Kingdom of Saudi Arabia
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Study of Visible light photodegradation of Congo red dye using ZrO_2@g-C_3N_4 nanocomposite

A graduation research project

Submitted to the department of Chemistry in partial fulfillment of the requirements for the completion of the degree of Bachelor of Science in Chemistry

by

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Abstract

This study investigated the photocatalytic degradation of Congo Red (CR) dye using ZrO_2@g-C_3N_4 nanocomposite under visible light irradiation. Kinetic analysis revealed that the Elovich model best describes the degradation process, suggesting the significance of adsorption and chemisorption. The intra-particle diffusion (IPDT) model further confirmed the role of diffusion, with a two-stage mechanism governed by different rates and boundary layer effects.

The ZrO_2@g-C_3N_4 nanocomposite exhibited exceptional photocatalytic activity, achieving a degradation capacity of 27.31 mg/g for CR. This performance is comparable to many reported photocatalysts, highlighting its potential for practical water treatment applications. Future research should focus on optimizing the synthesis process, investigating the long-term stability and reusability of the material, and exploring its applicability to other dye pollutants.

الخلاصة

تناولت هذه الدراسة التحلل الضوئي لصبغة الكونغو الأحمر (CR) باستخدام مركب نانوي من أكسيد الزركونيوم ($ZrO_2@g-C_3N_4$) تحت إشعاع الضوء المرئي. كشف التحليل الحركي أن نموذج إيلوفيتش يصف بشكل أفضل عملية التحلل، مما يشير إلى أهمية الامتصاص والامتصاص الكيميائي. كما أكد نموذج الانتشار داخل الجسيمات (IPDT) دور الانتشار، مع آلية من مرحلتين يحكمها معدلات مختلفة وتأثيرات الطبقة الحدودية.

أظهر المركب النانوي من أكسيد الزركونيوم ($ZrO_2@g-C_3N_4$) نشاطًا ضوئيًا استثنائيًا، حيث حقق قدرة تحلل تبلغ 27.31 مجم / جم لـ CR. هذا الأداء مماثل للعديد من المحفزات الضوئية المبلغ عنها، مما يسلط الضوء على إمكاناته لتطبيقات معالجة المياه العملية. يجب أن تركز الأبحاث المستقبلية على تحسين عملية التخليق، والتحقيق في الاستقرار الطويل الأمد وقابلية إعادة استخدام المادة، واستكشاف إمكانية تطبيقها على ملوثات الصبغة الأخرى.

Chapter 1

Introduction

1. Introduction

1.1. Introduction:

Water pollution, caused by rapid industrialization and population growth, poses a significant threat to the health of ecosystems and human populations. Synthetic dyes, such as Congo Red, are particularly harmful due to their toxicity, carcinogenicity, and long-term environmental impacts. Traditional water treatment methods often struggle to effectively remove these persistent pollutants.

Nanotechnology offers promising solutions for water purification through the use of nanomaterials with high surface area and reactivity. These materials can effectively adsorb and degrade pollutants, addressing the limitations of traditional methods. For example, studies have demonstrated the effectiveness of carbon nanotubes and metal oxide nanoparticles in removing various pollutants from water such as heavy metals and synthetic dyes [1, 2].

Synthetic dyes, particularly azo dyes, are a significant source of water pollution, primarily from the textile, leather, and paper industries. Due to their complex molecular structures, these dyes are resistant to conventional treatment methods and can have severe environmental and health consequences. Congo Red, a representative azo dye, is known for its persistence, toxicity, and carcinogenicity. It poses a significant threat to aquatic ecosystems and public health due to its high solubility and resistance to biodegradation.

Researchers have explored various advanced treatment technologies to address the challenge of Congo Red contamination. Among these, photocatalysis, which utilizes light energy to initiate chemical reactions, has emerged as a promising approach. Notably, ZrO_2@g-C_3N_4 composites have shown significant potential for degrading Congo Red, offering a promising solution to this pressing environmental issue.

Zirconium oxide (ZrO_2) is a ceramic material of significant technological importance due to its many valuable properties. ZrO_2 is a refractory material exhibiting high thermal resistance and a high dielectric constant (~25) [3]. It also possesses excellent mechanical behavior, chemical stability (except in acidic media), and non-toxicity [4]. Moreover, ZrO_2 is biocompatible, making it suitable for biomedical applications such as implants [5].

