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Kinetics Study and Degradation Pathway of Methyl Orange Photodegradation in The Presence of C-N-codoped TiO$_2$ Catalyst

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This work investigated the photodegradation of azo dye, methyl orange, without and with the addition of C-N-codoped TiO$_2$ catalyst using a visible halogen-lamp as a light source. C-N-codoped TiO$_2$ was prepared by free-organic solvent peroxo sol-gel method. The effects of initial dye concentration, catalyst dosage, and pH solution on the photodegradation of methyl orange were studied. Photodegradation process for methyl orange solution at acidic condition showed high removal percentage. 5 mg L-1 methyl orange achieved color removal until 94% for 180 min irradiation in photodegradation process with the presence of C-N-codoped TiO$_2$ catalyst, and approximately 70% TOC removed as the results of mineralization process. The kinetics reaction rate of photodegradation of methyl orange dye with the addition of C-N-codoped TiO2 followed pseudo-first order represented by Langmuir-Hinshelwood model, the kinetics constant of photodegradation became higher by decreasing the initial concentration of methyl orange. Three organic byproducts of methyl orange formed during photodegradation process was identified by LC-MS/MS system then degradation pathway of methyl orange photodegradation in the presence of C-N-codoped TiO$_2$ catalyst was proposed.

Keywords: Methyl orange, Photodegradation, C-N-codoped TiO2, Degradation-pathway

Introduction

The presence of synthetic organic dye in wastewater discharge from textile industries leads to a huge environmental hazard. The wastewater not only causes disruption of aquatic ecosystem because dye-bearing effluents inhibit the penetration of sunlight, but also visually reduces the esthetic quality of water. One of the main pollution from textile wastewater constitute of azo dyes [1]. These dyes have been confirmed to be toxic, mutagenic, and carcinogenic [2-4]. Thus remediation of these dyes from textile wastewater is an imperative research.

Methyl orange (MO), a simple azo dyes, was chosen as an artificial wastewater pollutant in this study. Conventionally, remediation methods for methyl orange such as coagulation [5], flocculation [6] and adsorption using chitosan [7, 8] and activated carbon [9] are currently used. However, these methods only transfer the dye from one phase to another, producing a secondary pollution [10]. Nowadays, photocatalysis have developed as promising solution to solve these pollution problems [11].

Titanium dioxide (TiO$_2$) is one of the most frequently studied as semiconductor photocatalytic

material for decomposition of organic compounds, due to its environmental friendly properties, high chemical stability, and relatively low cost [12-14]. Owing to the broad band gap of titania (anatase, ~3.2 eV) there are some disadvantages to its effectiveness in photocatalysis applications [11] such as titania is active only in ultraviolet-light irradiation with high energy [15-17]. Another disadvantages, the high recombination of photo-generated electron-hole pair of titania resulting in low photocatalytic activity and low affinity [18, 19]. Modification of TiO_2 with non-metals dopant such as nitrogen and carbon have been proposed to enhance photocatalytic activity in visible-light irradiation to degrade organic and inorganic pollutant [20-23].

This publication focused on reported the kinetics reaction of methyl orange photodegradation in the presence of C-N-codoped TiO_2 catalyst. To optimize the kinetics model, parameters of photodegradation process were investigated such as C-N-codoped TiO_2 dosage, initial concentration of methyl orange, and initial pH of methyl orange solution. In addition, the transformations of methyl orange molecule during photodegradation process were identified through the analysis of molecular structure by LC-MS/MS system. Then, the possible photodegradation pathway of methyl orange in the presence of C-N-codoped TiO_2 was proposed.

Experimental

Reagents

Methyl orange, MO, $(C_{14}H_{14}N_3SO_3Na)$ ACS grade was purchased from Sigma Aldrich used as model pollutant without further purification. Simulating pollutant solution were prepare by dissovling accurately weighted ammount of methyl orange in deionized water (R = 18.2 MΩ cm^{-1}, Milli-Q). Graphite carbon-powder (10 wt.%) were used as the source of carbon dopant and ammonia solution (*Merck*, 25%) as the source of nitrogen dopant. C-N-codoped TiO_2 was prepared from carbon-nitrogen-aqueous peroxotitanate solutions (CN-PTA) using sol-gel organic-free preparation [20, 21].

Characterization

The morphology of C-N-codoped TiO_2 particle was observed with transmission electron microscope (TEM HT7700) and SEM JEOL JSM-6510LA equipped with energy dispersive

X-ray spectroscopy (EDX) for chemical analysis was used. The X-ray diffraction (XRD) patterns of C-N-codoped TiO_2 powder were obtained with Philips X'pert Powder, PANalytical, X-ray difractometer using Cu-Kα radition sources (λ = 0.1540 nm).

Photolysis experiment of methyl orange

The photodegradation experiments were performed at room temperature (293 K) and atmospheric pressure inside black irradiation box equipped with a visible-halogen lamp (Phillips, 500 W) as a light source. The distance between lamp and dye solution was kept at 10 cm. For each experiments, the initial concentration of 5 mg L^{-1} methyl orange was used with the natural pH of methyl orange dye solution was 5.6. The amount of C-N-codoped TiO_2 was 0.4 g L^{-1} for every photocatalysis and adsorption experiments. Some parameters of photodegradation process were studied such as the effect of C-N-codoped TiO_2 catalyst dosage, the effect of initial dye concentration, the effect of initial pH of methyl orange solution. The photodegradation process of methyl orange was evaluated by monitoring the color removal by HPLC (High Performance Liquid Chromatography) system.

