



Degradation and mineralization of violet-3B dye using C-N-codoped TiO₂ photocatalyst

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ABSTRACT

The present study investigated the photodegradation of synthetic organic dye; violet-3B, without and with the addition of C-N-codoped TiO₂ catalyst using a visible halogen-lamp as a light source. The catalyst was synthesized by using a peroxo sol-gel method with free-organic solvent. The effects of initial dye concentration, catalyst dosage, and pH solution on the photodegradation of violet-3B were examined. The efficiency of the photodegradation process for violet-3B dye was higher at neutral to less acidic pH. The kinetics reaction rate of photodegradation of violet-3B dye with the addition of C-N-codoped TiO₂ followed pseudo-first order kinetics represented by the Langmuir-Hinshelwood model, and increasing the initial concentration of dyes decreased rate constants of photodegradation. Photodegradation of 5 mg L⁻¹ violet-3B dye achieved 96% color removal within 240 min of irradiation in the presence of C-N-codoped TiO₂ catalyst, and approximately 44% TOC was removed as a result of the mineralization.

Keywords: C-N-codoped TiO₂, HPLC, Kinetics, TOC, Vat-dye, Visible halogen-lamp

1. Introduction

Violet-3B, a group of anthraquinones vat dyes, is widely used for fabric dyeings such as cotton, viscose, and silk [1]. This dye can be produced during coloring and dyeing processes of fabric and become a pollutant when it is discharged into river water without an effective treatment. The wastewater effluent from dyeing industry can contain a large amount of azoic, anthraquinonic, and hetero-polyaromatic dyes [2-4] which are hazardous to the aquatic life because of its toxicity and carcinogenicity [5-6]. Besides, the color of dyes can damage the aesthetic aspect of water and reduces light penetration causing the inhibition of photosynthesis process of the aquatic organism [7]. These wastewater effluents from dyeing industry can be a serious environmental pollution if there is no treatment before releasing to the waterways [8]. Therefore, many researchers are looking for appropriate treatments in order to remove these dyes.

The conventional technologies, such as adsorption [9-10], coagu-

lation/flocculation [11] and conventional chemical oxidation [12] have been used for the removal of dyes. However, these techniques are ineffective because they are non-destructive and produce secondary pollution requiring further treatment for their safe disposal [13]. Therefore, the alternative treatment which can solve the problem in conventional technologies is required. Advanced oxidation processes (AOPs) based on the generation of highly reactive hydroxyl radicals (•OH) to reduce more number of recalcitrant pollutants [14]. This process can reduce pollutant into environment-friendly products without the generation of waste.

Heterogeneous photocatalysis is one of the best AOP processes to degrade organic pollutants [15]. The key to the photocatalysis process is the combination of semiconductor photocatalyst and light sources [16]. Titanium dioxide (TiO₂) is the most promising and widely used as a photocatalyst in wastewater treatment among the various semiconductors. Titania (TiO₂) has strong catalytic activity, its low cost, and photo-stability [17]. As a photocatalyst, TiO₂ has its own deficiency because of its large bandgap energy



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(~3.2 eV for the anatase phase) [18]. Thus, it should be activated and applied by UV light only. In a consequence, modification of TiO₂ to enhance photoactivity under visible light has been developed. The simplest and most potential approach to modify TiO₂ seems to be doped with non-metal elements [19], transition metal elements [20], and the combination of both elements [21-22].

In our previous researches, C-N-codoped TiO₂ has been applied to degrade other vat dyes such as orange-F3R [23] and yellow-GCN [24], but the kinetics of photodegradation reaction has not been studied. Moreover, to our best knowledge, there have been no researches related to the treatment of violet-3B dye using photodegradation in the presence of C-N-codoped TiO₂. Thus, the purpose of this research is to examine the kinetics reaction of violet-3B dye photodegradation in the presence of C-N-codoped TiO₂ catalyst. To achieve color removal, various parameters which affect the photodegradation process such as catalyst dosage, initial dye concentration, pH of the solution, and adsorption on C-N-codoped TiO₂ are investigated. Finally, the mineralization of dyes during the degradation is assessed by the Total Organic Carbon (TOC) analysis.