One of the most notable features of ZrO_2 is its optical properties, particularly its high refractive index and large optical bandgap. ZrO_2's high refractive index (~2.15–2.18 eV) and optical transparency (~42%) make it valuable for optical applications [6]. As an n-type semiconductor, ZrO_2 also possesses a wide bandgap. This bandgap varies slightly depending on its crystalline structure, with the tetragonal phase typically having a bandgap energy of around 3.0–3.2 eV, while the monoclinic phase is somewhat higher at 3.3–3.4 eV [7]. These properties allow ZrO_2 to absorb light predominantly in the ultraviolet region, which is critical for applications in photocatalysis [8].

ZrO_2 is widely used in various fields, including energy storage (fuel cell electrolytes), gas sensors (oxygen sensors), and as a catalytic support in heterogeneous catalysis [9].

Graphitic carbon nitride (g-C_3N_4) has gained significant attention recently due to its promising photocatalytic properties and environmentally friendly synthesis. Composed of earth-abundant elements—carbon and nitrogen—g-C_3N_4 forms strong covalent bonds within its conjugated layer structure, making it highly stable under various chemical and thermal conditions [10]. One of its most appealing features is its narrow bandgap of approximately 2.7 eV, allowing for efficient visible light absorption (~460 nm) [11]. This feature makes g-C_3N_4 an ideal candidate for photocatalysis, especially in the degradation of pollutants through visible-light-driven processes. Its unique conjugated system, consisting of stacked layers interconnected with nitrogen-containing functional groups, enables efficient pollutant adsorption, enhancing photocatalysis's effectiveness [12]. However, despite its potential, g-C_3N_4 suffers drawbacks such as high electron-hole recombination, low absorption coefficients, and a limited specific surface area. These limitations can be mitigated by doping g-C_3N_4 with metals or metal oxides, improving its overall photocatalytic performance [12].

Due to their unique properties, zirconium oxide (ZrO_2) and graphitic carbon nitride (g-C_3N_4) are promising materials for photocatalytic applications. ZrO_2 exhibits high thermal resistance, chemical stability, and a wide bandgap, making it an excellent photocatalytic support [11-13]. g-C_3N_4, on the other hand, possesses a narrow bandgap, allowing for efficient visible light absorption and effective pollutant adsorption.

The combination of ZrO_2 and g-C_3N_4 in a composite material leverage both advantages, addressing some of their limitations. The resulting ZrO_2@g-C_3N_4 composite benefits from the

high stability and wide bandgap of ZrO_2 while overcoming g-C_3N_4's electron-hole recombination issue through the formation of heterojunctions. This enhances charge separation and overall photocatalytic activity [9, 12].

Beyond photocatalysis, ZrO_2@g-C_3N_4 composites have potential applications in energy storage, gas sensing, and other fields [13]. Further research is needed to explore this promising material's full potential and optimize its performance for specific applications.

This project investigates the photocatalytic properties of ZrO_2@gC_3N_4 nanoparticle to degrade Congo Red dye. By studying the structural, morphological, and optical properties of these nanomaterials, this research aims to contribute to developing more effective water treatment technologies.

1.2. Objective and scope

Objective:

The primary objective of this study is to investigate the **photocatalytic efficiency** of the **ZrO_2@g-C_3N_4 nanocomposite** for the degradation of **Congo Red (CR)** dye under **visible light** irradiation. The study focuses specifically on the **kinetic behavior** of the photodegradation process, aiming to identify the most appropriate kinetic model to describe the degradation rates and mechanism based on experimental data.

Scope:

The scope of this research includes:

1. To investigate the photocatalytic activity of ZrO_2@g-C_3N_4 nanoparticles for the degradation of Congo Red dye under visible light irradiation.
2. Analyzing the kinetics of photodegradation using pseudo-first-order, pseudo-second-order, and Elovich models and determining the best-fitting model based on statistical criteria.
3. To investigate the mechanism of Congo Red degradation by ZrO_2@g-C_3N_4 nanoparticles, including the role of charge separation and reactive oxygen species.
4. To compare the performance of ZrO_2@g-C_3N_4 with other reported photocatalysts for Congo Red degradation.

1.3. Arrangement of project

This project includes five chapters.