Sample analysis

All alliquotes samples were filtered by 0.45 µm dismic filter (Advantec, Japan) to separate C-N-codoped TiO_2 particles prior to analysis. The methyl orange dye concentration before and after degradation were determined by HPLC using a Summit™ HPLC system (Dionex, USA). A ODS-hypersyl (Thermo Scientific) column (150 mm × 4.6 mm) with 5 µm particle size was used. The mixture solvents of acetonitrile: 0.01 M ammonium acetate (30:70, v/v %) were used as the mobile phase. The detector was performed with visible lamp and was set at 460 nm. The degradation percentage of dye from each solution at different time interval and condition is calculated by Eq. 1:

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

where C_o is the initial concentration of methyl orange dyes and C_t is concentration of methyl orange dyes after photolysis process at different condition. The reaction kinetics was evaluated based on the Langmuir-Hinshelwood kinetic model.

By-products analysis

Organic by-products during photocatalysis process as intermediate compounds were measured by LC-MS/MS system. Mass spectra were obtained by direct injection into a mass spectrometer using a Harvard syringe pump (Model 975 Harvard Apparatus, Dover, Mass., USA). The fragmentation of precursor ions was performed to identify product ions using collision energy provided by nitrogen gas. The negative ion mode was then used to scan the entire m/z value from 60 to 400 to obtain fragmentation data of the degradation by-products.

Results and Discussion

Characterization of C-N-codoped TiO₂ catalyst

X-ray diffractometry was used to investigate the crystal identity of TiO_2 samples before and after doping by carbon and nitrogen elements. Figure 1 compares the XRD patterns of the C-N-codoped and undoped TiO_2. Compared to TiO_2-anatase standard (ICSD no. 82084), both undoped and C-N-codoped TiO_2 showed anatase crystalline peaks at 2θ values of 25° (101); 37° (004); 48° (200); 54° (105); 55° (211). Thus, doped by carbon and nitrogen elements maintained the anatase phase of TiO_2 crystalline [21]. From difractogram patterns, C-N-codoped TiO_2 have a clear peak broadening due to the smaller crystalline size of TiO_2 nanoparticles versus to undoped TiO_2. Based on the calculation of Scherrer formula, the crystalline size of undoped and C-N-codoped TiO_2 were 18 nm and 9 nm, respectively.

Figure 2a-b represents the typical TEM images of TiO_2 particles before and after doped by carbon and nitrogen elements. It can be observed that the aggregation of C-N-codoped TiO_2 particles is more serious than undoped TiO_2 particles. The reason due to carbon species can locate at the surface of TiO_2 partcles and act a role of linker between the aggregated particles. The EDX spectra in Fig. 2c confirmed that TiO_2 after doping process contained carbon and nitrogen elements.
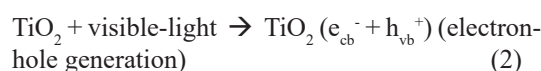
Effect of C-N-codoped TiO₂ catalyst dosage

The effect of C-N-codoped TiO_2 dosage on the photodegradation of methyl orange was investigated in the variation of 0.1 g L^{-1} to 1.0 g L^{-1}. The dye removal results are presented in Fig. 3. It was observed that maximum methyl orange dye removal is achieved in the concentration of 0.45 g L^{-1} C-N-codoped TiO_2 catalyst. The photodegradation of organic pollutant in the presence of catalyst has exhibited the dependency on the catalyst dosage. This can be explained on the increase of catalyst dosage, total active surface area of catalyst increases hence more active sites are available on catalyst surface which resulted in increasing of hydroxyl radicals thus the number of degraded dye molecules increases [24, 25]. However more addition of catalyst may not be useful in photodegradation of methyl orange dye because high dose of catalyst will establish turbidity suspension which cause inhibition in the penetration of visible light [26, 27].

Effect of C-N-codoped TiO₂ in the photocatalysis process

Figure 4 shows the comparison of methyl orange degradation in the process of adsorption, photolysis, and photocatalysis. The adsoprtion was performed by exposed methyl orange to C-N-codoped TiO_2 in the dark condition. The result shows that only small amount of methyl orange dye (about 5%) was adsorbed on the C-N-codoped TiO_2 surface after 210 minutes. Meanwhile, the photolysis experiment which was performed by exposing methyl orange dye to visible light without the addition of C-N-codoped TiO_2 shows approximately 10% of methyl orange removed. About 96% of methyl orange was removed in photocatalysis process. The dye removal percentage increase significantly in the presence of C-N-codoped TiO_2 due to the more highly reactive species, hydroxyl radicals (•OH), were produced. The hydroxyl radical will react to methyl orange dye molecules and achieve mineralization process. During visible-light penetration to C-N-codoped TiO_2, the hydroxyl radical was produced by the reaction between electron vacancy or hole site (h^+) of TiO_2 with water molecules [28, 29]. The reaction was shown at Eq. (2-3):

$$TiO_2 + \text{visible-light} \rightarrow TiO_2\,(e_{cb}^- + h_{vb}^+) \text{ (electron-hole generation)} \quad (2)$$