2. Experimental Section

2.1. Chemicals

Violet-3B dye (Vat Violet 9) (C.I. number 60005, CAS number 1324-17-0) was purchased from indiamart (India) and used in this research without further purification. The molecular formula of Violet-3B is C₃₅H₁₉BrO₂, the molecular weight is 551.43 g mol⁻¹. 100 mg L⁻¹ of violet-3B dye stock solution was prepared by dissolving 100 mg of violet-3B dye powder into 1 L of deionized water. C-N-codoped TiO₂ was synthesized in the laboratory and prepared using sol-gel organic-free preparation [25, 26]. Graphite carbon-powder (10 wt %) was sonicated for 1 h in distilled water then titanium (IV) chloride (Merck) was added to carbon suspension. The pH of the solution was adjusted to 10 by dropwise addition of ammonia solution (Merck, 25%). The carbon-nitrogen-aqueous peroxotitanate solution (CN-PTA) was obtained after stirring for 24 h. The solution was centrifuged and washed thoroughly with distilled water then the precipitates were solved with distilled water and hydrogen peroxide (Merck, 30%). After stirring for 4 h the solvents were vaporized by using rotary evaporator then the precipitates were calcined in the air at 500°C for 1 h.

2.2. Photodegradation Process of Violet-3B Dye

All experiments were performed under atmospheric pressure at 293 K inside black irradiation box. Visible halogen-lamp (500 W, Phillips) was used as light-sources for photodegradation process, and the distance to dye solution was 10 cm. The initial concentration of 5 mg L⁻¹ violet-3B dye was used in every experiment except for investigating the effect of the initial dye concentration. The dosage of C-N-codoped TiO₂ was 0.3 g L⁻¹ for every photocatalysis and adsorption experiment. The initial pH of the reaction solution was the natural pH of violet-3B dye solution (pH 5.6) except for investigating the effect of pH. The degradation products were analyzed by HPLC system.

2.3. Sample Analysis

All liquids samples were centrifuged (1,700 rpm for 10 min) to separate C-N-codoped TiO₂ particles prior to analysis. The violet-3B dye was analyzed by high performance liquid chromatography using a Summit™ HPLC system (Dionex, USA), the injection volume was 500 μL. An ODS-Hypersyl (Thermo Scientific) column (150 mm × 4.6 mm) with 5 mm particle size was used. The mixture of deionized water and methanol (70:30, v/v%) was used as mobile phase, and the flow rate was 0.8 mL min⁻¹. The detector was performed with visible lamp and was set at 540 nm. Mineralization analysis of the violet-dye samples during photodegradation was performed on a Shimadzu TOC analyzer (Shimadzu, Japan). The degradation percentage of dye from solution at different time interval and condition is calculated by Eq. (1);

$$\% \text{removal} = \frac{C_t}{C_o} \times 100\% \quad (1)$$

where C_o is the initial concentration of violet-3B dyes and C_t is the concentration of violet-3B dyes after photolysis process at different condition.

3. Results and Discussion

3.1. Degradation of Violet-3B Dye

HPLC-system is used at wavelength 540 nm to calculate the change of violet-3B dye concentration during the photodegradation process. Fig. 1 shows the chromatogram of violet-3B dye with a single peak obtained. The peak of violet-3B appears at 0.78 min of retention time. However, after photolysis, in the presence of C-N-codoped TiO₂ catalyst, the intensity of the peak decreased significantly showing high removal of violet-3B dye.

3.2. Effect of Catalyst Dosage

The effect of C-N-codoped TiO₂ dosage on the degradation of violet-3B dye was investigated by varying the concentration of TiO₂ catalyst from 0.05 to 1.2 g L⁻¹ in the photolysis process for 180 min. The removal percentage of violet dye shows that, as the amount of catalyst increase up to 0.3 g L⁻¹, with the removal percentage of violet-3B dye, increased up to 83%. The increasing amount of catalyst produces the number of sites available for photons absorption thus more hydroxyl radical (•OH) is formed to degrade the organic molecule of violet-3B dye [27, 28]. However, the addition of C-N-codoped TiO₂ dosage higher than 0.3 g L⁻¹ caused the decrease in removal percentage of violet-3B dye to 71%. This phenomenon could be due to the turbidity of dye solution resulting in less light penetration and blocking the light scattering [27, 29]. Hence, the optimum dosage of C-N-codoped TiO₂ catalyst used in the violet-3B dye photodegradation is 0.3 g L⁻¹.

