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Kinetics of Phenol Degradation Using TiO_2/Zeolite Composite

Andi Eka Kartika[1], Sumiati Side[1*], Diana Eka Pratiwi[1], Nur Afni[1]

[1]Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Negeri Makassar,Makassar, South Sulawesi,

Corresponding Address:sumiati.side@unm.ac.id

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ABSTRACT

Phenol is a hazardous organic pollutant commonly found in industrial wastewater and is difficult to degrade through conventional treatment methods, thus requiring more effective and sustainable approaches. Photocatalytic degradation using TiO_2 has been widely explored; however, its performance is limited by rapid electron–hole recombination and low surface area. Combining TiO_2 with zeolite enhances adsorption capability and increases the availability of active sites, offering a promising strategy to improve photocatalytic efficiency. This study aims to analyze the kinetic behavior of phenol degradation using a TiO_2/zeolite composite and to determine the optimum irradiation time based on a pseudo-first-order kinetic model. Irradiation times of 15, 30, 45, 60, and 75 minutes were applied, and phenol concentrations were measured using UV–Vis spectrophotometry at 270,20 nm. The results show rapid degradation during the first phase (15-30 minutes), with removal efficiency increasing from 83.014% to 87.315%. After 30 minutes, the degradation rate becomes nearly constant, indicating the attainment of photocatalytic dynamic equilibrium. The -ln(Ct/C0) plot reveals two distinct reaction phases: an initial high-rate phase followed by a plateau phase. Therefore, 30 minutes is identified as the most efficient irradiation time, representing the point at which maximum degradation is achieved before the reaction rate significantly decreases. These findings provide meaningful insight into the photocatalytic kinetics of TiO_2/zeolite composites and support their potential application in phenolic wastewater treatment.

Keywords: *Photocatalysis, TiO_2/Zeolite, Phenol Degradation, Kinetics, Wastewater Treatment*

I. INTRODUCTION

Clean water is a fundamental resource that significantly determines the quality of life and public health. However, various reports indicate that the quality of waters in Indonesia remains concerning. The Directorate of Water Pollution Control of the Ministry of Environment and Forestry reported that the national Water Quality Index (WQI) in 2023 only reached 54.59, which is lower than the target value of 55.4. This reflects that many rivers in Indonesia are still categorized as polluted with an increasing pollution load, especially from domestic waste and industrial activities in urban and coastal areas (Direktorat Pengendalian Pencemaran Udara, 2023) This. condition is particularly evident in the coastal areas of Makassar City, where rivers and the sea become the final discharge point for various waste disposals, requiring serious attention, especially concerning the presence of toxic pollutants like phenol compounds (hydroxybenzene, C6H5OH), which are dissolved organic pollutants frequently found in industrial effluents.

Water quality monitoring data conducted in the coastal region of Makassar shows that the phenol concentration at all observation stations has exceeded the quality standard for marine biota, which is 0.002 mg/L, as regulated in the Decree of the Minister of Environment

No. 51 of 2004. In tourism areas, ports, and aquaculture zones, phenol levels were recorded to reach 1.52 mg/L, 1.03 mg/L, and up to 0.08 mg/L, values that signify significant pollution and indicate a strong pressure from domestic waste, industrial activities, and sea transportation (Suharto et al., 2018).

Phenol is an aromatic organic compound widely used in the chemical industry, such as in the production of resins, plastics, pesticides, and pharmaceuticals. However, waste containing phenol is toxic, carcinogenic, and difficult to decompose naturally, making its presence in aquatic environments a serious threat to human health and the ecosystem. Therefore, the development of effective and environmentally friendly methods for degrading phenol is crucial in industrial waste management (Mohd, 2022; Setyaingtyas et al., 2018).

