

Photocatalytic Kinetics of Sago Wastewater Using Titanium Dioxide

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Abstract. Sago processing is an important industry in Malaysia. However, it generates a complex, starch-rich wastewater with high organic matter content that requires in-depth investigation to develop effective treatment strategies. In this study, sago wastewater was treated via photocatalysis using titanium dioxide (TiO₂) under controlled ultraviolet (UV) irradiation from a 20 W UV light source and under natural sunlight irradiation. While previous studies on sago wastewater treatment have mainly focused on pollutant removal efficiency, limited attention has been given to the kinetics of photocatalytic degradation. Photocatalytic performance was evaluated based on reductions in chemical oxygen demand (COD), biological oxygen demand (BOD), and total suspended solids (TSS). Under controlled UV irradiation, reductions of 72%, 61%, and 53% in COD, BOD, and TSS, respectively, were achieved after 150 min. Photocatalytic treatment under natural sunlight irradiation was slower, resulting in a 44% COD reduction over the same duration. Kinetic analysis using the pseudo-first-order and pseudo-second-order kinetic models showed good agreement with the experimental results. The pseudo-first-order rate constants ranged from 0.0046 to 0.0085 min⁻¹, whereas the pseudo-second-order rate constants ranged from 8×10^{-6} to 1×10^{-5} L mg⁻¹ min⁻¹. The kinetic parameters provide valuable insights into the photocatalytic degradation behavior of sago wastewater beyond removal-efficiency evaluation and support the assessment of treatment approaches for sustainable sago wastewater management.

Keywords: Biological Oxygen Demand, Chemical Oxygen Demand, Kinetics, Photocatalysis, Pseudo-First-Order Model, Pseudo-Second-Order Model, Sago Wastewater

INTRODUCTION

The sago industry is an important agro-based sector in Malaysia with export volumes ranging from 24,000 to 40,000 tons per year, primarily from Sarawak (Mohamad *et al.*,

2024). Despite its economic importance, sago processing generates substantial volumes of wastewater. Approximately 30,000 to 35,000 L of wastewater can be produced per ton of sago processed (Anbukumar *et al.*, 2014). This wastewater is typically acidic and

contains high concentrations of organic matter, suspended solids, lipids, proteins, and carbohydrates (Rashid *et al.*, 2024), with reported COD, BOD, and TSS ranging from 11,600 to 75,000 mg/L, 2,500 to 32,000 mg/L, and 300 to 6,700 mg/L, respectively (Srinivasan *et al.*, 2020). If inadequately treated, sago wastewater undergoes rapid fermentation, produces foul odors, and causes severe oxygen depletion in receiving water bodies. Previous studies have reported its adverse effects on soil fertility and seed germination (Ayyasamy *et al.*, 2016; Sivananda, 2010) as well as toxic and genotoxic impacts on aquatic organisms (Ramesh & Nagarajan, 2016). These environmental risks highlight the need for effective and reliable treatment strategies for sago wastewater.

Researchers have investigated various treatment technologies for sago wastewater, including biological, physical, and chemical methods. Biological treatments such as aerobic and anaerobic digestion can achieve COD removal efficiencies up to 95% (Jaganathan *et al.*, 2025) but are often associated with generating large quantities of sludge (Aura *et al.*, 2024), which may require additional handling and disposal costs. Moreover, studies have shown that anaerobically treated sago wastewater may still retain suspended solids, turbidity, and high levels of residual nitrogen and phosphorus, which may cause eutrophication and oxygen depletion in receiving water bodies (Jaganathan *et al.*, 2025). Physical and chemical methods, such as coagulation–flocculation and membrane filtration, can effectively remove particulates but are limited in removing dissolved organic pollutants and are associated with high operational and maintenance costs. These limitations have driven interest in advanced oxidation

processes as alternative or complementary treatment options.

Among advanced oxidation processes, photocatalysis using TiO_2 has attracted considerable attention due to its strong oxidative capability and potential to mineralize organic pollutants into harmless end products such as carbon dioxide and water. Numerous studies have demonstrated the effectiveness of TiO_2 -based photocatalysis in degrading a wide range of pollutants (Kanaraju *et al.*, 2019; Ren *et al.*, 2021; Shareef & Ayesha, 2023; Rostami *et al.*, 2021), confirming its robustness as a wastewater treatment technology. However, most reported studies focus on synthetic wastewater systems or emphasize pollutant removal efficiencies, while systematic kinetic evaluations using the real agro-industrial wastewater remain limited. In this study, the photocatalytic degradation of real sago wastewater was evaluated in terms of COD, BOD, and TSS reduction under controlled ultraviolet (UV) irradiation, with additional experiments conducted under natural sunlight. Understanding the performance differences between these irradiation sources is important for assessing the potential transition from laboratory-scale UV photocatalysis toward sustainable solar-driven wastewater treatment, particularly in tropical regions with abundant solar availability. Therefore, additional experiments under natural sunlight irradiation were conducted to evaluate the feasibility of solar-driven photocatalytic treatment of sago wastewater. Kinetic analysis employing pseudo-first-order and pseudo-second-order kinetic models was carried out for the controlled UV irradiation data, providing quantitative insight into degradation dynamics rather than removal performance alone. The resulting kinetic parameters

improve understanding of photocatalytic treatment behavior for complex agro-industrial wastewater.