Chapter 1: Introduction and Literature Review

This chapter outlines the environmental hazards of Congo Red dye and introduces photocatalysis as a solution. It focuses on ZrO_2@g-C_3N_4 nanoparticles for their visible light activity. It highlights kinetic models like P-F-O, P-S-O, and Elovich, setting up the study's objective to evaluate photocatalytic efficiency and kinetic behavior.

Chapter 2: Experimental Methods and Materials

This chapter focuses on the synthesis of ZrO_2@g-C_3N_4 nanoparticles and the experimental setup for Congo Red photodegradation under visible light. It describes the preparation of dye solutions, dark adsorption tests, and degradation experiments. Methods for fitting experimental data to the P-F-O, P-S-O, and Elovich kinetic models are also outlined, along with data analysis techniques for calculating kinetic constants and evaluating the models' performance.

Chapter 3: Results, Discussion, and Conclusion

This chapter presents the experimental findings, showing the successful degradation of Congo Red using ZrO_2@g-C_3N_4 nanoparticles. Kinetic analysis reveals that while the P-S-O model fits well ($R^2 = 0.9812$), the Elovich model offers the best description of the photodegradation process ($R^2 = 0.9906$, RCS = 0.776). The chapter discusses the implications of these results, emphasizing the significant role of adsorption in the initial phase, and providing a deeper understanding of the degradation process. It concludes with a summary of key findings and recommendations for future research.

Chapter 2

Experimental section

2. Experiment and analysis:

2.1. Synthesis and mean structural and morphological characteristics

In a previous study, a mesoporous ZrO_2@g-C_3N_4 nanocomposite was synthesized using a one-step ultrasonication technique [14] and investigated for its potential as a sorbent material for copper ions elimination [15]. A previous study detailed the procedure for producing the nanomaterial. The ZrO_2@g-C_3N_4 nanocomposite was synthesized using a simple and efficient ultrasonication-assisted method. This method involved dispersing g-C_3N_4 nanosheets and ZrO_2 nanoparticles in methanol and subjecting the mixture to sonication. The final product was obtained through drying and annealing.

The structural and morphological characterization of the nanomaterial, as previously described by Khezami L. et al. [15], revealed its well-defined crystalline structure, as confirmed by X-ray diffraction (XRD), which showed peaks corresponding to both ZrO_2 and g-C_3N_4 with a crystallite size of approximately 14 nm for ZrO_2. The material demonstrated a specific surface area of 95.7 m^2/g and a pore volume of 2.16×10^{-7} m^3/g, indicating its mesoporous nature. Scanning electron microscopy (SEM) images displayed a network of interconnected nanoscale particles. At the same time, energy-dispersive X-ray spectroscopy (EDX) and elemental mapping confirmed the uniform distribution of C, N, O, and Zr throughout the composite.

In the current study, we are extending the investigation to assess the photocatalytic efficiency of this ZrO_2@g-C_3N_4 nanocomposite under visible light for the degradation of Congo Red dye, focusing on its ability to degrade the dye and its potential for effective environmental remediation.

2.2. Congo red photodegradation experiments

To investigate the photocatalytic degradation of Congo Red (CR) dye, ZrO_2@g-C_3N_4 nanoparticles were employed as the photocatalyst. A 20 ppm CR solution was prepared and mixed with the photocatalyst, followed by a 30-minute equilibration period in the dark to establish adsorption-desorption equilibrium. Subsequently, the suspension was exposed to visible or light irradiation from an OSRAM 58 LM/W lamp Samples were withdrawn at regular intervals (e.g., 5 minutes, 10 minutes, 30 minutes, etc.) and centrifuged to separate the photocatalyst. Concurrently, a control beaker containing the same solution without adding the photocatalyst was exposed to light irradiation to evaluate the photolysis effect. The remaining CR concentration in

the supernatant was quantified using a UV-vis spectrophotometer at 620 nm. Multiple trials were conducted under varying experimental conditions, including visible light, to evaluate the photocatalytic performance of the ZrO_2@g-C_3N_4 nanoparticles.

The equation used to calculate q_e (mg/g), which represents the amount of dye adsorbed per unit mass of adsorbent based on the dye's initial and equilibrium concentrations in the solution, is as follows:

$$qt=(Ci-Ct)\cdot V/m \quad (1)$$

Where:

- C_i (ppm) is the initial concentration of the dye.
- C_t (ppm) is the concentration of the dye at equilibrium.
- V (L) is the volume of the solution.
- m (g) is the mass of the adsorbent.