$$TiO_2\,(h_{vb}^+) + H_2O \rightarrow TiO_2 + H^+ + \cdot OH \quad (3)$$

Then, hydroxyl radicals attack the oraganic molecule of methyl orange producing inorganic salts and hydrogen dioxide [30, 31]. The reaction was shown at Eq. 4:
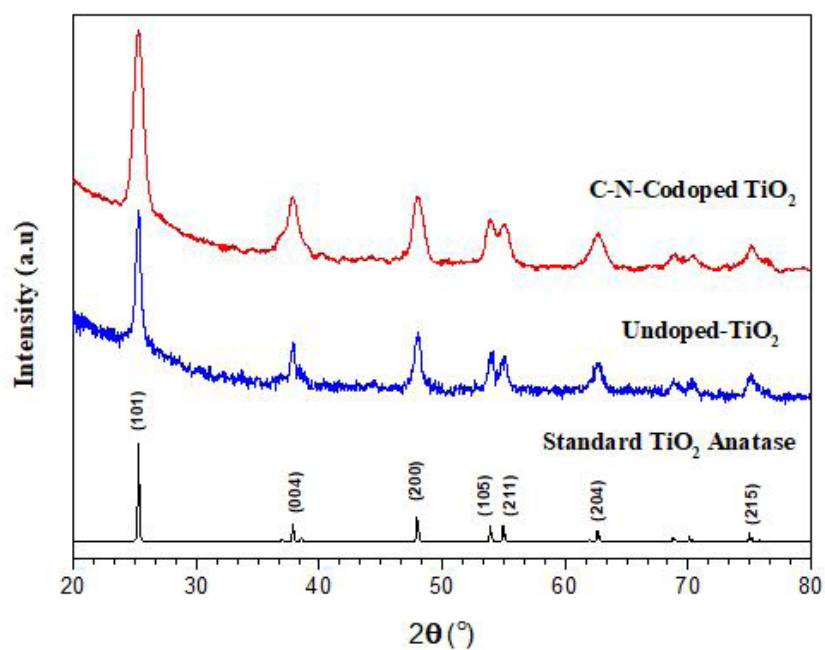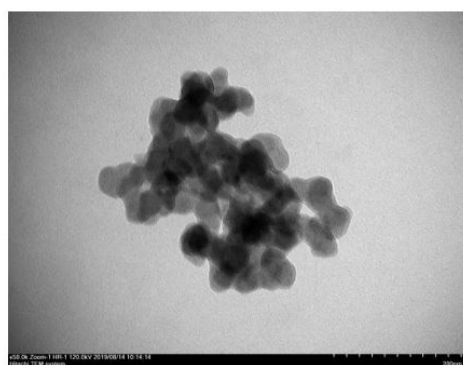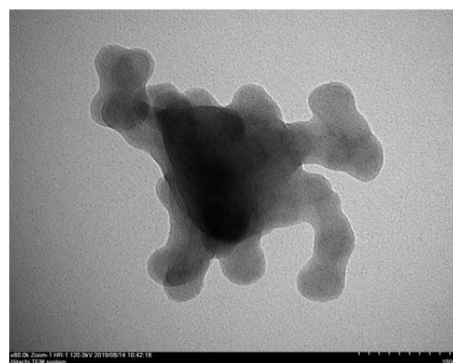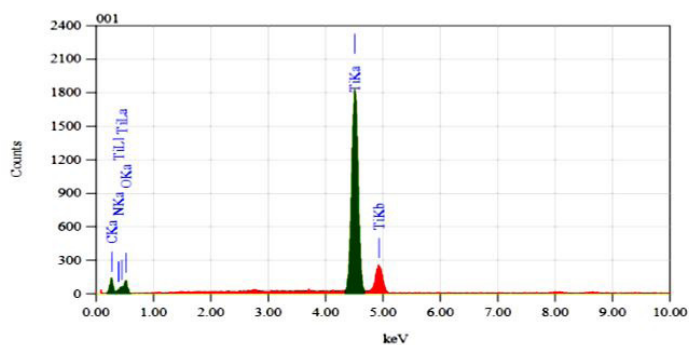
$$\cdot OH + C_{14}H_{14}N_3SO_3^- \rightarrow CO_2 + \text{Inorganic salts} + H_2O \quad (4)$$
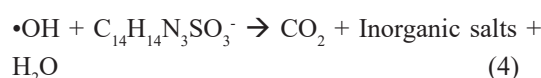
Fig. 1. The comparison XRD patterns of C-N-codoped TiO$_2$; undoped-TiO$_2$; and standard TiO$_2$-anatase

(a)   (b)

(c)