Kinetic Modelling

Understanding the kinetics of photocatalytic degradation is essential for process optimization, reactor design, and scale-up, as kinetic analysis provides quantitative information on degradation rates, treatment duration, and catalyst performance. The kinetics of photocatalysis can be modeled using the Langmuir-Hinshelwood (L-H) model, which was originally developed for catalytic surface reactions. This model accounts for the adsorption of organic pollutants on the catalyst, the reaction of the adsorbed species, and product desorption. Several authors adopt the L-H model for photocatalytic degradation kinetics, including Tran *et al.* (2023), Khezrianjoo & Revanasiddappa (2012), Bloh (2019), Ayu Murti *et al.* (2025), Loghambal *et al.* (2018), and Carrasco-Venegas *et al.* (2021). This model describes the degradation rate as shown in Eq. (1).

$$-\frac{dC}{dt} = \frac{k_r KC}{1 + KC} \quad (1)$$

Where C is the pollutant concentration, k_r is the surface reaction constant, and K is the adsorption equilibrium constant. When $KC \ll 1$, the denominator simplifies (~ 1), giving a first-order-like expression in C. Conversely, when $KC \gg 1$, the reaction approximates zero-order with respect to C. Although the L-H model accounts for adsorption and reaction effects, it does not consider other factors such as mass transport, light intensity, catalyst surface changes, or intermediate formation.

Given the complexity of heterogeneous

photocatalytic systems, some researchers adopt simplified kinetic models to describe pollutant degradation. The pseudo-first-order (PFO) kinetic model, derived from the Langmuir-Hinshelwood framework under low pollutant concentration is widely used for its simplicity and its ability to provide an apparent rate constant for comparing catalyst performance. In some cases, the pseudo-second-order (PSO) kinetic model is applied when the reaction rate appears to depend strongly on the pollutant concentration or when the catalyst surface significantly influences the overall reaction. Some studies show good fitting with PSO and PFO kinetic models, including those presented by Pang *et al.* (2022), Ramaprabha & Kumar (2025), Hadian *et al.* (2021), Rytwo & Zelkind (2021), Ahmad *et al.* (2023), Etay *et al.* (2023), and Susanti *et al.* (2021). The pseudo-first-order kinetic model is typically expressed as shown in Eq. (2) and can be simplified into Eqs. (3)-(4). The pseudo-second-order kinetic model is presented in Eq. (5) and can be rearranged into simplified forms, shown in Eqs. (6)-(7). Commonly, PFO and PSO kinetic models for describing adsorption include the term C_e , the equilibrium adsorption capacity, to account for adsorption toward equilibrium on the catalyst surface. However, in this study, the models are applied to describe the photocatalytic degradation kinetics, focusing on the decrease of pollutant concentration in solution rather than adsorption on the catalyst.

$$\text{PFO kinetic model, } n = 1; -\frac{dC}{dt} = k_1 C \quad (2)$$

$$\ln C = -k_1 t + \ln C_0 \quad (3)$$

$$C = C_0 e^{-k_1 t} \quad (4)$$

$$\text{PSO kinetic model, } n = 2; -\frac{dC}{dt} = k_2 C^2 \quad (5)$$

$$\frac{1}{C} = k_2 t + \frac{1}{C_0} \quad (6)$$

$$C = \frac{C_0}{k_2 C_0 t + 1} \quad (7)$$

Here, C_0 is the initial pollutant concentration (mg/L), C is the pollutant concentration at time t , and k_1 (min^{-1}) and k_2 ($\text{L}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$) are the rate constants.

The use of pseudo-first-order and pseudo-second-order kinetic models in this study is justified by the characteristic degradation behavior commonly observed in photocatalytic wastewater treatment systems. In such systems, process performance is typically evaluated in terms of pollutant removal, where COD, BOD, and TSS decrease rapidly at the initial stage of treatment and progressively approach minimum values corresponding to an apparent steady-state condition. This behavior reflects the rapid degradation of readily oxidizable compounds, followed by a gradual slowdown as reactive species are depleted and reaction or surface limitations become dominant. The mathematical forms of both PFO and PSO kinetic models effectively capture this exponential-type degradation trend, thus providing a practical basis for describing photocatalytic degradation behavior. Accordingly, in this study, we applied both PFO and PSO kinetic models to analyze the temporal reduction of COD, BOD, and TSS during photocatalytic treatment of sago wastewater.

MATERIALS AND METHODS

Sago wastewater used in this study was collected from a nearby sago processing mill. The initial characteristics of the wastewater were measured before treatment: temperature 28°C , pH 7.5, BOD 1211 mg/L,

COD 1533 mg/L, TSS 755 mg/L, and turbidity 2927 NTU. These characteristics reflect the high organic and particulate content typical of sago processing effluent. All experiments were conducted at room temperature (approximately 25°C). 500 mL of sago wastewater was used and placed in an opaque container to prevent external light interference and ensure the photocatalytic reaction was driven solely by the intended irradiation source. Titanium dioxide (TiO_2) powder (Sigma-Aldrich, 99% purity) was added at a dosage of 2 g (equivalent to 4 g catalyst per L of wastewater) to provide sufficient catalytic surface area for effective photocatalytic reactions while avoiding excessive turbidity that could limit light penetration. Continuous mixing was maintained at 200 rpm using a magnetic stirrer to ensure homogeneous suspension of the TiO_2 particles. For controlled photocatalytic treatment, a 20 W UV bulb was immersed directly into the wastewater. Experiments were also conducted under direct natural sunlight without artificial UV illumination using similar operating conditions to assess the potential applicability of solar-driven photocatalysis under practical conditions. This study did not directly measure solar irradiation intensity. However, the average solar irradiation reported for a comparable area was approximately 16 MJ/m^2 (Jakhrani *et al.*, 2012), which can be used as a reference. The total reaction time was set to 150 minutes. COD, BOD, and TSS were measured every 30 minutes. The degradation rate was calculated based on the change in measured COD, BOD, and TSS between two consecutive sampling points over a 30-minute interval using Eq. (8).

$$\text{degradation rate} = \frac{C_t - C_{t+\Delta t}}{\Delta t} \quad (8)$$

where C_t and $C_{t+\Delta t}$ represent the values of

COD, BOD, and TSS measured in mg/L at two sampling times, and t represents the time interval (min). The calculated rate is expressed as mg/L.min. Kinetic analysis was studied using PFO and PSO kinetic models, as described in the Introduction section. Further evaluation was also conducted using the Solver function in Microsoft Excel to perform non-linear fitting of the kinetic models. The Solver function minimized the root mean square error (RMSE) by iteratively adjusting the rate constants to obtain the best fit between the experimental and predicted values.