Chapter 3

Results and discussion

3. Result and discussion

3.1. Calibration curve

According to **Beer-Lambert's Law**, the optical density (OD) is proportional to the concentration **C** (within a certain concentration range):

$OD = \varepsilon \cdot l \cdot C$

Where:

- **ε**: extinction coefficient, expressed in $l \cdot mol^{-1} \cdot cm^{-1}$ or $l \cdot mg^{-1} \cdot cm^{-1}$.
- **l**: path length of the cuvette used, in cm.
- **C**: concentration of the substance, in $mg \cdot l^{-1}$ or $mol \cdot l^{-1}$.

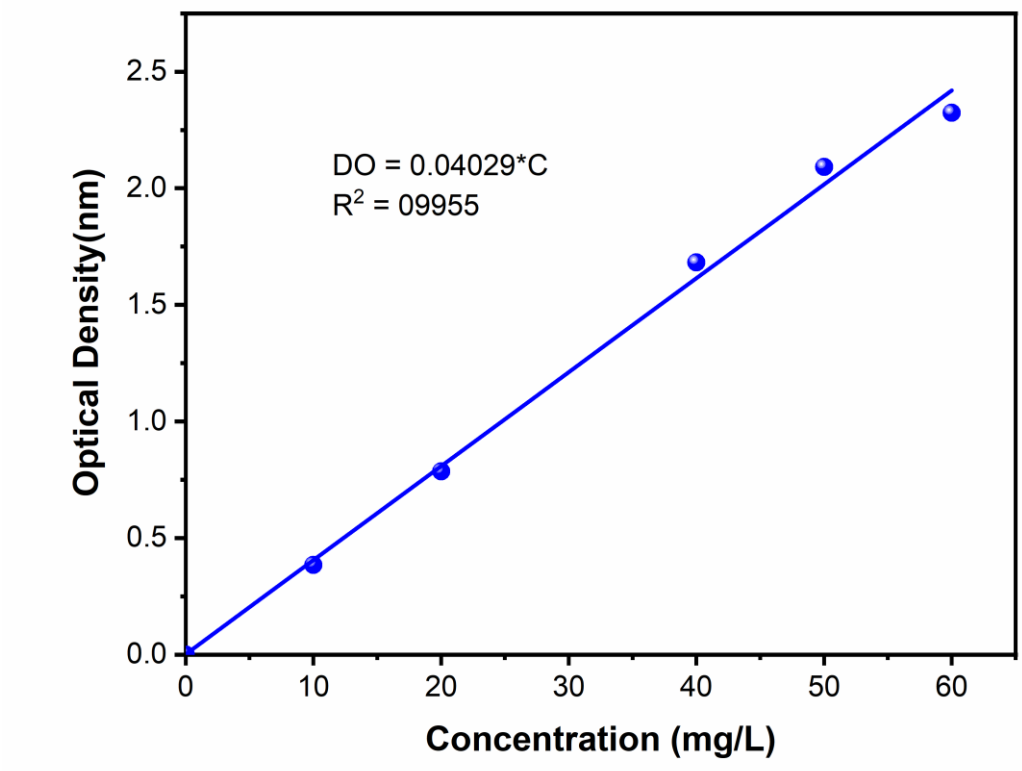

Figure 1: calibration curve of the optical density versus the dye concentration.

Thus, it is possible to establish a calibration curve for each of the CR dyes (**OD = f(C)**). Using this curve (or by determining the extinction coefficient), the concentration of the substance can be calculated by simply measuring the optical density at the same wavelength used to create the calibration curve (Figure 1).

The well-fitted calibration curve demonstrates a strong linear relationship between the absorbance at 620 nm and the concentration of Congo Red. This result confirms the applicability of Beer-Lambert's Law in this specific case and ensures the accuracy of Congo Red concentration determinations based on absorbance measurements.

3.2. Dark adsorption, photolysis, and photodegradation of CR dye

Figure 2 shows how Congo Red (CR) was absorbed in the dark for 30 minutes, followed by photodegradation with ZrO_2@g-C_0N_4 nanoparticles acting as a catalyst in visible light. During the dark phase, a plateau is observed, indicating the establishment of adsorption-desorption equilibrium between CR and the catalyst surface.