Elements	Atom (%)
Ti	39.6
O	41.79
C	16.59
N	2.02

Fig. 2. TEM image (a) undoped-TiO$_2$ and (b) C-N-codoped TiO$_2$; (c) EDX spectrum of C-N-codoped TiO$_2$
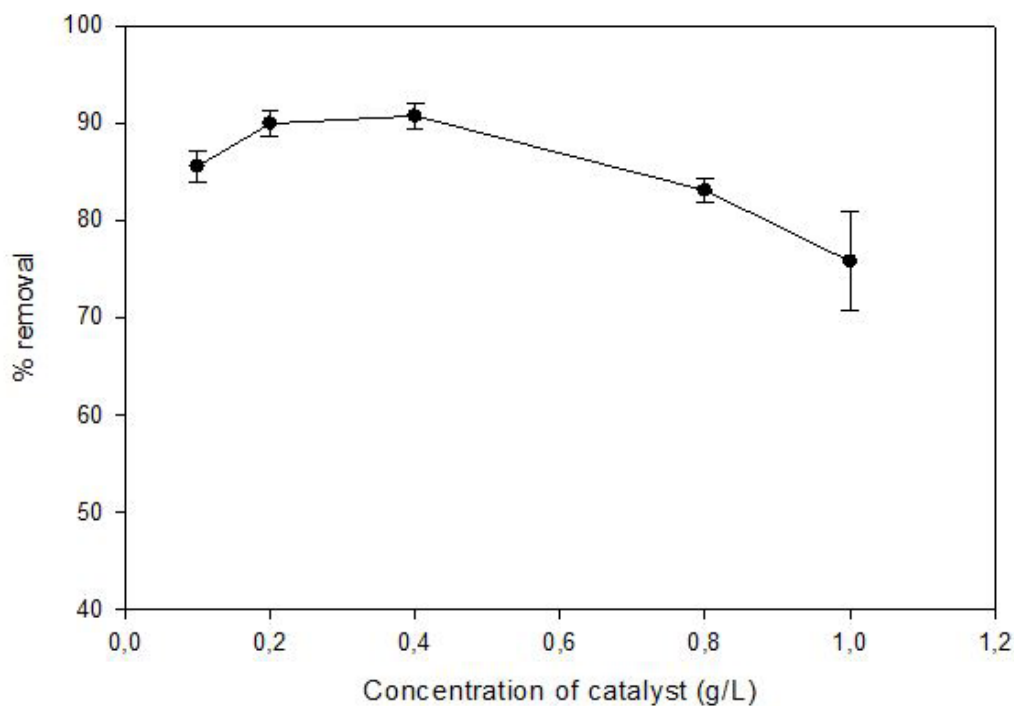
Fig. 3. Effect of C-N-codoped TiO$_2$ dosage in the photodegradation for 180 min.
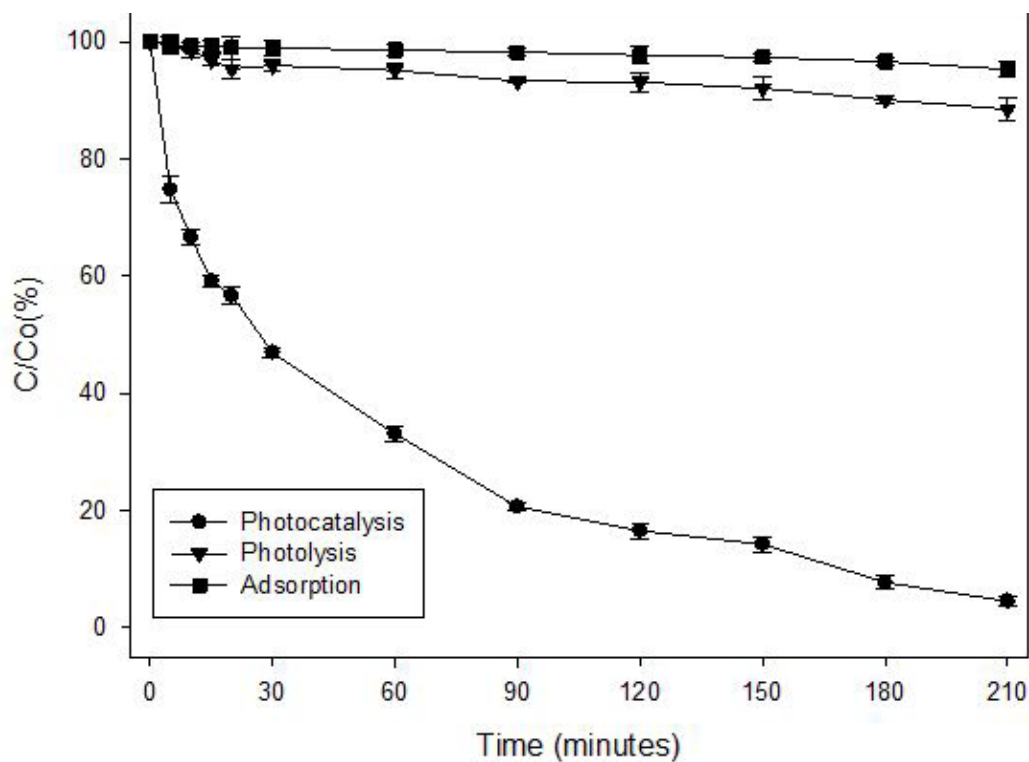 **(MO = 5 mg L^{-1}; pH = 5.6; n*=2) *n: number of sample size**

Fig. 4. Comparison of adsorption, photolysis, and photocatalysis in degradation of methyl orange
 (MO = 5 mg L^{-1}; pH = 5.6; n=2)

Effect of initial methyl orange concentration

The degradation of different methyl orange initial concentrations were studied, the results are shown in Fig. 5. It has been found that the color removal efficiency of methyl orange was decreased with increasing the initial concentration of methyl orange dye. High concentration of methyl orange causes declining transparency of the solution thus penetration of visible light to organic molecules of methyl orange dye decreased [32, 33]. Therefore, the time to complete removal of methyl orange dye longer for higher initial dye concentration.