RESULTS AND DISCUSSION

Photocatalytic Degradation Performance

Pollutant degradation was evaluated based on reductions in COD, BOD, and TSS; lower values indicate higher photocatalytic degradation performance. Tables 1-2 present the measured COD, BOD, and TSS values of the treated sago wastewater. The results show that photocatalytic degradation occurred more slowly under sunlight compared to experiments conducted using a 20 W UV bulb. Although the same amount of catalyst was used in both experiments, the UV illumination intensity that triggered the reaction differed. This observation is consistent with findings by Yuceturk (2024), who showed that photocatalytic reactions can be optimized more effectively under controlled artificial light sources such as UV bulbs than under natural sunlight. The UV bulb provided stronger and more consistent UV radiation. In contrast, sunlight intensity varies with time of day and weather conditions, and the ozone layer attenuates part of its UV components. These factors may reduce the photocatalytic efficiency under solar irradiation. Despite these limitations,

the results obtained under natural sunlight demonstrate the feasibility of solar-assisted photocatalytic treatment of sago wastewater. However, photocatalytic performance under sunlight should be interpreted cautiously, as fluctuations in solar irradiance can affect degradation efficiency compared with controlled UV illumination.

Table 1. COD of treated wastewater

Time (min)	COD			
	Light bulb		sunlight	
	mg/L	%	mg/L	%
0	1533	0	1553	0
30	1218	22	1289	17
60	793	49	1118	28
90	664	57	1041	33
120	543	65	931	40
150	438	72	870	44

Table 2. BOD and TSS of treated wastewater

Time (min)	BOD		TSS	
	(light bulb)	(light bulb)	(light bulb)	(light bulb)
	mg/L	%	mg/L	%
0	1211	0	755	0
30	987	18	627	17
60	803	34	544	28
90	778	36	498	34
120	650	46	453	40
150	477	61	355	53

Under sunlight exposure, COD decreased by approximately 44% after 150 minutes. In contrast, photocatalytic degradation under the 20 W UV bulb resulted in approximately 72% reduction over the same treatment duration. These results indicate that the COD reduction under the 20 W bulb was nearly twice that achieved under sunlight for an equivalent time. Nevertheless, despite the slower photocatalytic degradation observed under sunlight irradiation, solar-driven treatment may offer a

potential cost advantage by eliminating the need for artificial UV sources. For experiments conducted under the 20 W bulb, the estimated reductions in BOD and TSS were 61% and 53 %, respectively, after 150 minutes. The percentage reductions in COD, BOD, and TSS at different times are presented in Figures 1-4.

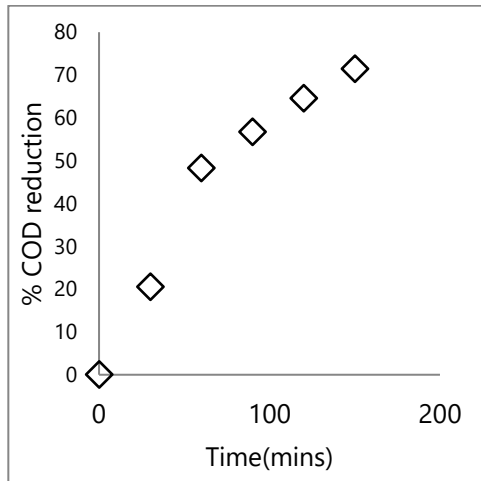


Fig. 1: COD versus time under the 20W bulb

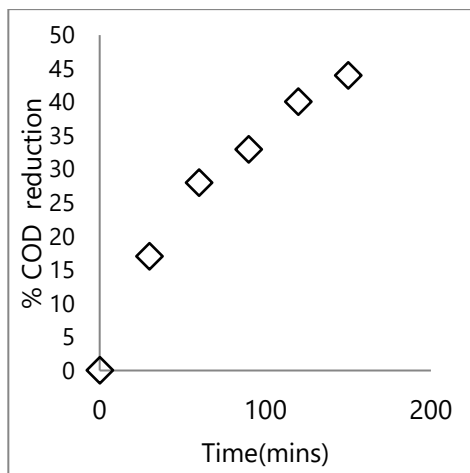


Fig. 2: COD versus time under sunlight

Figures 5-8 show the degradation rate, indicating that the initial rapid reaction phase within the first 60 minutes corresponds to the steep increase in COD, BOD, and TSS reduction in Figures 1-4, followed by a gradual decline. Initially, a high concentration of photogenerated electrons and hydroxyl radicals enhances the oxidation of the

organic compounds, which relates to the increase in the degradation rate. As the reaction proceeds, active catalytic sites become increasingly occupied, and the concentration of easily oxidizable organics decreases, resulting in a decline in reaction rates. The degradation rate for COD was higher than that estimated for BOD and TSS. COD degradation refers to the oxidation of biodegradable and non-biodegradable compounds. At the same time, BOD measures only the biodegradable portion, and TSS measures solid particles suspended in the wastewater and does not include dissolved organic matter.