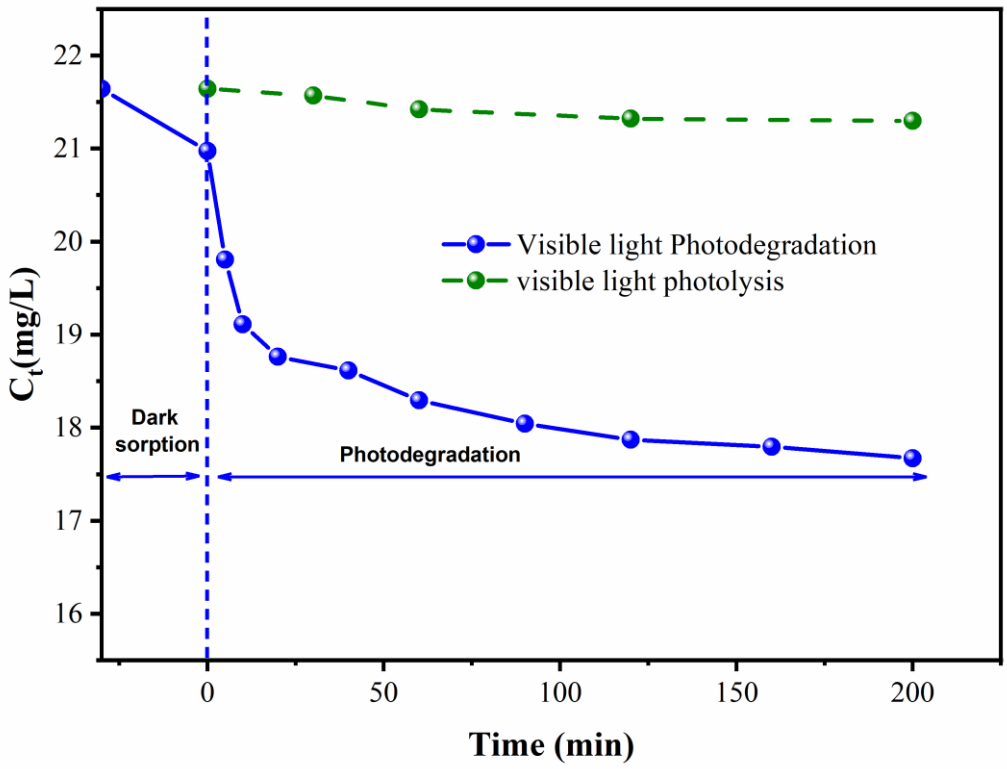

Figure 2. Adsorption, photolysis, and photodegradation of Congo Red Using ZrO_2@g-C_3N_4 Nanocomposite Under Visible Light Irradiation.

This finding ensures that any subsequent changes in CR concentration are solely due to photocatalytic degradation. A significant decrease in CR concentration is observed upon exposure to visible light, indicating efficient photocatalytic degradation by ZrO_2@g-C_3N_4. The green curve represents the photolysis effect, where CR is exposed to light without a catalyst. This

control experiment demonstrates CR's much slower degradation rate in the absence of the catalyst, highlighting the superior photocatalytic performance of ZrO_2@g-C_3N_4. The experimental results demonstrate the effectiveness of ZrO_2@g-C_3N_4 nanoparticles in degrading Congo Red dye under visible light irradiation. The enhanced photocatalytic activity compared to photolysis highlights the potential of this material for water treatment applications.

3.3. Study of photodegradation kinetics

Table 1 presents the analysis of Congo Red dye photodegradation kinetics under visible light irradiation using ZrO_2@g-C_3N_4 as a photocatalyst, which is further illustrated in **Figure 3**.

Table 1. Various parameters of kinetic models for photodegradation CR dye.