Study of Kinetic Order

The Langmuir-Hinshelwood kinetic model can be applied for photodegradation of methyl orange in the presence of C-N-codoped TiO_2 catalyst in the correlation between the degradation rate and the initial dye concentration [34]. In this research the initial concentrations of methyl orange dye used were relatively low, hence the kinetics data were modelled using pseudo first-order. The kinetics can be expressed by the following formula:

$$C = C_o \, e^{-kt} \qquad (5)$$

where C is the concentration of methyl orange at time t, C_o is the initial concentration of methyl orange and k (min^{-1}) is the degradation rate constant. The integration of Eq. 5 results in Eq. 6:

$$\ln\left(\frac{C}{C_o}\right) = -kt \qquad (6)$$

Based on Eq. 6, a plot of $\ln(C/C_o)$ versus irradiation time represents a straight line showing in Fig. 6. The value of methyl orange degradation rate constant at each concentration was shown in Table 1. From the pseudo-first-order constant, the contribution of adsorption and oxidation in the photodegradation of methyl orange could be estimated by the equation of Langmuir-Hinshelwood model [35, 36], Eq. 7:

$$\frac{1}{k} = \frac{1}{K_{MO}k_{rxn}} + \frac{C_o}{k_{rxn}} \qquad (7)$$

where K_{MO} (L mg^{-1}) is equilibrium adsorption constant of methyl orange on C-N-codoped TiO_2 and k_{rxn} (mg L^{-1} min^{-1}) is the reaction rate between methyl orange and •OH radicals.

As shown in Fig. 7, the degradation rate constant of pseudo first-orrder for photodegradation of methyl orange at various initial concentration in the presence of C-N-codoped TiO_2 was fitted to Eq. 7. The resulting values of k_{rxn} and K_{MO} obtanied were 0.236 mg L^{-1} min^{-1} and 10.436 L mg^{-1} with the R^2 value of 0.9142, respectively.

Effect of initial pH methyl orange solution

The effect of pH on methyl orange photodegradation was investigated in the presence of C-N-codoped TiO_2 catalyst. The acidic condition was made by the addition of HCl (0.1 M) and base condition by the adition of NaOH (0.1 M). The results obtained in the pH range 3-9 are shown in Fig. 8. It was observed that the best degradation efficiency was obtained at pH 3.6. It is known that TiO_2 has amphoteric character in aqueous solution. The point of zero charge (p_{zc}) of C-N-codoped TiO_2 was found at acidic pH (5.29) [37]. Since the pH condition of dye solution near the p_{zc} can be favorable to adsorb the molecule of methyl orange and therefore the highest degradation percentage was achieved at pH 3.6. Base pH condition decreased the degradation efficiency due to the coulombic repulsion between negative charge of catalyst surface (TiO$^-$) at alkaline condition [38] and the OH$^-$ species in photocatalytic mechanism [35]. The degradation percentage at natural pH of methyl orange (5.6) was slightly different to acidic pH thus this pH was chosen for investigation of kinetics reaction since no need HCl addition.

Byproducts analysis and photodegradation mechanism

To confirm the mineralization process in the photodegradation of methyl orange using C-N-codoped TiO_2 catalyst, the reaction were carried out up to 180 min and the irradiated samples were analyzed by TOC (Total Organic Carbon) analyzer. The TOC-removal percentage of methyl orange gradually increased with time. After 180 min reaction, the TOC-removal percentage reached approximately 70%, the results are shown in Fig. 9. However, compared with the color removal of methyl orange, the removal percentage of TOC was slightly lower under the same conditions. This occurred mainly because the methyl orange macromolecule broke into an organic small molecular substances and was finally oxidized to form an inorganic substance (CO_2) during the photocatalytic degradation of MO. The small molecular substances were detected in the analysis of HPLC system. Fig. 10 shown the chromatogram of methyl orange during photodegrdation process for 180 min. Some peaks were inidcated as by-products of methyl orange then identified by LC-MS/MS system.