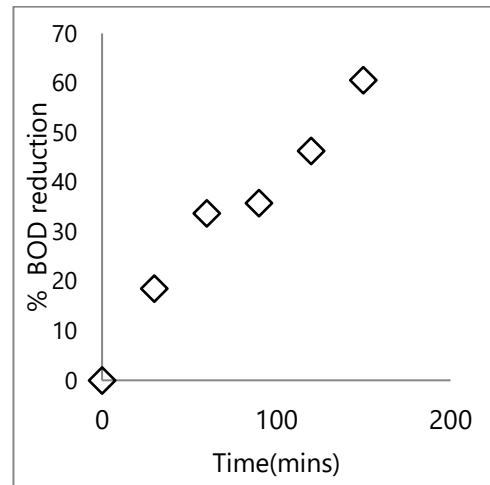


Fig. 3: BOD versus time under the 20 W bulb

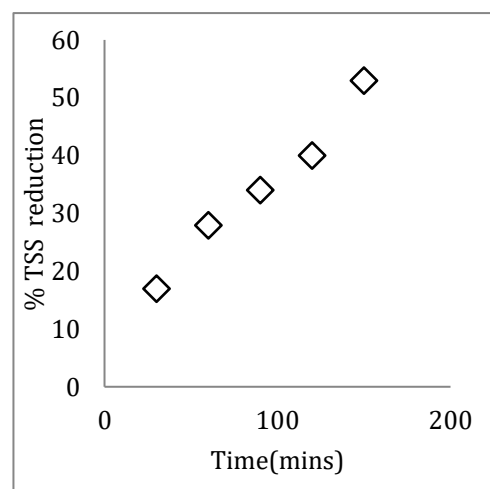


Fig. 4: TSS versus time under the 20 W bulb

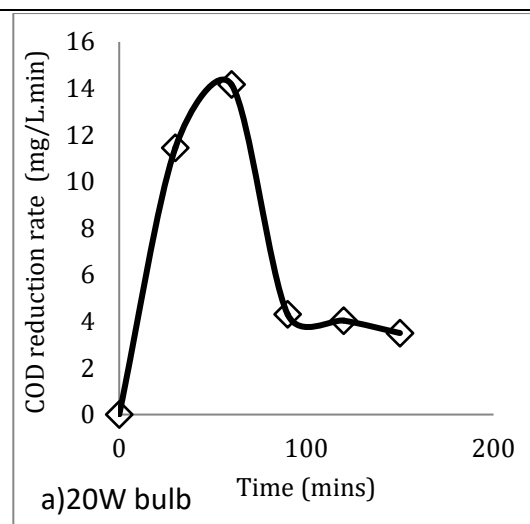


Fig. 5: COD reduction rate versus time under the 20 W bulb

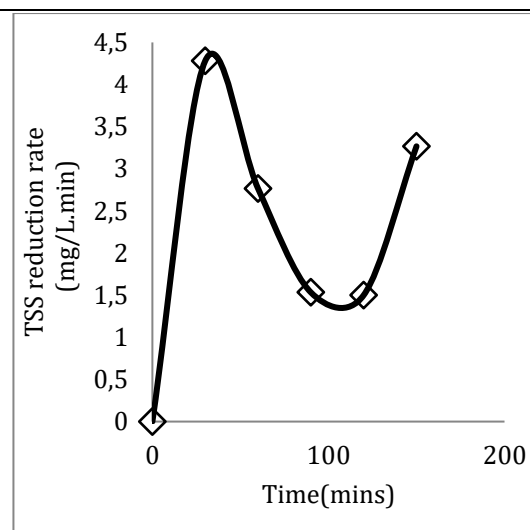


Fig. 8: TSS reduction rate versus time under the 20 W bulb.

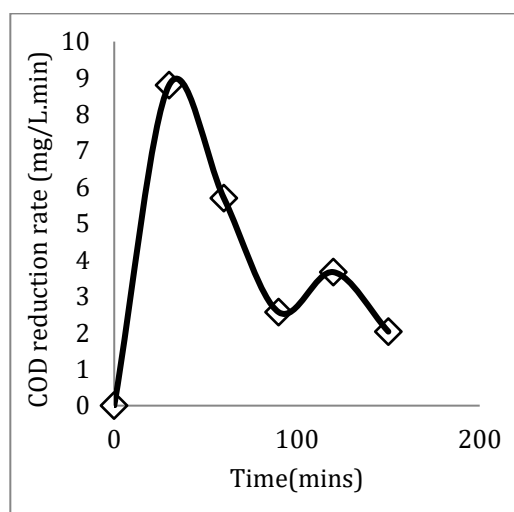


Fig. 6: COD reduction rate versus time under sunlight

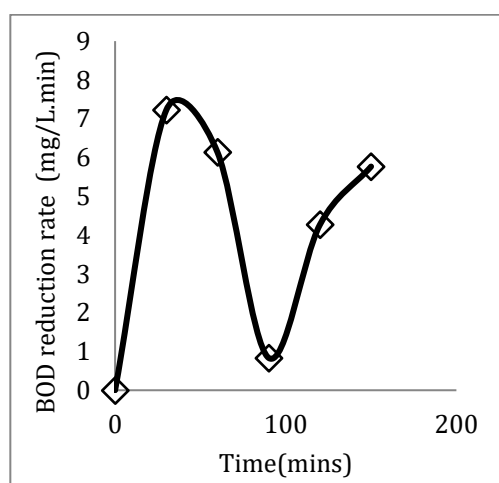


Fig. 7: BOD reduction rate versus time under the 20 W bulb

Beyond 100 minutes, the COD reduction rate slowed, suggesting that the remaining organic compounds were more resistant to oxidation, which may have limited further degradation. In contrast, both BOD and TSS increased again. This may be attributed to partial oxidation of persistent organics producing new low-molecular-weight intermediates, and to possible desorption or resuspension of fine particles from the catalyst surface. Thus, although the overall organic load (as indicated by COD) continues to decrease or remain stable, transient formation of biodegradable and particulate fractions causes the secondary peaks observed in BOD and TSS.