Kinetics Models	Nonlinear model	Eq. No.	Variables	Parameters Unit	Calculated Values
P-F-O	$q_t = q_e(1 - e^{-k_1 t})$	(3)	q_e	$mg.g^{-1}$	24.65 ± 0.98
			k_1	min^{-1}	0.082 ± 1.5 x 10^{-2}
			RCS	-	**5.161**
			R^2	-	**0.9389**
P-S-O	$q_t = k_2 q_e^2 t/(1 + k_2 q_e t)$	(4)	$q_{e\ (calculated)}$	$mg.g^{-1}$	27.51 ± 0.32
			$q_{e\ (experimental)}$	$mg.g^{-1}$	27.31 ± 0.77
			k_2	$mg.(mg.min)^{-1}$	3.86x10^{-3} ± 6.5x10^{-4}
	$h_0 = k_2 q_e^2$	(5)	$t_{1/2}$	*min*	9.49
			h_0	$mg.(g.min)^{-1}$	2.88
	$t_{1/2} = 1/k_2 q_e$	(6)	*RCS*	-	**1.588**
			R^2	-	**0.9812**
Elovich	$q_t = \frac{1}{\beta} Ln(\alpha\beta t)$	(7)	β	$g.mg^{-1}$	0.217 ± 0.013
			α	$mg.(g.min)^{-1}$	9.72 ± 2.25
			RCS	-	**0.776**
			R^2	-	**0.9908**
IPDT	$q_t = k_{dif} t^{\frac{1}{2}} + C$	(8)	C_1	$g.mg^{-1}$	2.131
			K_{dif1}	$mg.g^{-1}.min^{-1/2}$	3.774
			RSS	-	**2.578**
			R^2	-	**0.9189**
			C_2	$g.mg^{-1}$	16.751
			K_{dif2}	$mg.g^{-1}.min^{-1/2}$	0.779
			RSS	-	**0.0091**
			R^2	-	**0.9579**

The kinetic models used include the pseudo-first-order (P-F-O), pseudo-second-order (P-S-O), and Elovich models, each providing insight into photodegradation. In these models, qe and qt represent the quantities of CR dye photodegraded at equilibrium (mg/g) and time t (min). k_1 and

k_2 are the pseudo-first and pseudo-second order rate constant, and is the initial adsorption rate ($mg/(g.min)^{-1}$), and β is the desorption constant. The model with the highest regression coefficient (R^2) and the lowest Reduced Chi-Sqr. (RCS), was considered the best fit. This approach comprehensively assesses the photocatalytic process and helps elucidate the underlying mechanisms.

The Pseudo-First-Order (P-F-O) model, commonly applied in systems where reactant concentration decreases exponentially with time, provides a reasonable fit with an R^2 value of 0.9389. However, this model is less optimal than others in describing the photodegradation process. The P-F-O model suggests that the degradation rate depends primarily on the remaining dye concentration. Still, it fails to capture the complexity of the reaction mechanism and interactions on the catalyst surface.

The Pseudo-Second-Order (P-S-O) model, assuming chemisorption as the rate-limiting step, offers a highly accurate description of the photodegradation kinetics. With a higher R^2 value of 0.9812 than the P-F-O model, this model highlights the role of surface reactions and active sites on the photocatalyst, suggesting that the degradation process is governed by chemisorption mechanisms. The kinetic constants for the P-S-O model, including k2=3.86×10−3 mg/g.min and a half-life t1/2= 9.49 min, further support the idea that chemisorption significantly influences the degradation kinetics of Congo Red (CR).

However, the Elovich model provides the best overall fit for the photodegradation of Congo Red under visible light irradiation, with an even higher R^2 value of 0.9906 and a lower reduced chi-square (RCS) value of 0.776. The Elovich model, which is often used to describe heterogeneous adsorption processes, suggests that the initial stages of the reaction are dominated by adsorption, where the dye molecules strongly adhere to the surface of the ZrO_2@g-C_3N_4 photocatalyst. The Elovich model, therefore, provides a more statistically significant and detailed description of the experimental data than the P-S-O model, particularly in explaining the early stages of the degradation process.

