



Role of active oxidative species on TiO_2 photocatalysis of tetracycline and optimization of photocatalytic degradation conditions

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Abstract

The optimum operating conditions for TiO_2 photocatalytic degradation of tetracycline antibiotic (TC) in aqueous solution and the role of active oxidative species (AOS) from UV/ TiO_2 in its degradation were investigated. Response surface methodology (RSM) and central composite design (CCD) were adopted to optimize three parameters: TiO_2 concentration, initial pH and UV irradiation time. Radical scavengers were added to reaction solution to assess the photocatalytic reaction mechanism of TC. The results showed that 93.1% degradation efficiency was obtained under optimum conditions established during experimentation (TiO_2 concentration = 2.09 g l^{-1} , pH = 5.56 and $t = 20.95 \text{ min}$). These results agree with the prediction made by the proposed model. Photocatalytic degradation of TC followed a pseudo first-order reaction rate. Photogenerated holes (h^+_{vb}) with minor participation from superoxide anions (O_2^-), were responsible for TC oxidation on TiO_2 , while hydroxyl radicals ($\cdot\text{OH}$) played a negligible role in titania-TC oxidation.

Key words

Active oxidative species, Photocatalytic degradation, Response surface methodology, Tetracycline, UV/ TiO_2 process

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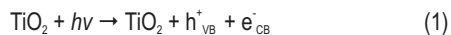
Introduction

Over the past decade, antibiotics have been widely used in animal farming and poultry industries. As a broad-spectrum bacteriostatic agent, tetracycline is widely used in aquaculture and veterinary medicine. Due to its high water solubility and bio-refractory nature, tetracycline residue has been detected in a multitude of matrices (Karcı and Balcıođlu., 2009; Wei, *et al.*, 2011). Because this residue is poorly metabolized, conventional water treatment technologies cannot efficiently remove these residues (Luo, *et al.*, 2008; Wei, *et al.*, 2011). The potential risk of tetracycline residues in aquatic environments constitutes a rising public health concern (Luo *et al.*, 2008; Watkinson, *et al.*, 2009). Therefore, more effective treatment technologies are expected. Photocatalytic oxidation in TiO_2 suspension might be an efficient way to increase its degradation rate because some refractory

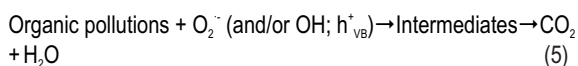
pollutants have been reported to efficiently decompose in the presence of TiO_2 (Ikehata and El-Din, 2004; Luo *et al.*, 2008; Watkinson *et al.*, 2009).

Photocatalytic degradation of various organic systems, using irradiated TiO_2 , is well documented in literature (Ahmed, *et al.*, 2014; Gaya and Abdullah, 2008; Leong, *et al.*, 2014). Briefly, when a semiconductor such as TiO_2 absorbs a photon with energy equal to or greater than its band gap width, an electron may be promoted from the valence band to the conduction band (e^-_{cb}), leaving behind an electron vacancy (h^+_{vb}) in the valence band. If charge separation is maintained, the electron and hole may migrate to the catalyst surface, where they participate in redox reactions with adsorbed species (Gaya and Abdullah, 2008). Specifically, h^+_{vb} may react with surface-bound H_2O or OH^- to produce hydroxyl radical ($\cdot\text{OH}$), and e^-_{cb} reacts with oxygen to

generate a superoxide radical anion ($O_2^{\cdot-}$), as indicated in the following eqs. (1–4):



It has been suggested that these active oxidative species (AOS), h^+_{VB} , $\cdot OH$ and $O_2^{\cdot-}$, are primary oxidizing species in the photocatalytic oxidation processes, as shown in Eq. (5). However, the role that AOS plays in initial photoreaction process is still controversial (Chen, *et al.*, 2005; Zhang, *et al.*, 2009).



The major uncertainty is whether oxidation proceeds via direct electron transfer between the substrate and h^+_{VB} or via $O_2^{\cdot-}$ ion and $\cdot OH$ radical-mediated pathway.

Photocatalytic degradation processes are generally influenced by a number of parameters involving synergistic effects (Abella'n *et al.*, 2007; Elmolla and Chaudhuri, 2009; Fernandez, *et al.*, 2004). To find optimum conditions, response surface methodology (RSM) can be adopted. RSM is an experimental strategy used to determine optimum conditions for a multivariable system. This strategy has been successfully applied to a different process to achieve experimental design optimization in recent years (Betianu *et al.*, 2008; Zuurro *et al.*, 2013). Central compositional design (CCD) is the most popular design due to its ease use in sequential experimentation (Betianu *et al.*, 2008; de Franco *et al.*, 2014). As photocatalytic process is affected by a large number of parameters, it is rather difficult to optimize an experimental design containing all these parameters. Therefore, the most important factors affecting the photocatalytic degradation were selected for optimization.