Overall, these contrasting trends indicate that COD, BOD, and TSS each represent different aspects of the photocatalytic transformation. COD measures the amount of organic matter that can be oxidized chemically, while BOD reflects the biodegradable portion of organic matter, and TSS corresponds to the suspended particles. Consequently, the single-peak COD pattern reflects the overall oxidation kinetics. At the same time, the double-peak behavior in BOD and TSS indicates cyclic formation and

degradation of intermediates, particle release, and resuspension.

Relationship Between COD, BOD, and TSS During Photocatalytic Treatment

The relationship between COD, BOD, and TSS was analyzed to understand the interdependence between organic oxidation, biodegradability, and particulate removal during photocatalytic treatment, as shown in Table 3 and Figures 9-11. A strong negative correlation was observed between COD and BOD ($R^2 = 0.969$) and between COD and TSS ($R^2 = 0.972$), both following a logarithmic trend. This indicates that as the concentrations of biodegradable organic matter (BOD) and suspended solids (TSS) decreased, the overall organic load represented by COD also decreased. The logarithmic nature of these relationships suggests that the rate of COD removal was initially rapid and gradually slowed as pollutant concentration declined. In contrast, BOD and TSS exhibited a strong positive linear correlation ($R^2 = 0.994$), implying that higher levels of suspended solids contributed to increased biodegradable content in the wastewater. Overall, these correlations confirm that reducing suspended and biodegradable matter plays a significant role in lowering total chemical oxygen demand during photocatalytic degradation.

Table 3. Relationship between COD, BOD and TSS

	Relationship	R^2
COD vs BOD	$COD = 527.97\ln(BOD) - 2701.5$	0.969
COD vs TSS	$COD = 287.42\ln(BOD) - 1377.2$	0.972
BOD vs TSS	$BOD = 0.542TSS + 95.456$	0.994

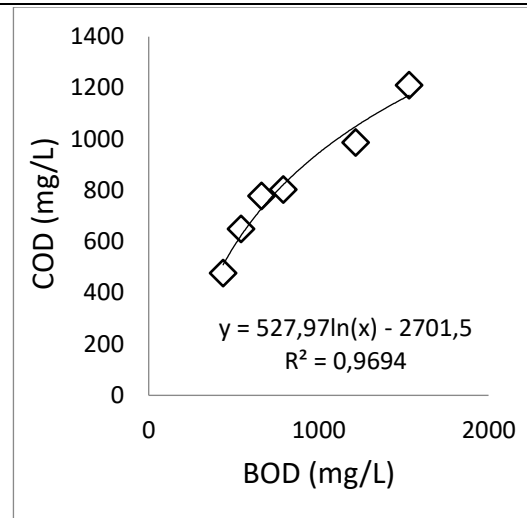


Fig. 9: Relationship between COD and BOD

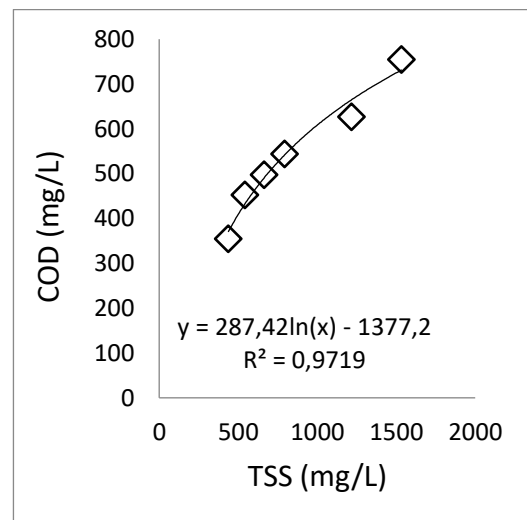


Fig. 10: Relationship between COD and TSS

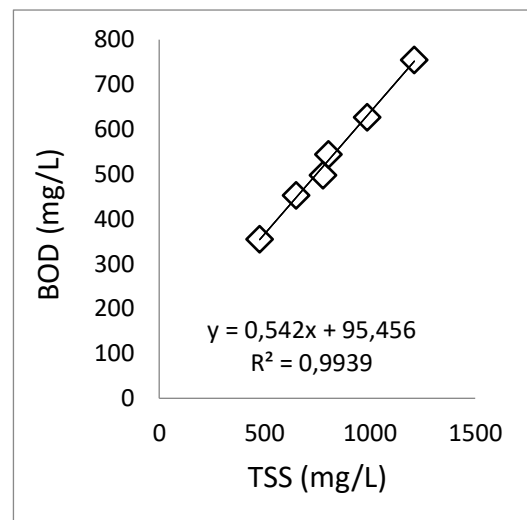


Fig. 11: Relationship between BOD and TSS

Kinetic Analysis of Photocatalytic Oxidation

The degradation kinetics were evaluated using pseudo-first-order and pseudo-second-order kinetic models, as shown in Figures 12-23. The fitted kinetic parameters are summarized in Tables 4-5. Both models showed good agreement with the experimental data, with coefficients of determination (R^2) exceeding 0.90 (Table 4), indicating that both models can adequately describe the degradation behavior under the investigated conditions.