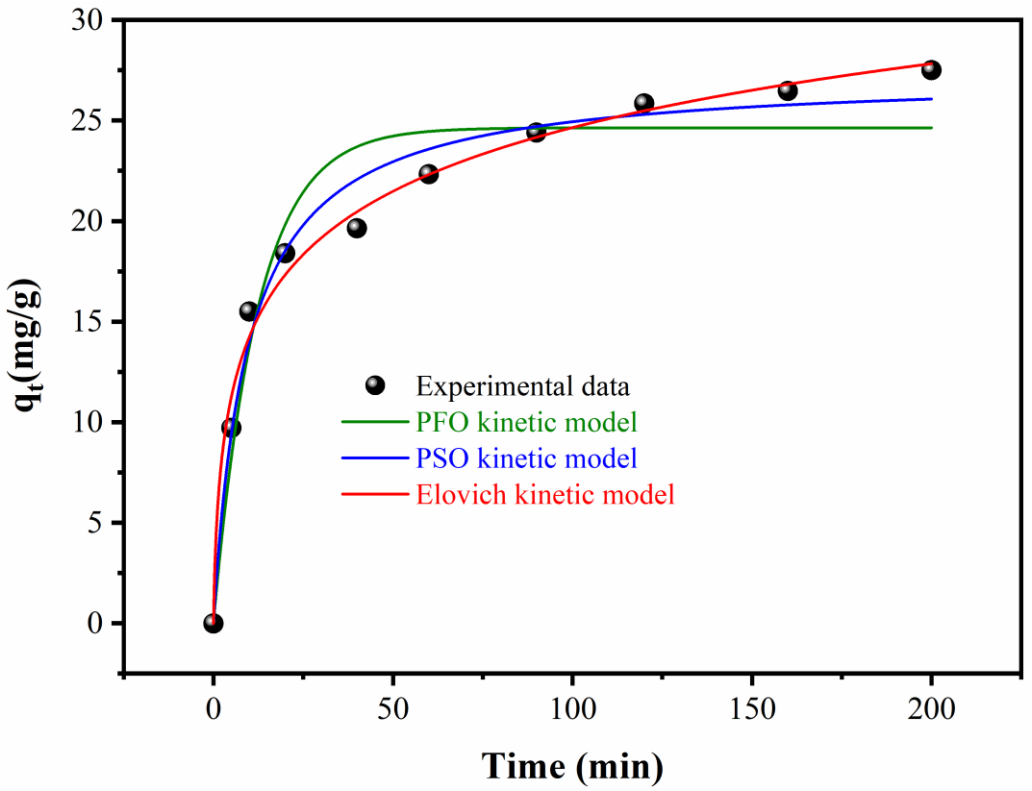

Figure 3: Fitting experimental data of different non-linear kinetic model PFO, PSO, Elovich, for Congo Red photodegradation under visible light.

Figure 3 illustrates the experimental data and the fitted curves for all three kinetic models. It clearly shows that both the P-S-O and Elovich models provide excellent fits for Congo Red photodegradation under visible light. However, the Elovich model stands out as the most reliable for describing the process in its entirety.

The Elovich model not only captures the adsorption phenomena occurring during the early stages of photodegradation but also reflects the overall degradation kinetics more comprehensively than the other models. Its superior fit, indicated by a lower RCS and the highest R^2, underscores the importance of adsorption in the efficiency of ZrO_2@g-C_3N_4 as a photocatalyst for dye degradation, providing a comprehensive and reliable description of the process.

3.4. Study of photodegradation mechanism:

The intra-particle diffusion (IPDT) model was used to analyze the photodegradation mechanism of Congo Red (CR) dye onto the ZrO_2@g-C_3N_4 photocatalyst (Table 1). The diffusion constants

(k_{dif}) and the boundary layer thickness parameter (C) are derived from the slope and intercept of the linear plot of Q_t versus $t^{1/2}$, as depicted in **Figure 4**. The analysis revealed that intra-particle diffusion is a significant factor in the photodegradation process. The diffusion parameters, k_{dif} and C, were determined from the slope and intercept of the plot, respectively (Table 1).