Conventional waste treatment methods such as coagulation-flocculation, activated carbon adsorption, and biological processes are generally unable to remove phenol effectively because they only transfer the pollutant to sludge, produce hazardous residues, and are incapable of reducing the toxicity of non-biodegradable aromatic compounds. Several studies have shown that phenol, which has a stable aromatic structure, is difficult to degrade through biological processes and often escapes conventional treatment systems (Ahmaruzzaman et al., 2024; Saputera et al., 2021)

One of the most promising approaches for wastewater treatment is the photocatalytic process, particularly utilizing titanium dioxide (TiO_2) as the catalyst. TiO_2 is renowned for its high chemical stability, non-toxicity, and ability to generate highly reactive hydroxyl radicals (•OH) under UV irradiation (Kholidah et al., 2021). However, pure TiO_2 possesses significant limitations that hinder its effectiveness in degrading organic pollutants. These major constraints include the rapid recombination of electron–hole (e^-/h^+) pairs, low quantum yield, limited activity only under ultraviolet (UV) light, and poor reusability. Consequently, the ability of pure TiO_2 to utilize sunlight and generate active oxidative species is restricted, resulting in low overall photocatalytic efficiency (Wang et al., 2025). Therefore, modification of TiO_2 with other materials is essential to enhance its overall photocatalytic performance.

Recent studies show that TiO_2 can be enhanced through structural modification or the creation of composites with support materials, one of which is Zeolite, which serves a dual function as an adsorbent and a photocatalyst support. Zeolite is a porous aluminosilicate material characterized by a high surface area, excellent adsorption capacity, and superior thermal and chemical stability. The combination of TiO_2/Zeolit is expected to enhance photocatalytic efficiency through the synergy between zeolite's adsorption ability and the photocatalytic activity of TiO_2 (Armaković & Armaković, 2025).

Although various studies have explored the use of TiO_2/Zeolit composites in the photodegradation process, the research focus is generally still limited to degradation efficiency and material characterization. For instance, a study by Xue et al., (2025) demonstrated that using fly ash-based zeolite supports the uniform distribution of TiO_2, resulting in a 98.36% removal rate for methylene blue and showcasing very high photodegradation efficiency.

Nevertheless, an in-depth study concerning the photodegradation rate and the reaction kinetic characteristics within the TiO_2/Zeolit composite system still needs to be strengthened. This aligns with the findings of Liu et al., (2022), which showed that 3D-zeolite-TiO_2 composites significantly increased the photodegradation efficiency of Rhodamine B, with the highest reaction rate constant achieved at a 5 wt% (kapp = 0.188 min^{-1}). That study emphasizes the critical importance of kinetic modeling and reaction rate analysis for a more comprehensive understanding of the photocatalytic mechanism. Comprehension of kinetic parameters is crucial for designing optimal, efficient, and applicable wastewater treatment systems both at the industrial scale and in real-world environments.

Therefore, this research is designed to conduct a kinetic analysis of phenol degradation using the TiO_2/Zeolit composite. By applying the first-order reaction kinetic model, this study

aims to identify the optimum irradiation time at which the degradation efficiency reaches a steady state. These results will provide fundamental data that can complement existing literature and contribute to the development of a more efficient and sustainable phenol wastewater treatment technology.

II. METHODS

II.1 Instruments and Materials

The instruments utilized in this study included a set of standard glassware, a magnetic stirrer, a shaker, an analytical balance, a stopwatch, a UV reactor, a Phillips TUV 15W/G15 T8 lamp (λ = 360 nm), a spray bottle, and a UV-Vis spectrophotometer (Shimadzu UV-2450). The materials used were TiO_2/zeolite composites obtained from previous research (Side & Putri, 2020), distilled water (H_2O), hydrochloric acid solution (HCl, 6 M), ethanol (C_2H_5OH, 96%), phenol, aluminum foil, filter paper, and Whatman filter paper.

II.2 Experimental Procedure

II.2.1 Preparation of Standard Curves

The standard curve for phenol was established by first preparing a 1000 ppm stock solution through the dissolution of 1 g of phenol powder in deionized water to a final volume of 1000 mL. From this stock solution, a series of phenol solutions with concentrations ranging from 2 to 10 mg/L at 2 mg/L intervals were prepared. The absorbance of each solution was measured using a UV-Vis spectrophotometer at a wavelength of 270.20 nm to construct the calibration curve.