3.3. Effect of C-N-codoped TiO₂ in the Photolysis

To confirm the role of C-N-codoped TiO₂ in the photodegradation reaction, three sets of experiment were performed to compare violet-3B dye degradation rates with and without a catalyst. The first

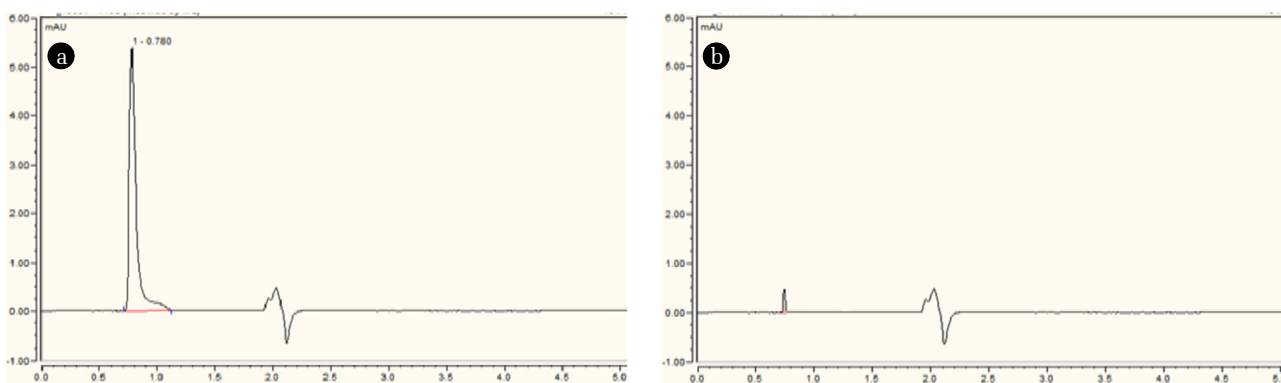


Fig. 1. Chromatogram of 5 mg L⁻¹ violet-3B dye. (a) Before degradation and (b) After degradation for 300 min by the addition of C-N-codoped TiO₂.

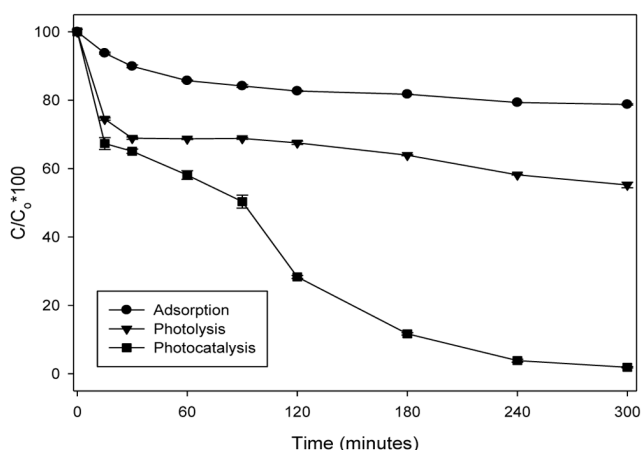


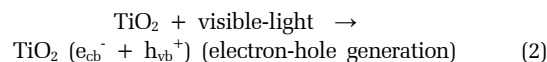
Fig. 2. Photodegradation of 5 mg L⁻¹ violet dyes under photocatalysis, photolysis and adsorption condition (pH = 5.6, C-N-codoped TiO₂ = 0 g L⁻¹ in photolysis, 0.3 g L⁻¹ in photocatalysis and adsorption) (n = 3).

set was performed by exposing violet-3B dye (5 mg L⁻¹) with the addition of 0.3 g L⁻¹ C-N-codoped TiO₂ under visible-light irradiation (photocatalysis condition). The second set was performed by exposing violet-3B dye to visible light without C-N-codoped TiO₂ catalyst (photolysis condition). Then, the third set was adsorption condition by exposing violet-3B to C-N-codoped TiO₂ without visible-light irradiation. The results of violet-3B dye removal are shown in Fig. 2.

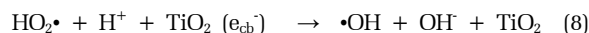
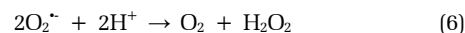
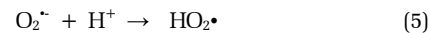
The experiment with C-N-codoped TiO₂ showed that the small amount of violet-3B dye (about 20%) was adsorbed on the C-N-codoped TiO₂ surface after 300 min. The adsorption phenomenon might be caused by carbon dopant in TiO₂ crystal. During photolysis condition, about 45% of the violet dye was removed after 300 min of irradiation. High irradiation energy from visible lamp could degrade the molecules of violet-3B dye. Approximately, 98% of the violet dye was removed by the addition of C-N-codoped TiO₂ in the photodegradation process.