As seen from Fig. 10a, methyl orange has a strong peak at retention time RT 4.120 min. After photdegradation process for 180 min the peak significantly decreased and some peaks were formed indicating as byproducts (in Fig. 10b-e). The peaks were identified in MS/MS system then known as organic compounds with m/z 290; 158; and 123. Other small peak at 120 min degradation was also identifed with m/z 276. After 180 min degradation the organic structure with m/z 276 was not showed up and transferred into other molecules. Hence, the tentative molecular strucure and proposed pathway for methyl orange photodegradation in the presence of C-N-codoped TiO_2 are shown in Fig. 11.
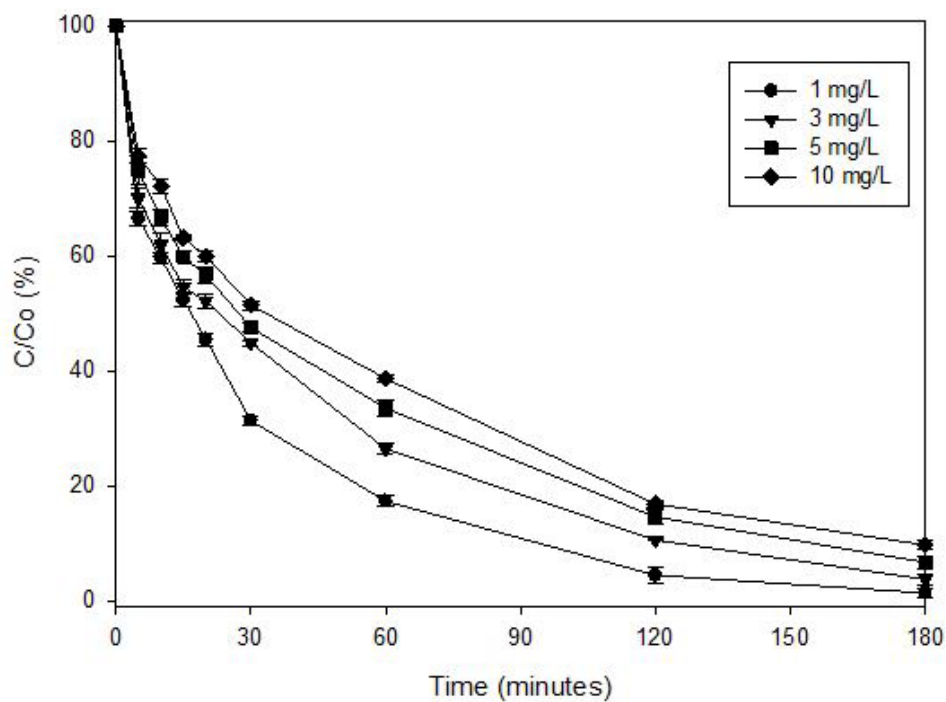
Fig. 5. Effect of methyl orange initial concentration to color removal (C-N-codoped TiO$_2$= 0.45 g L^{-1}; pH = 5.6; n=2)

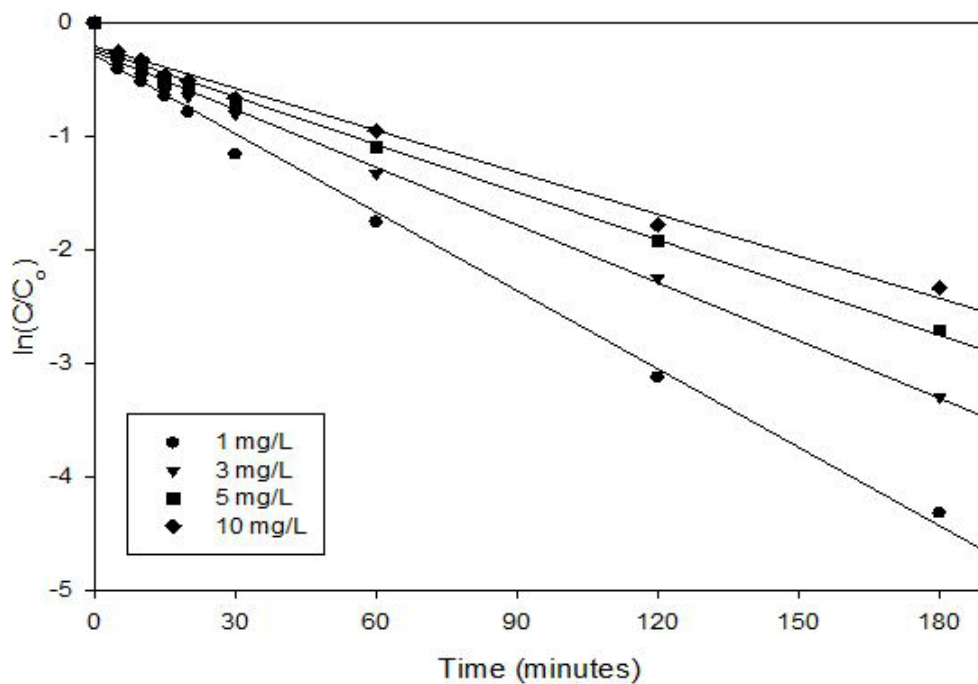**Fig. 6. Photodegradation kinetics model in various concentration of methyl orange in the present of catalyst (pH= 5.6, C-N-codoped TiO$_2$ = 0.45 g L^{-1}, n=2)**
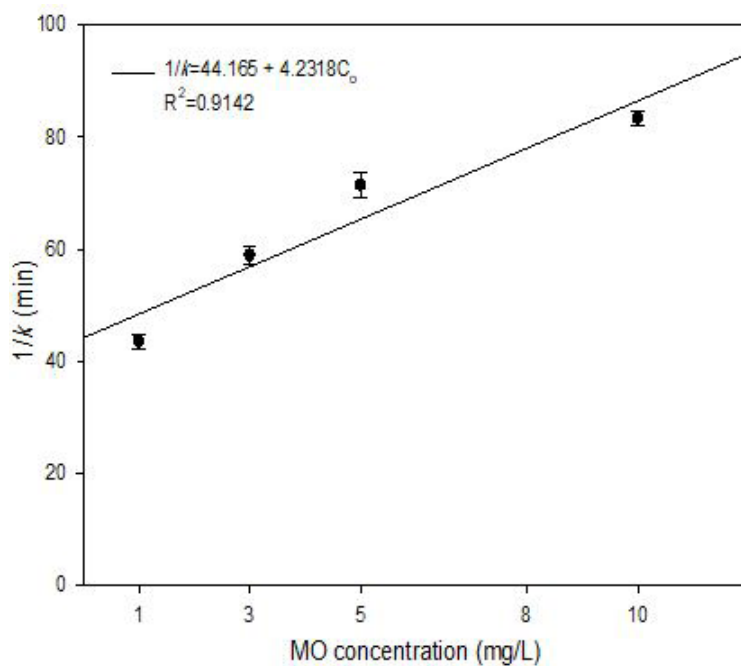
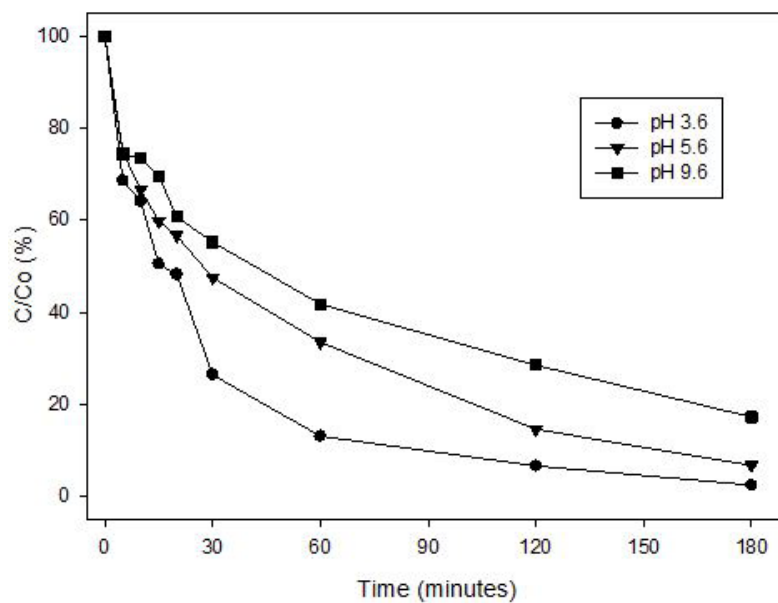**Fig. 7. Plot of the initial MO concentration versus the reciprocal of pseudo-first-order rate constant (1/k)**