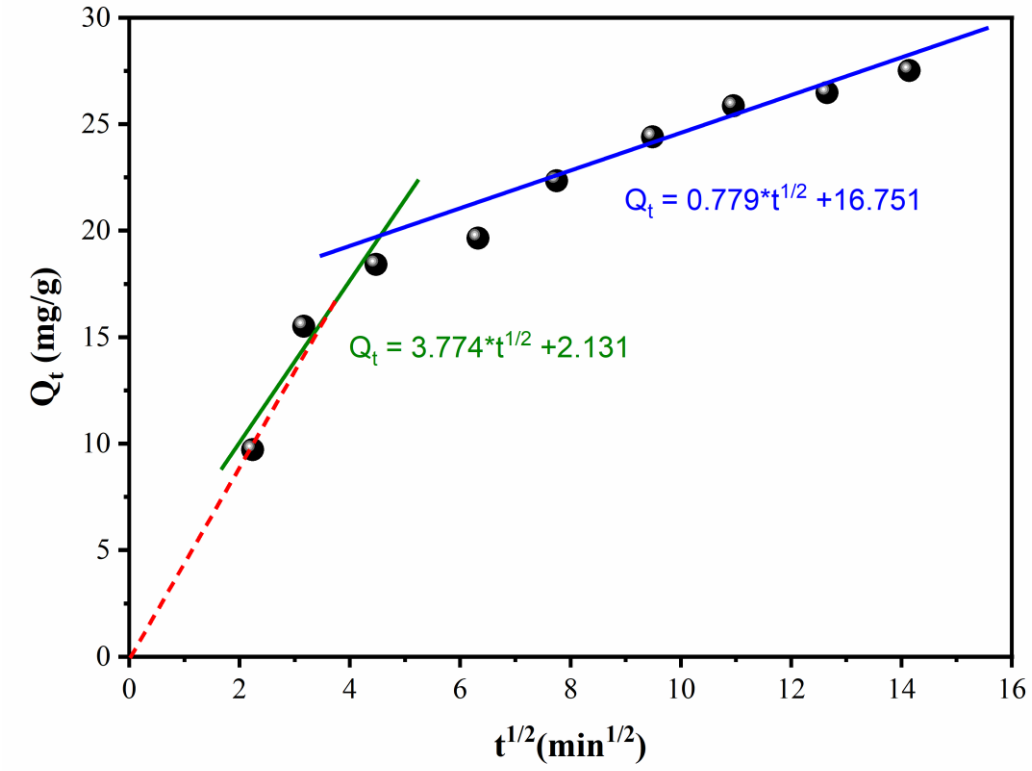

Figure 12: Intra-particular diffusion/transport model plots.

In the first stage, the diffusion constant kdif1 = 3.774 $mg.g^{-1}.min^{-1/2}$ and boundary layer parameter C_1 = 2.131 indicate rapid dye migration to the photocatalyst surface. As adsorption progresses, kdif2 decreases to 0.779 $mg.g^{-1}.min^{-1/2}$, while C_2 rises to 16.751, showing a more substantial boundary layer effect near equilibrium.

The linear relationship between Q_t and $t^{1/2}$ and a high R^2 = 0.9579 confirm intra-particle diffusion's key role. Initially, the high adsorption rate (with k_{dif1} = 3.774) slows as equilibrium is reached due to reduced concentration gradients and fewer available mesopores.

The IPDT model effectively captures the CR dye photodegradation, with diffusion playing a critical role**.**

The kinetic analysis revealed that the Elovich model best describes the photodegradation of Congo Red (CR) dye by ZrO_2@g-C_3N_4, indicating the significant role of both diffusion and chemisorption in the overall process. The intra-particle diffusion (IPDT) model further supports the importance of diffusion, as evidenced by the linear relationship between Q_t and $t^{1/2}$.

Conclusions

4. Summary and Conclusion

The present study demonstrates that ZrO_2@g-C_3N_4 nanocomposite is an effective photocatalyst for degrading Congo Red (CR) dye under visible light. Adsorption experiments conducted in dark conditions for 30 minutes, followed by photodegradation under visible light, revealed significant degradation efficiency. The maximum amount of CR dye removed during the photodegradation process was qe ≈ 27.31 mg/g, calculated using the PSO model. The kinetic analysis revealed that the Elovich model provided the best fit for the photodegradation data, with a high regression coefficient R2=0.9906 and the lowest reduced chi-square RCS = 0.776, outperforming both the pseudo-first-order and pseudo-second-order models.

The pseudo-second-order kinetic constants were also determined, showing that k_2 = 3.86×10^{-3} mg/g.min, with a calculated half-life time $t_{1/2}$ = 4.25 min. Despite these results, the Elovich model better captured the complexity of the surface interactions and chemisorption mechanisms during the degradation process.

Additionally, the Intra-particle Diffusion/Transport (IPDT) model highlighted the crucial role of diffusion in the overall process. The diffusion constants, k_{dif}, along with boundary layer thickness parameters, C, suggest that intra-particle diffusion was a significant factor in controlling adsorption kinetics. This finding further confirms the effectiveness of ZrO_2@g-C_3N_4 as a photocatalyst, particularly in processes where diffusion limitations influence the degradation rate.

The study conclusively shows that ZrO_2@g-C_3N_4 is a highly efficient photocatalyst for degrading CR dye, removing significant quantities of dye from aqueous solutions. These findings offer a promising route toward developing effective catalysts for wastewater treatment and environmental remediation applications.

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