Higher removal percentage of violet dyes was achieved during photocatalysis condition due to that more hydroxyl radical (•OH) radicals can react with violet-3B dye molecules and achieve mineral-

ization process. The •OH radical was produced by the reaction between electron vacancy or hole site (h⁺) of TiO₂ with water. Since carbon and nitrogen dopant was inserted to TiO₂, visible light could be absorbed by TiO₂ and causing the excitation process of the electron from valence band to conduction band [30]. The reaction was shown at Eq. (2) and (3) [17];



while the excited electron in the conduction band can produce •OH radical by reacting with oxygen shown in Eq. (4) to (8) [17, 31];



3.4. Effect of Initial Dye Concentration

Various violet-3B dye concentrations in the range 5 to 30 mg L⁻¹ were tested to investigate the effect of initial dye concentration during photocatalysis condition for 420 min in the presence of C-N-codoped TiO₂ catalyst. The results are shown in Fig. 3. It was found that the low concentration of violet-3B dye was favorable for the photodegradation process.

By increasing the initial concentration of dye lead to a decrease in violet-3B degradation rate. This effect can be explained by the increase in the dye concentration, caused the decrease in the light penetration that reaches the organic molecule of violet-3B dye due to the declining transparency of the solution into a more concentrated solution [27-28]. Thus, the time for complete degradation of violet-3B dye would be longer for higher initial violet-3B concentrations [29, 32]. The result of the effect of initial dye concentration showing in Fig. 3 indicates that violet-3B degradation kinetics are not simple first-order but pseudo-first-order.

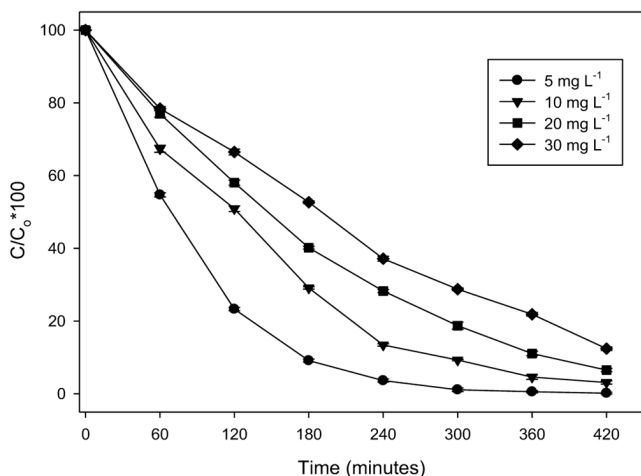


Fig. 3. Effect of initial dye concentration on removal efficiency under photocatalysis condition (pH= 5.6, C-N-codoped TiO₂ = 0.3 g L⁻¹, n=3).

3.5. Reaction Kinetics

Photodegradation reaction using C-N-codoped TiO₂ as a catalyst is known to be a heterogeneous reaction between violet-3B dye and TiO₂, and the •OH radicals produced from the reaction between TiO₂ and H₂O is the main key in the oxidation reaction of dye degradation. The Langmuir-Hinshelwood kinetic model can be applied for heterogenous photodegradation in the correlation between the initial degradation rate and the initial concentration of dyes [33], in this model, the reaction rate for second-order catalyst surface decomposition of violet-3B dye is expressed as follows;

$$\text{rate} = -\frac{d[\text{dye}]}{dt} = k_c \frac{K_{\text{dye}}[\text{dye}]}{1 + K_{\text{dye}}[\text{dye}]_0} \quad (9)$$

where $[\text{dye}]$ is the concentration of violet-3B dye at time t and $[\text{dye}]_0$ is the initial concentration of violet-3B dye, k_c is the second-order rate constant, K_{dye} is the equilibrium adsorption constant of dye onto the surface of C-N-codoped TiO₂. In this research since the initial concentrations of violet-3B dye used were relatively low, based on the Eq. (9) the kinetics data were modeled using pseudo-first-order;

$$-d\frac{[\text{dye}]}{dt} = k_{\text{obs}}[\text{dye}] = k_c \frac{k_{\text{dye}}}{1 + k_{\text{dye}}[\text{dye}]_0}[\text{dye}] \quad (10)$$

where k_{obs} is the observed pseudo-first-order rate constant for the photodegradation oxidation of violet-3B dye using C-N-codoped TiO₂ as a catalyst. The integration of Eq. (10) results in Eq (10);

$$\ln\left(\frac{[\text{dye}]}{[\text{dye}]_0}\right) = -kt \quad (11)$$

Based on Eq. (11), a plot of $\ln([\text{dye}]/[\text{dye}]_0)$ versus irradiation time represents a straight line showing in Fig. 4 and Table 1. The relationship between k_{obs} and the initial concentration of violet-3B dye $[\text{dye}]_0$ from Eq. (11) can be expressed by;