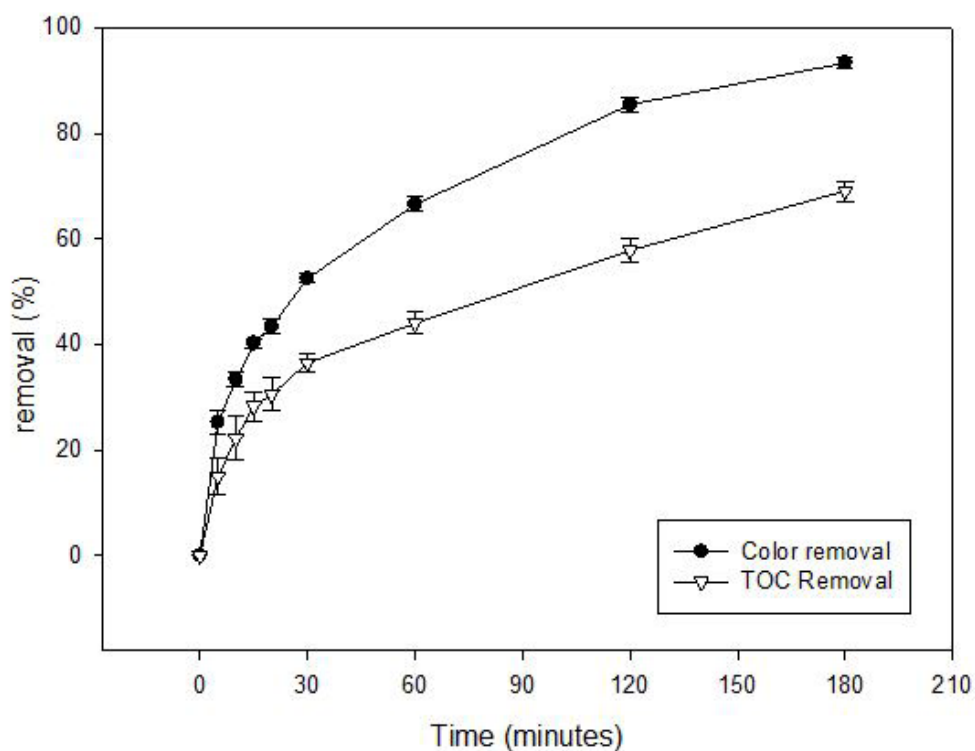**Fig. 8. Effect of methyl orange initial pH to color removal (MO= 5 mg L^{-1}; C-N-codoped TiO$_2$= 0.45 g L^{-1}; n=2)**

Fig. 9. Color and TOC removal comparison of methyl orange during photodegradation (MO= 5 mg L^{-1}; C-N-codoped TiO$_2$= 0.45 g L^{-1}; pH= 5.6; n=2)
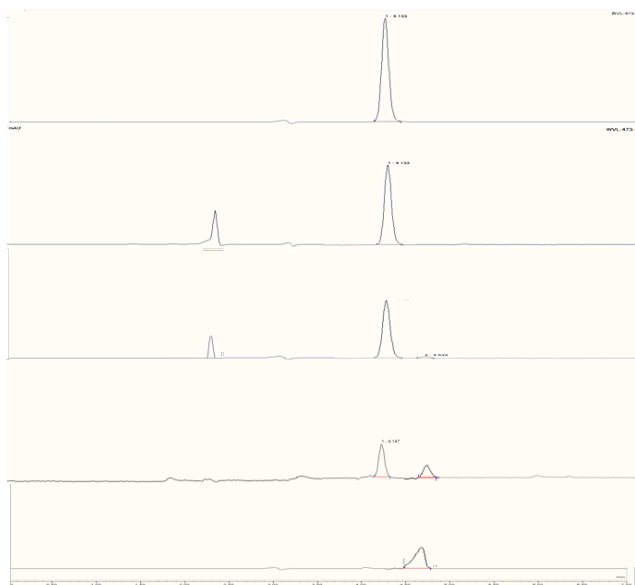