The present study aimed at investigating the photocatalytic degradation of TC by UV/TiO₂ processes. Multivariate analysis using RSM was employed, simultaneously varying the pH, TiO₂ concentration and irradiation time, to determine optimal conditions for degradation of TC. Kinetics of photodegradation of TC was also analyzed and role of main AOS during photodegradation of TC under UV light illumination was also investigated in detail.

Materials and Methods

Procedures and analysis : Experiments were conducted in a beaker of 100ml capacity in room temperature. A UV lamp (Philips, PL-L 18 W) emitting mostly monochromatic radiation at 365 nm was placed above the beaker. Distance between lamp

and surface of the reaction solution was 5 cm.

In all experiments, 100ml of 42 μM TC (Solarbio Co. Ltd., China) solution containing the appropriate amount of TiO₂ powder (P-25, Degussa, Germany) was magnetically stirred (125 rpm) before and during irradiation. Before irradiation, the solution was stirred in dark for 30 min to allow the system to reach adsorption equilibrium. Samples were taken at designed time intervals during irradiation, followed by centrifugation and filtration through a 0.5 μm cellulose filter to remove solid particles. The treated sample was analyzed by high performance liquid chromatography (Shimadzu, HPLC, LC-20AT), using UV detector and a C18 column (Shim-Pack, VP-ODS, 250*4.6 mm). A 11:22:67 (v/v) methanol/acetonitrile/0.1 M aqueous oxalic acid mixture was used as mobile phase at 25°C with a constant flow rate of 0.8 ml min⁻¹. The retention time of TC was 6.3 min.

For control led pH in TC solutions, H₂SO₄ (0.1 N) and NaOH (0.1 N) were used. The pH values of solutions were monitored with Jenco 6010M pH-meter.

Response surface methodology : To find the optimum conditions for degradation of TC in TiO₂/UV system, the experimental design as a function of selected main factors was determined. The factors (variables) in the present study were TiO₂ concentration (X_1), initial pH value (X_2) and irradiation time (X_3). These experiments were carried out as a CCD consisting of 20 experiments determined by 23 full factorial designs with 6 axial points and 6 center points. The coded levels and experimental factors are given in Table 1.

Design Expert 8.05b (Stat-Ease, America) was used for data analysis and response surface optimization. Through analysis of variance (ANOVA), relationships between parameters and response variables were obtained. Regression coefficient (R^2) was used to measure the fits of the experimental data.

Kinetic analysis of the photocatalytic degradation of TC: To determine the kinetics of photodegradation processes, a pseudo-first-order equation is used (Bensaadi *et al.*, 2014; Bosco, *et al.*, 2006). Half-life of TC degradation was calculated using equation (6) and (7).

$$\ln \frac{C_0}{C} = kt \quad (6)$$

$$t_{1/2} = \frac{\ln 2}{k} \quad (7)$$

Where, C_0 and C are TC concentration at times zero and t ; k is the rate constant and $t_{1/2}$ is the half-life time.

Identification of role of AOS : To identify the roles played by h^+_{VB} , $\cdot OH$ and $O_2^{\cdot-}$ in photocatalytic degradation of TC (4.2 μM), isopropanol (4.2 mM), benzoquinone (4.2 μM) and iodide ions (I^-) (0.42 mM) were added to antibiotic solution respectively. Acetonitrile was used as a solvent in a separate experiment to

Table 1 : Experimental factors and their coded levels

Factors	Factors and code level				
	$-\alpha$	-1	0	1	$+\alpha$
TiO ₂ concentration (g l ⁻¹): X ₁	0.5	0.9	1.5	2.1	2.5
Initial pH value: X ₂	2	3.8	6.5	9.2	11
Irradiation time (min): X ₃	5	9	15	21	25

Table 2 : Parameters and appropriate degradation rate

Run	X ₁	X ₂	X ₃	Y (%)
1	1.5	6.5	15	81.84
2	2.1	3.82	21	95.81
3	0.9	3.82	9	52.01
4	0.9	9.18	9	71.02
5	0.9	9.18	21	81.79
6	1.5	6.5	5	73.38
7	1.5	6.5	25	85.36
8	1.5	11	15	65.21
9	0.5	6.5	15	74.57
10	2.1	9.18	21	81.16
11	1.5	2	15	53.23
12	0.9	3.82	21	67.09
13	2.5	6.5	15	88.58
14	1.5	6.5	15	81.25
15	1.5	6.5	15	81.12
16	1.5	6.5	15	81.96
17	2.1	3.82	9	72.55
18	1.5	6.5	15	80.94
19	2.1	9.18	9	75.56
20	1.5	6.5	15	81.56

minimize the formation of ·OH. The influence of additives and changes in the parameters provided information about the mechanisms and reactive species involved in the reaction.