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k_c K_{\text{dye}}} + \frac{[\text{dye}]_0}{k_c} \quad (12)$$

The linear expression was obtained by plotting the proportion of degradation rate ($1/k_{\text{obs}}$) versus the initial concentration of violet-3B dye, the curve is shown in Fig. 4. By fitting the Eq. (12), the values of the adsorption equilibrium constant (K_{dye}) and the second-order constant (k_c) were obtained, and the value found to be $K_{\text{dye}} = 0.129 \text{ L mg}^{-1}$ and $k_c = 0.18 \text{ mg L}^{-1} \text{ min}^{-1}$ ($R^2 = 0.987$), respectively.

Table 1. Effect of Initial Concentration to Rate Constant of Violet-3B Dye Photodegradation

Initial dye (mg L ⁻¹)	k _{obs} (min ⁻¹)	1/k _{obs} (min)	t _{1/2} (min)	R ²
5	0.0152	65.79	45.60	0.996
10	0.0092	108.69	75.34	0.984
20	0.0067	149.25	103.45	0.975
30	0.0047	212.76	147.48	0.976

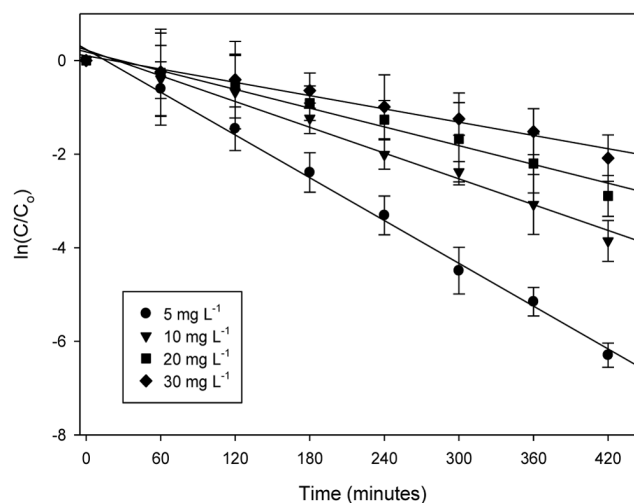


Fig. 4. Photodegradation kinetics model in various concentration of violet-3B dye in the present of catalyst (pH = 5.6, C-N-codoped TiO₂ = 0.3 g L⁻¹, n=3).

The pseudo-first-order rate constant (k_{obs}), half-time ($t_{1/2}$), and the correlation coefficients (R^2) for photodegradation of violet-3B dye at different initial concentration, experimental conditions: the mass of C-N-codoped TiO₂ = 0.3 g L⁻¹, natural pH; n = 3

3.6. Effect of Initial pH

To investigate the effect of initial pH on degradation of violet-3B dye, the experiments were conducted by changing the pH of dye solution from 3 to 10. The concentration of violet-3B dye was kept constant at 5 mg L⁻¹ and the mass of C-N-codoped TiO₂ catalyst is 0.3 g L⁻¹. Fig. 5 shows the results of degradation efficiency for every pH condition and Table 2 shows the pseudo-first-order rate constant. The order of degradation efficiency follows pH 5 > pH 7 > pH 3 > pH 10. It is known that TiO₂ has an amphoteric

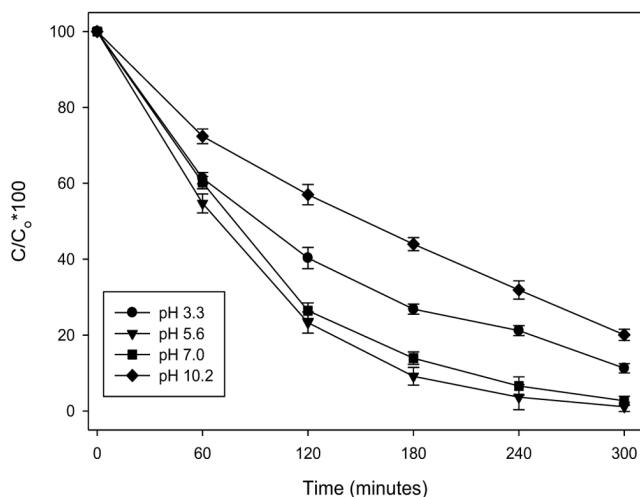


Fig. 5. Effect of pH solution on degradation efficiency, under photocatalysis condition (violet-3B dye = 5 mg L⁻¹, C-N-codoped TiO₂ = 0.3 g L⁻¹, n=3).