II.2.2 Degradation of Phenol

The degradation of phenol dye was investigated under varying irradiation times. The time variation study (15, 20, 45, 60, and 75 minutes) was performed by preparing 50 mL of 10 mg/L phenol solution and adding 0.1 g of the TiO_2/zeolite composite catalyst. Each dye solution was placed in a degradation reactor and continuously stirred during UV irradiation at a wavelength of 280 nm for the specified durations. After irradiation, the suspension was separated by centrifugation at 7000 rpm for 15 minutes. The absorbance of the supernatant was then analyzed using a UV-Vis spectrophotometer to determine the residual dye concentration.

II.2.3 Determination of Rate Constant

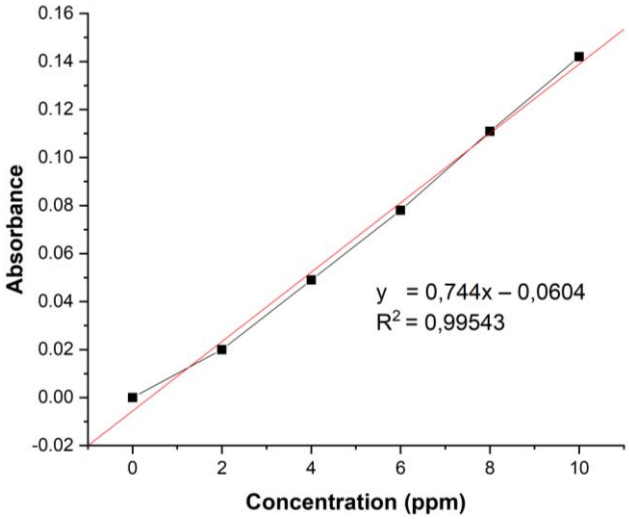
The experimental data were analyzed according to a pseudo-first-order kinetic model to determine the degradation rate constant, as expressed in Equation (1):

$$C_t = C_0 e^{-kt} \text{ atau } ln\frac{C_t}{C_0} = -kt \quad (1)$$

where C_t is the concentration of phenol remaining at time t, C_0 is the initial concentration of phenol, and *k* is the constant of the reaction rate. By making the curve - ln (C_t/C_0) *vs*. t it is possible to determine the slope of the curve which represents the constant of the reaction rate.

III. RESULTS AND DISCUSSION

The standard curve was obtained by measuring the absorbance of phenol solutions at various concentrations, 0-10 ppm at 2 ppm intervals, at a wavelength of 270.20 nm. Phenol absorbs light in the UV region because it has conjugated double bonds in the benzene group. The maximum absorption at the wavelength ($\boldsymbol{\lambda}_{max}$) 270.20 nm is the result of the $\pi \rightarrow \pi^*$ electronic transition. This transition is consistent with literature stating that benzene derivative compounds with a hydroxyl substituent **(-OH)** in a polar solvent show absorption in that region (Pareek, 2021).



IV. V. **Figure 1.** Fenol standard curve VI.

The relationship between the phenol concentration and the absorbance value obtained is presented in Figure 1. The graph shows a very good and linear correlation between phenol concentration (X-axis) and absorbance (Y-axis). From this standard curve, the linear regression equation is obtained as follows:

$$y = 0.744x – 0.00604$$

with a determination coefficient of 0.99543, the R^2 value that is very close to 1 indicates that the phenol absorbance data are highly accurate and precise, fully complying with the Lambert–Beer Law within the concentration range of 0-10 ppm.

The percentage of phenol degradation as a function of irradiation time using the TiO_2/Zeolite catalyst is presented in detail in Table 1 and visualized in Figure 2. The data show that the degradation percentage increases sharply in the initial minutes and then reaches a stable condition. At the initial time (15 minutes), the degradation of phenol was around 83.014%. This sharp increase indicates that the photocatalytic reaction rate proceeds rapidly during the early phase, likely because the phenol concentration is still high and the active surface of the photocatalyst has not yet reached saturation (Seloglu et al., 2024). In addition, this strong adsorption capability results from the synergistic effect of the surface area and pore characteristics of TiO_2 and zeolite, which function as pre-concentration agents, attracting phenol molecules to the active sites of the catalyst before the photodegradation process begins (Tsaplin et al., 2023).