Results and Discussion

Optimization of the reaction : According to the response surface design, 20 experiments were conducted. The specific

parameters and degradation rate for these experiments are listed in Table 2. According to the most common values reported in previous studies, a TiO₂ concentration range of 0.5 - 2.5 g l⁻¹ and a pH range of 2 - 11 were chosen.

$$Y (\%) = \left[1 - \frac{C_t}{C_0} \right] \times 100\% \quad (8)$$

In equation (8), Y(%) is percentage of TC removal rate; C_t is residual concentration of TC after designed irradiation time and C₀ is initial concentration of TC.

According to the experimental design presented in Table 2, the following response quadratic model was established, which could be written in terms of coded factors:

$$Y = -47.2658 + 27.53544 \cdot X_1 + 22.69633 \cdot X_2 + 2.197977 \cdot X_3 - 3.56 \cdot X_1 \cdot X_2 + 0.10642 \cdot X_1 \cdot X_3 - 0.17261 \cdot X_2 \cdot X_3 + 1.159078 \cdot X_1^2 - 1.04671 \cdot X_2^2 - 0.01046 \cdot X_3^2 \quad (9)$$

Where, Y is removal rate of TC; X₁ is TiO₂ concentration; X₂ is initial pH value and X₃ is UV irradiation time (min).

ANOVA was used to evaluate statistical significance of second-order polynomial model (Table 3). According to ANOVA table, F-value (26.41) was quite high, and P-value was smaller than 0.0001, which is accepted by most investigators. Moreover, an R² value of 0.9589 was close to 1, indicated that the empirical model was effective. Relationship between RSM model's predicted removal rate of TC and the experimental removal rate of TC is shown in Fig. 1. The data were distributed along 45° diagonal lines, confirming that the model satisfied assumptions of ANOVA and was appropriate for model simulation of this study.

The effect of design variables, TiO₂ concentration, initial pH and UV irradiation time on TC removal rate (response) was investigated by means of graphical response surface analysis. The response surfaces using three-dimensional and contour line plots are shown in Fig. 2-4.

Fig. 2 shows the effect of TiO₂ concentration and solution pH on TC removal rate for an irradiation time of 15 min. It is

Table 3 : Analysis of variance (ANOVA) of response surface model

Source	Sum of squares	Degree of freedom	Mean square	F-value	P-value
Model	2120.264	9	235.5849	25.96673	<0.0001
X ₁	431.1232	1	431.1232	47.51943	<0.0001
X ₂	130.5095	1	130.5095	14.38507	0.0035
X ₃	410.3216	1	410.3216	45.22662	<0.0001
X ₁ ·X ₂	257.0778	1	257.0778	28.33573	0.0003
X ₁ ·X ₃	1.132512	1	1.132512	0.124828	0.7312
X ₂ ·X ₃	60.33511	1	60.33511	6.65028	0.0275
X ₁ ²	2.420128	1	2.420128	0.266752	0.6167
X ₂ ²	809.3148	1	809.3148	89.20462	<0.0001
X ₃ ²	1.970659	1	1.970659	0.217211	0.6512
Res	90.72567	10	9.072567		
Lack of Fit	89.89252	5	17.9785	107.8948	<0.0001

evident that the removal rate increased linearly with increasing concentrations of TiO_2 ; however, this trend plateaus, approaching an asymptote for TiO_2 concentrations $>2.0 \text{ g l}^{-1}$. Some researchers pointed out that catalyst concentration had optimum value, because excess catalyst inhibited photocatalytic reaction as a result of the light attenuation and shadowing effect (de Franco *et al.*, 2014; Haque and Muneer, 2007; Mohebbali, 2013).