Table 4. Fitted parameters

PFO	$\ln C = -k_1 t + \ln C_0$	R^2
	$\ln \text{COD} = -0.0085t + 7.3084$	0.98
	$\ln \text{BOD} = -0.0056t + 7.0852$	0.96
	$\ln \text{TSS} = -0.0046t + 6.6066$	0.96
PSO	$\frac{1}{C} = k_2 t + \frac{1}{C_0}$	R^2
	$1/\text{COD} = 1\text{E-}05t + 0.0006$	0.99
	$1/\text{BOD} = 8\text{E-}06t + 0.0008$	0.91
	$1/\text{TSS} = 9\text{E-}06t + 0.0013$	0.95

Table 5. Fitted rate constants

	k_1		% difference
	Linear	Non linear	
PFO	0.0085	0.0091	7
	0.0056	0.0057	2
	0.0046	0.0048	4
	k_2		
	Linear	Non linear	
PSO	1E-05	9E-06	10
	8E-06	6E-06	25
	9E-06	8E-06	11

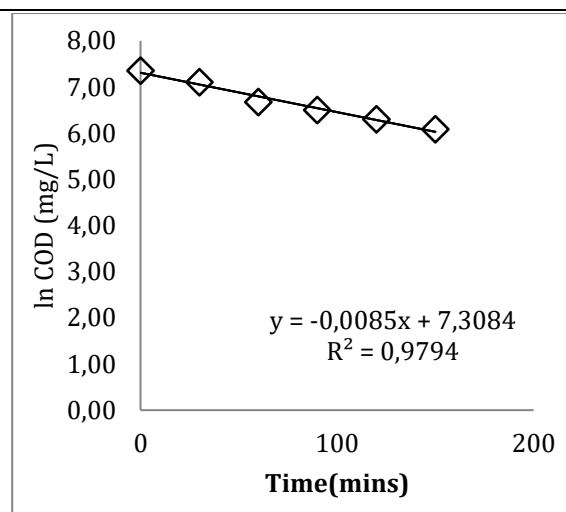


Fig. 12: ln COD versus time – PFO

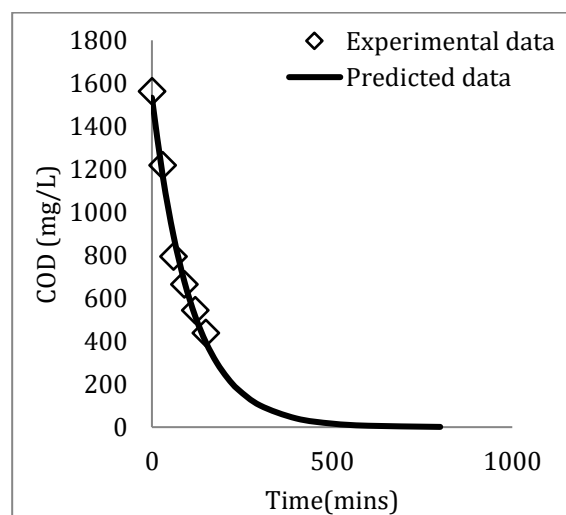


Fig. 13: COD versus time - PFO

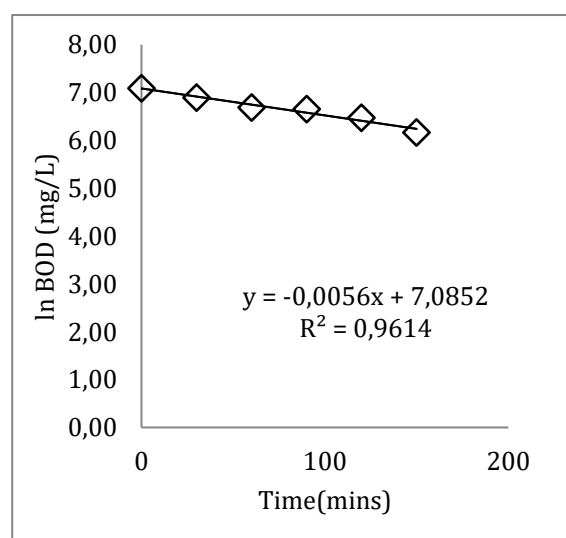


Fig. 14: ln BOD versus time - PFO

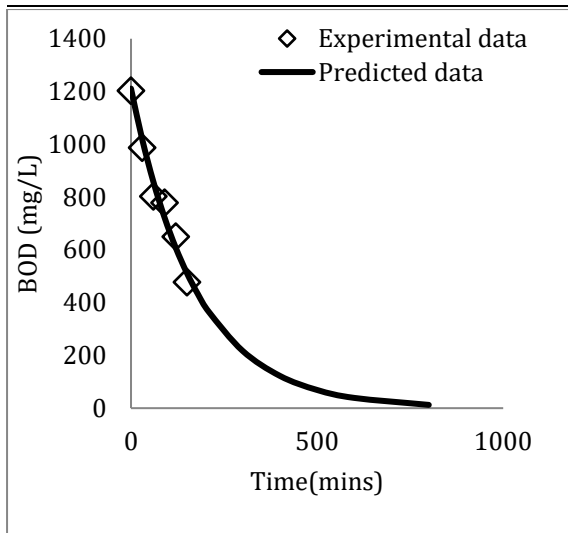


Fig. 15: BOD versus time - PFO

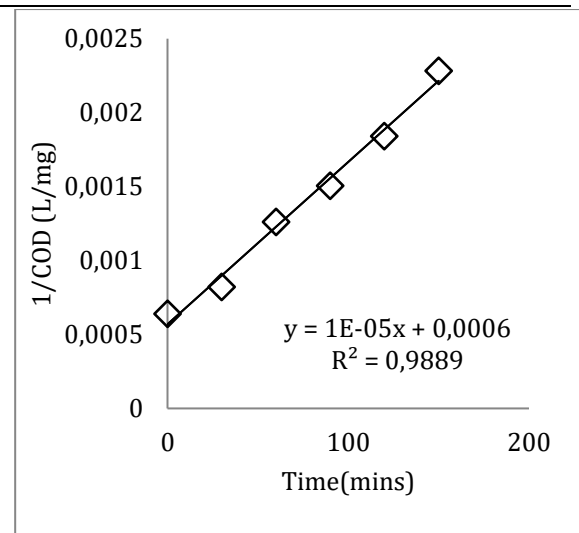


Fig. 18: 1/COD versus time - PSO

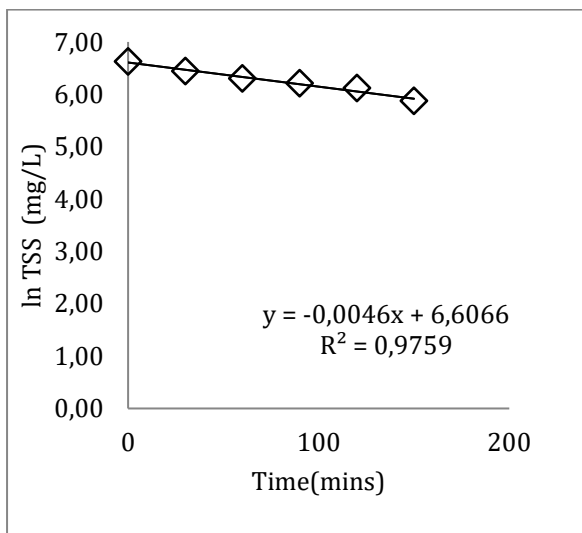


Fig. 16: ln TSS versus time - PFO

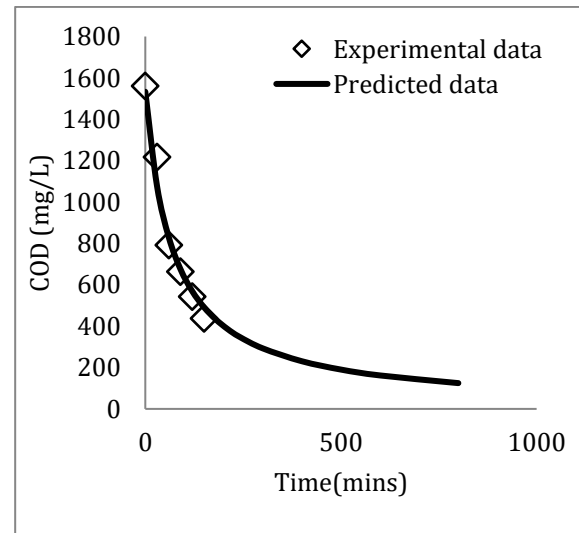


Fig. 19: COD versus time - PSO

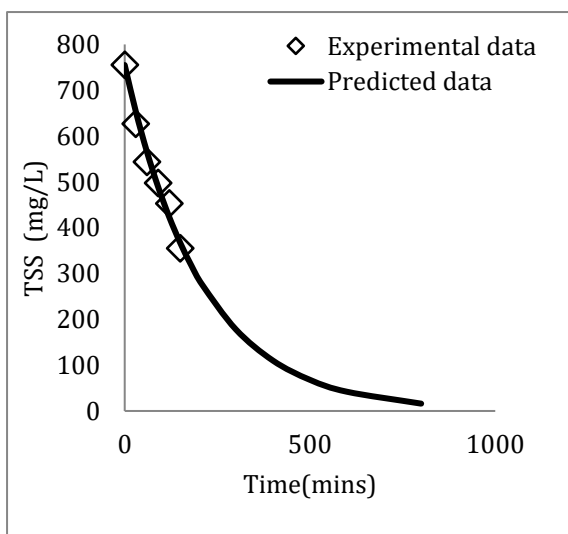


Fig. 17: TSS versus time - PFO

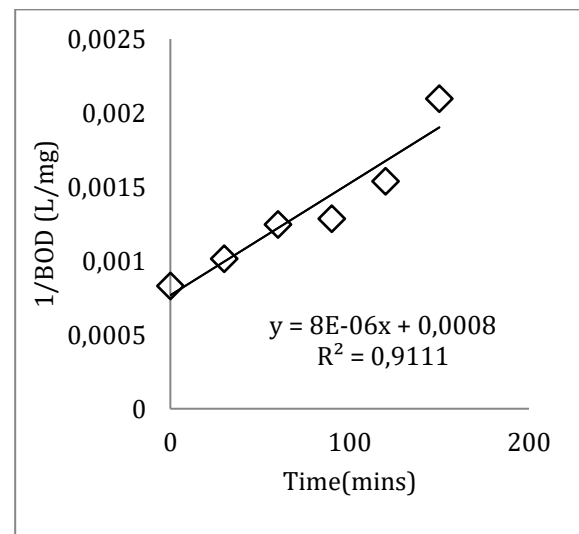


Fig. 20: 1/BOD versus time - PSO

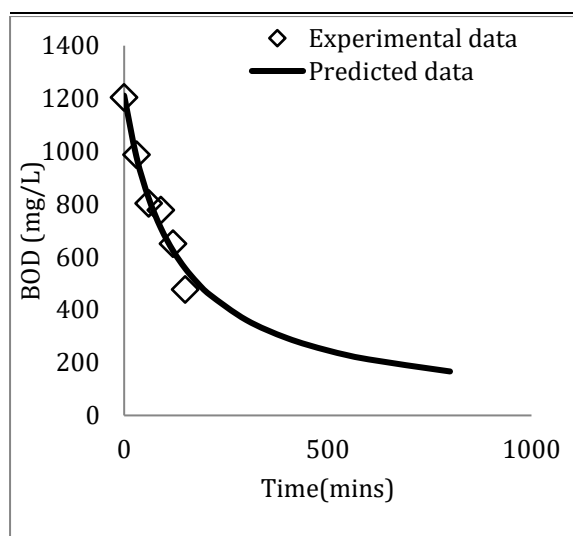


Fig. 21: BOD versus time – PSO

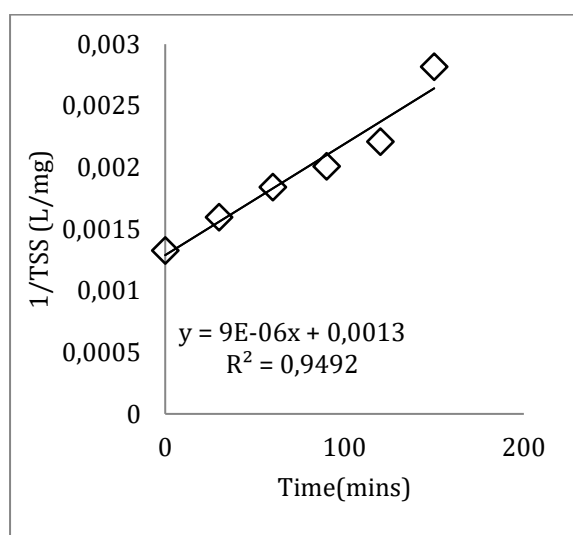


Fig. 22: 1/TSS versus time – PSO

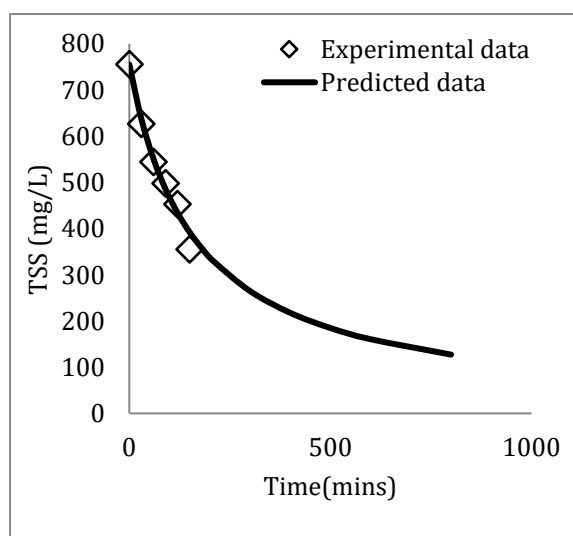


Fig. 23: TSS versus time – PSO

Further evaluation was carried out using the Solver function in Microsoft Excel to perform non-linear fitting of the kinetic models. The rate constants obtained from the linearized and non-linear approaches were compared, as shown in Table 5, to assess the influence of the fitting method on the estimated kinetic parameters. The percentage differences were relatively small for the pseudo-first-order kinetic model (2–7%), whereas larger differences were observed for the pseudo-second-order kinetic model (10–25%). These findings suggest that linearization had a smaller effect on kinetic parameter estimation for the PFO kinetic model but a more pronounced effect for the PSO kinetic model. The COD, BOD, and TSS concentrations predicted using the non-linear fitting approach showed good agreement with the experimental values, as demonstrated in the corresponding figures. The average percentage errors calculated between the predicted and experimental values from the non-linear fitting analysis ranged from 3.18 to 6.12%.

The kinetic constants obtained from both models provide additional insight into the degradation behavior of the wastewater constituents during photocatalytic treatment. The rate constants (k_1) for the PFO kinetic model were in the range of 0.0046–0.0091 mg/L.min, while the PSO kinetic model produced rate constants (k_2) in the range of 6×10^{-6} – 1×10^{-5} mg/L.min. These rate constants cannot be directly compared numerically because the two models are derived from different kinetic expressions and represent different kinetic parameters. The PFO rate constant (k_1) represents the apparent degradation rate associated with concentration-dependent pollutant reduction. In contrast, the PSO rate constant (k_2) relates to surface interaction processes

and is influenced by the equilibrium capacity term. Therefore, the lower numerical values of k_2 compared with k_1 do not indicate slower degradation. The good fit of both kinetic models may be related to the heterogeneous nature of sago wastewater, which contains various organic constituents that may degrade through different pathways. During photocatalysis, organic pollutants are oxidized by photogenerated reactive species, particularly hydroxyl radicals ($\bullet\text{OH}$). At the same time, adsorption and surface interactions between wastewater constituents and the TiO_2 catalyst may also contribute to the overall degradation process. Although both models provided satisfactory fitting, the PFO kinetic model showed more consistent agreement across the evaluated parameters, with relatively higher R^2 values and comparable or lower percentage errors for most datasets.