Table 2. Effect of Initial pH to Rate Constant of Violet-3B Dye Photodegradation

pH	k_{obs} (min ⁻¹)	$t_{1/2}$ (min)	R ²
3.3	0.0069	100.46	0.989
5.6	0.015	46.21	0.991
7.0	0.012	57.76	0.995
10.2	0.0051	135.91	0.967

character in aqueous solution. The point of zero charges (p_{zc}) of C-N-codoped TiO₂ was found at pH 5.29 [34]. Since the pH condition of dye solution near the p_{zc} can be favorable to adsorb the molecule of violet-3B and therefore the highest degradation percentage was achieved at pH 5.6. While at neutral pH, the efficiency of TiO₂ catalyst in photodegradation was not changed [35], however further increase in pH will decrease the degradation efficiency due to the electrostatic repulsion between negative charge of catalyst surface (TiO) at alkaline condition [36] and the OH species in photocatalytic mechanism [37]. Therefore, the optimum pH condition for photodegradation of violet-3B using C-N-codoped TiO₂ was at circumneutral pH (between 5 and 7).

The pseudo-first-order rate constant (k_{obs}), half-time ($t_{1/2}$), and the correlation coefficients (R^2) for photodegradation of violet-3B dye at different pH (experiment conditions: dye = 5 mg L⁻¹, C-N-codoped TiO₂ = 0.3 g L⁻¹)

3.7. Mineralization

To confirm the mineralization, the photodegradation of violet-3B using C-N-codoped TiO₂ catalyst reaction were carried out up to 300 min and the irradiated samples were analyzed by TOC analyzer. Fig. 6 shows the comparison of removal efficiency of violet-3B dye and TOC reduction in photolysis with the addition of C-N-codoped TiO₂ catalyst. The results showed 45% reduction in TOC under irradiated of visible-light for 300 min. This result indicates

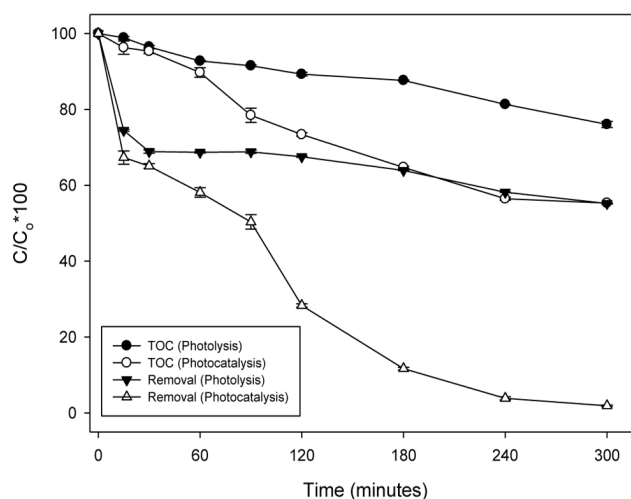


Fig. 6. TOC reduction and removal efficiency comparison for photo-degradation of violet-3B dye (experimental conditions: dye = 5 mg L⁻¹, mass of C-N-codoped TiO₂ = 0.3 g L⁻¹, natural pH, n = 3).

that, although 98% of the color removal was achieved within 300 min with the irradiation of visible light, the organic compound of the violet-3B is not completely mineralized.

4. Conclusions

The experimental results of this study show that photodegradation using C-N-codoped TiO₂ as a catalyst could be applied to the treatment of violet-3B dye wastewater. The combination between C-N-codoped TiO₂ and visible light in photodegradation showed more efficient to degrade violet-3B dye than visible light and catalyst alone. For 300 min photodegradation process, 5 mg L⁻¹ violet-3B dye was adsorbed as much 21% onto 0.3 g L⁻¹ C-N-codoped TiO₂ surface, 45% of color removal was achieved by irradiation of visible-light only and increased to 98% by photocatalysis. The photodegradation of violet-3B using C-N-codoped TiO₂ was fitted to the Langmuir-Hinshelwood model and obeyed the pseudo-first-order kinetics. In the mineralization study, the photodegradation process in the presence of C-N-codoped TiO₂ achieved an approximately 45% TOC removal. The mechanism of violet-3B dye photodegradation is still in studying.

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