The highest removal rate was observed pH 5.5–7.5. Optimum pH of 5.56 was obtained by model analysis in the present study. pH is known as an important parameter in the photocatalytic reactions, since it determines the surface charge properties of the photocatalyst, and therefore the adsorption behavior of the pollutants (Haque and Muneer, 2007). The zero point charge (pH_{zpc}) of TiO_2 is 6.25, TiO_2 surface is positively charged for $\text{pH} < \text{pH}_{\text{zpc}}$ (Eq. (10)), and negatively for $\text{pH} > \text{pH}_{\text{zpc}}$ (Eq. (11)) (Bensaadi *et al.*, 2014; Lu *et al.*, 2014):

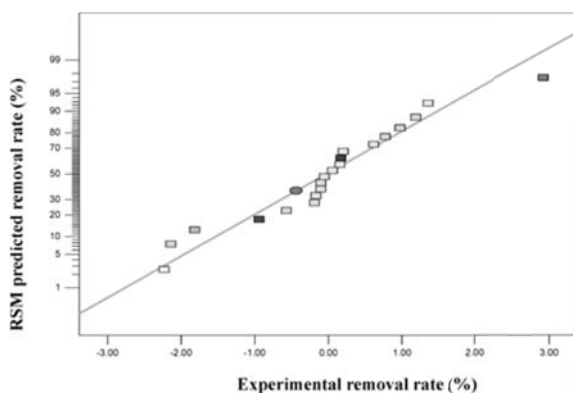
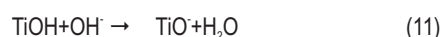


Fig. 1: RSM predicted removal rate of TC vs. the experimental removal rate of TC

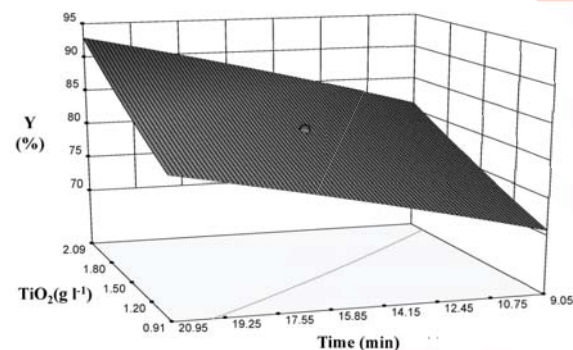


Fig. 3: Response surface for TiO_2 concentration and irradiation time with pH held constant at its median value of 6.5

Since TC is negatively charged in solution, with increased of pH, it was more negatively charged. Therefore, when TiO_2 surface was positively charged below pzc, an attractive force between TiOH_2^+ surface groups and TC molecules can favor adsorption, consequently leading to a better degradation rate. This might be the reason why the removal efficiency for TC in acidic solution was highest.

Fig. 3 shows the effect of TiO_2 concentration and irradiation time on TC removal rate at a solution with pH of 6.5. Fig. 4 shows the effect of solution pH and irradiation time on TC removal rate at a TiO_2 concentration of 1.5 g l^{-1} . From these two figures, it can be observed that irradiation time showed the greatest effect on the removal rate as compared with other designed variables. Increasing the irradiation time up to 21 min led to a strong increase of predicted response (removal efficiency), but this increasing trend moderates, approaching an asymptotic plateau for $t > 21$ min. The results revealed optimum irradiation time, which is important from an engineering point of view.

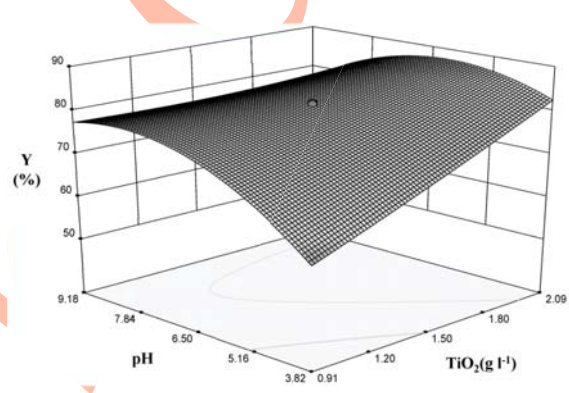


Fig. 2: Response surface for TiO_2 concentration and pH variables, with irradiation time held constant

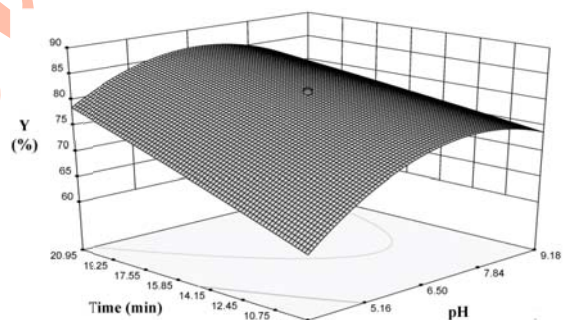


Fig. 4: Response surface for pH value and irradiation time with TiO_2 concentration held constant at its median value of $C = 1.5 \text{ g l}^{-1}$

According to model analysis, the optimized reaction conditions were: TiO₂ concentration of 2.09 g l⁻¹, pH of 5.56 and irradiation time of 20.95 min. Under optimized conditions, the experimental TC removal rate was 93.1%, close to the predicted removal rate of 93.85%. The difference between experimental and predicted optima was found within the limit of model error.