Fig. 10. chromatogram of methyl orange during photodegradation for (a) 0 min;(b) 30 min; (c) 60 min;(d) 120 min; (e) 180 min). (MO= 5 mg L^{-1}; C-N-codoped TiO$_2$= 0.45 g L^{-1}; pH= 5.6)
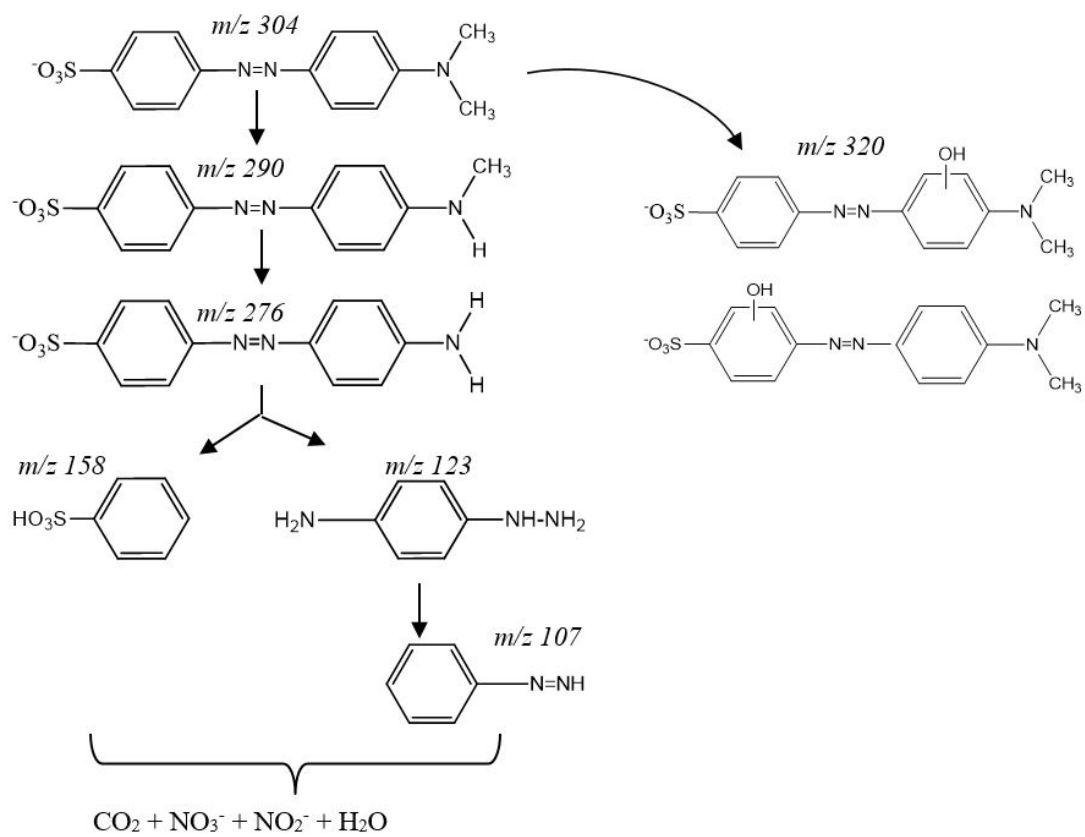
Fig. 11. Schematic illustration of the proposed degradation pathway

TABLE 1. Methyl orange degradation rate based on Langmuir-Hinshelwood model (experimental conditions: mass of C-N-codoped TiO_2 = 0.45 g L^{-1}, pH=5.6, n=2)

Initial dye(mg L^{-1})	k_{obs} (min^{-1})	$1/_{kobs}$ (min)	$t_{1/2}$ (min)	R^2
1	0.023	43.41	30.09	0.9912
3	0.017	58.94	40.86	0.9901
5	0.014	71.38	49.47	0.9877
10	0.012	81.01	56.15	0.9839

Conclusion

The experimental results of this study show that photo-degradation using C-N-codoped TiO_2 as a catalyst could be applied to the treatment of methyl orange wastewater. About 4% of methyl orange was adsorbed onto C-N-codoped TiO_2 surface, and 10% of methyl orange was degraded during photodegradation then by the addition of 0.45 g L-1 of C-N-codoped TiO_2 the color removal of methyl orange increase to 94% for 180 min visible-light irradiation. The photodegradation of methyl orange using C-N-codoped TiO_2 catalyst was fitted to the Langmuir-Hinshelwood model and obeyed the pseudo-first-order kinetics. In the mineralization study, the photolysis process in the presence of C-N-codoped TiO_2 achieved an approximately 70% TOC removal. The organic byproducts were identified by LC-MS/MS system then the degradation pathway of methyl orange was propoesed.

Acknowledgement

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