The observed rapid initial reduction followed by a gradual decrease in degradation rate reflects the abundance of readily oxidizable organic compounds during the early stage of treatment and their subsequent depletion, along with the increasing influence of mass transfer limitations and reduced availability of active reaction sites at later stages.

CONCLUSIONS

The results of this study demonstrate that photocatalytic treatment using TiO_2 under the investigated laboratory conditions effectively reduced organic and particulate pollutants in sago wastewater, as indicated by the observed decreases in COD, BOD, and TSS over time. Among the evaluated parameters, COD exhibited the highest overall removal efficiency (72%), followed by BOD (61%) and TSS (53%). These differences in degradation

behavior can be attributed to the nature of the pollutants: COD represents both biodegradable and non-biodegradable organic fractions, BOD reflects primarily biodegradable matter, and TSS is associated with suspended particulate removal. The rapid reduction observed within the first 60–90 minutes suggests that the photocatalytic process preferentially targets readily degradable organic compounds and larger suspended solids during the initial treatment stage. The subsequent decrease in degradation rate indicates the depletion of these components and the presence of more resistant fractions at later stages. Overall, the findings provide relevant insight into the photocatalytic degradation behavior of sago wastewater under the specific operating conditions examined and highlight the potential of kinetic analysis for evaluating treatment performance. The observed first-order-type degradation trends suggest predictable removal behavior within the experimental scope of this study.

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