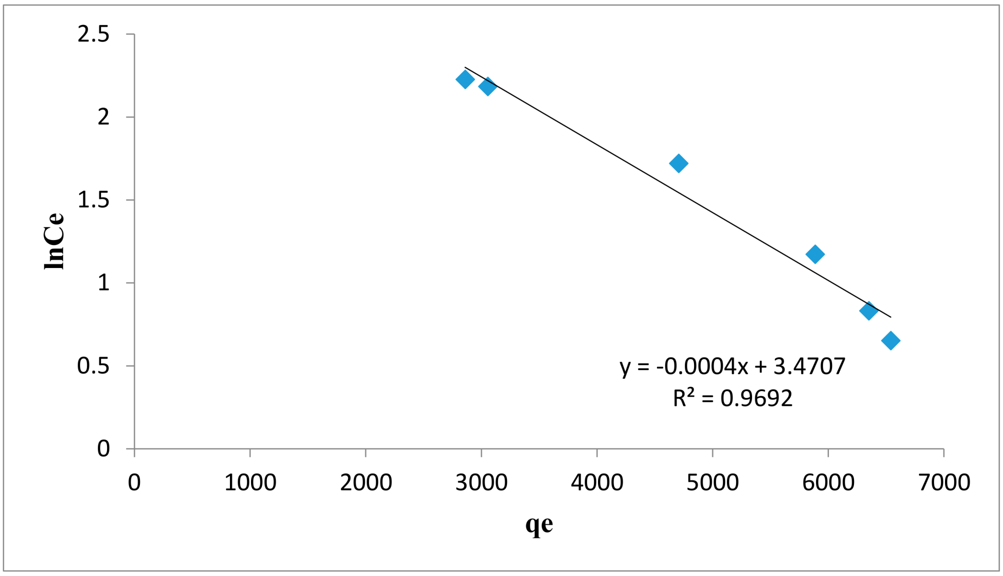


Figure 14. Temkin isothermal plot.

Table 5. Calculated parameters for isothermal models.

Sample No	Models	Parameters	Values
1	Freundlich isotherm	K_F	3×10^{85}
		N	−0.002
		R^2	1
2	Langmuir isotherm	K_L(mg/g)	0
		Q_0 (mg/g)	0
		aL	0
		R^2	0.972
3	Temkin isotherm	A_T	0
		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 Fruendlich 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 ΔH, ΔG and ΔS were calculated and the negative values of ΔH (−291.406 KJ/mol) showed the exothermic nature of the process while from negative values of Gibbs free energy (ΔG) 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.

Author Contributions: Conceptualization, S.J.; methodology, S.J.; software, M.S.K.; validation, S.S.d.R. and I.Z.; formal analysis, A.K., G.S.K. and J.B.; investigation, A.K. and R.K.; resources, M.Z.; data curation, N.P.; writing—original draft preparation, I.Z.; writing—review and editing, M.S.K. and M.M.G.; visualization, R.K. and M.S.K.; supervision, M.Z.; project administration, M.Z., A.K., N.P. and M.M.G.; funding acquisition, M.Z. All authors have read and agreed to the published version of the manuscript.

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