A significant increase occurs between 15 and 30 minutes, during which the average degradation reaches 87.315%. This sharp rise (approximately 4.3%) indicates that photocatalytic activation under UV irradiation has proceeded intensively, generating hydroxyl radicals (•OH) that quickly react with phenol adsorbed on the catalyst surface (Andari & Wardhani, 2018). After 30 minutes, the phenol degradation rate tends to stabilize primarily due to the saturation of active sites on the surface of the TiO_2/Zeolite catalyst. In the initial phase of the photoreaction, phenol molecules are rapidly adsorbed onto the active sites and react with hydroxyl radicals (•OH). However, as the process continues, most of these active sites become occupied by phenol or intermediate products, significantly reducing the catalyst's ability to adsorb new molecules. Once this condition is reached, the photodegradation reaction no longer increases even though UV irradiation continues, causing the degradation percentage to appear constant at longer irradiation times. This active-site saturation phenomenon has been reported as a major factor contributing to the decreased photodegradation rate in various TiO_2 composite

systems based on porous adsorbents (Diban et al., 2021). At 60 minutes, the degradation reaches 87.4945% and remains constant up to 75 minutes.

Table III.1 . Results of Contact Time Test (Kinetics) on Phenol Degradation Percentage

Time (minute)	Initial Concentration (mg/L)	Final Concentration (mg/L)	Degradation	Persen Degradation (%)	Average (%)
15	10	1.304301075	0.869569892	86.95698925	83.0143369
	10	1.694086022	0.830591398	83.05913978	
	10	2.097311828	0.790268817	79.02688172	
30	10	1.290860215	0.870913978	87.09139785	87.3154122
	10	1.223655914	0.877634409	87.76344086	
	10	1.290860215	0.870913978	87.09139785	
45	10	1.263978495	0.873602151	87.36021505	87.4050179
	10	1.263978495	0.873602151	87.36021505	
	10	1.250537634	0.874946237	87.49462366	
60	10	1.263978495	0.873602151	87.36021505	87.4946237
	10	1.237096774	0.876290323	87.62903226	
	10	1.250537634	0.874946237	87.49462366	
75	10	1.250537634	0.874946237	87.49462366	87.4946237
	10	1.277419355	0.872258065	87.22580645	
	10	1.223655914	0.877634409	87.76344086	

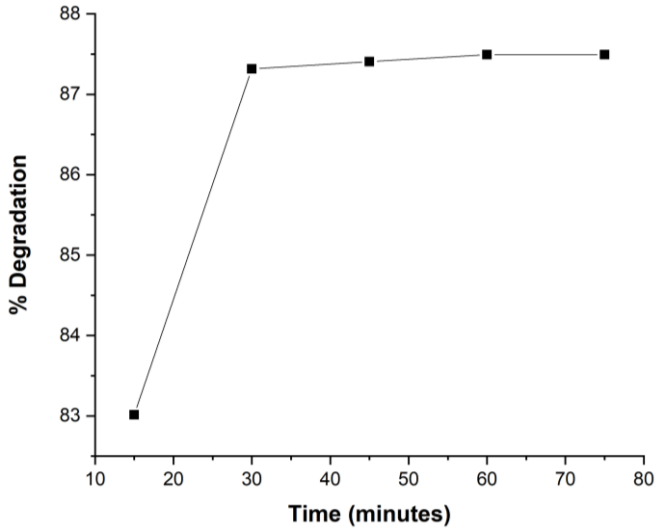


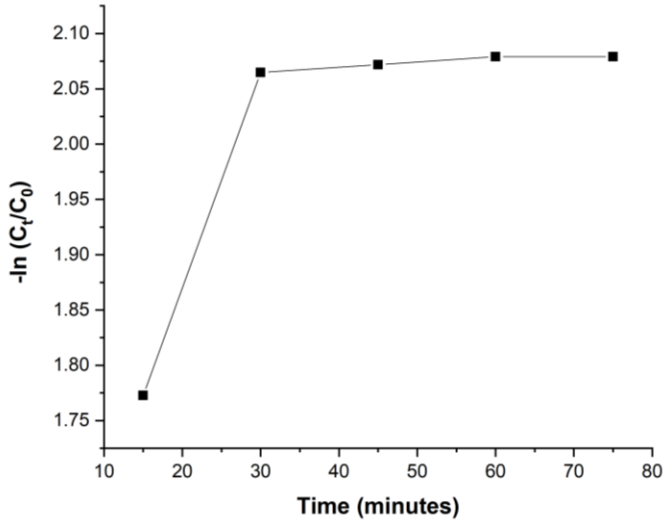
Figure 2. Plot Phenol Degradation vs. Variation in Irradiation Time

Based on the graph, the determination of the optimum time at 30 minutes is not only based on the highest degradation value achieved, but also takes into account energy efficiency and process time. Although there is a slight increase in the percentage of degradation after 30 minutes, the increase is insignificant (only about 0.1%). This stagnation phenomenon in degradation after 30 minutes of irradiation indicates the achievement of a photocatalytic dynamic equilibrium, as explained by Dang et al., (2016) and Z. Liu et al., (2024), where the phenol degradation rate becomes proportional to the rate of side reactions or diffusion limitations formed during the process.

The determination of the reaction rate and the photocatalytic degradation mechanism is crucial for evaluating catalyst performance. The experimental data were analyzed using a first-order reaction kinetics model, where the relationship between $-\ln(C_t/C_0)$ and time (t) is visualized through a linear regression graph. The reaction rate constant (k), which serves as an indicator of process efficiency, can be calculated from the slope of the resulting line (Putri et al., 2025).

Figure 3 shows the presence of two distinct phases in the degradation process. The first phase (15-30 minutes) is characterized by a sharp increase in the $-\ln(C_t/C_0)$ value, from approximately 1.77 to 2.06. The steepness of the graph in this interval indicates a high degradation rate and a large reaction rate constant **(k)** in the initial stage. This condition occurs because the reactant concentration is still relatively high and the entire active surface of the photocatalyst is still available, allowing the reaction to proceed optimally without significant hindrance.

Figure 3. Plot-ln (C_t/C_0) vs. t for photodegradation of Phenol



Conversely, the second phase (30-75 minutes) shows a very different behavior. The graph becomes almost flat (plateau), with a very small increase in -ln(Ct/C0), only from 2.06 to about 2.08. This drastic change in slope signifies that the reaction rate has slowed down significantly and approaches zero. This deceleration indicates that the majority of the degradation process has been achieved and the system has likely approached saturation or equilibrium conditions, so further increases in irradiation time no longer provide a meaningful increase in the total degradation (Fauzi et al., 2024). Thus, a contact time of 30 minutes can be declared as the most efficient optimum condition, because at this duration, the maximum degradation level is achieved before the reaction rate experiences a decline.

VII. CONCLUSION

The results of this study demonstrate that the TiO_2/zeolite composite exhibits strong photocatalytic performance in degrading phenol, achieving its highest efficiency of 87.314% at 30 minutes of irradiation. Kinetic evaluation using the pseudo-first-order model reveals the presence of two reaction phases: an initial rapid degradation phase followed by a plateau phase in which the reaction rate significantly declines. The minimal change in degradation after 30 minutes indicates that the system has reached a photocatalytic dynamic equilibrium, making additional irradiation time ineffective for further improvement. Therefore, 30 minutes is established as the optimum irradiation time when considering both efficiency and energy usage. Overall, these findings strengthen the potential application of TiO_2/zeolite composites as an

effective photocatalytic material for phenol-containing wastewater treatment and provide essential kinetic insights for future system design and optimization.

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