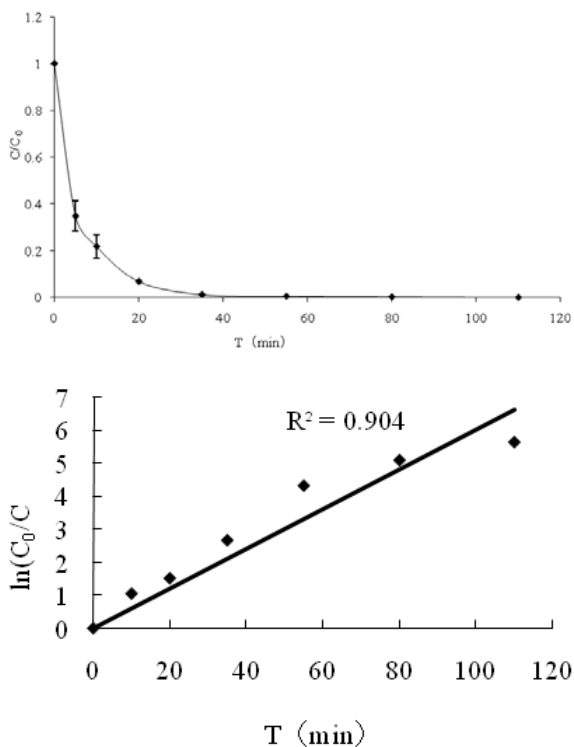


Fig. 5 : Plot of C/C₀ vs. T. The inset shows ln(C₀/C) vs. T, where initial concentration of TC was 42 μM, TiO₂ concentration was 2.0 g l⁻¹ and pH was 5.56

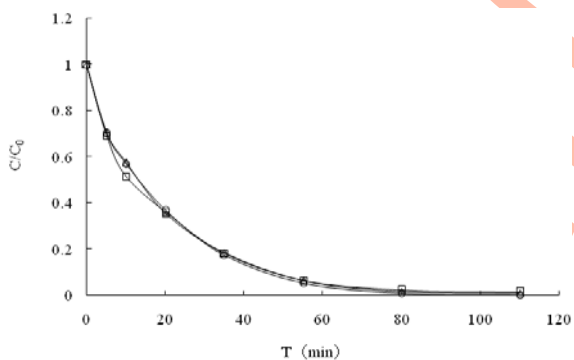


Fig. 6 : Effect of isopropanol and acetonitrile on titania-TC oxidation. Normalized TC concentration (%). TC in the presence of isopropanol (4.2 mM) (□) and acetonitrile (△)

Photocatalytic degradation kinetics of TC : Degradation of TC catalyzed by TiO₂/UV was found to follow pseudo-first-order kinetics, and there was a good linear relationship between ln(C₀/C) and T. Kinetic analysis of photocatalytic degradation of TC in TiO₂/UV system under optimum conditions is shown in Fig.5. According to linear fit of curve, pseudo-first-order model can be expressed as:

$$\ln \frac{C_0}{C} = 0.0604t \quad (12)$$

Rate constant, k, and half-life of TC degradation in TiO₂/UV system was 0.0604 min⁻¹ and 11 min, respectively

Roles of ·OH, h⁺_{VB} and O₂^{·-} : Isopropanol, a good scavenger, is easily oxidized by ·OH. Therefore, isopropanol has commonly been used to discern the role of ·OH in oxidation mechanisms (Chen *et al.*, 2005). Due to its weak adsorption power on TiO₂ surfaces in aqueous media, isopropanol is usually used as a diagnostic tool for ·OH radical-mediated mechanisms. Acetonitrile can be used as a solvent to confirm the participation of ·OH or h⁺_{VB} in photocatalytic reaction mechanism because there are no water molecules in acetonitrile to produce ·OH.

Fig.6 shows that the presence of isopropanol had no effect on degradation profile, indicating that ·OH play a negligible role in photoreaction. Furthermore, experiments carried out in an acetonitrile suspension showed almost same degradation profile, confirming that ·OH did not participate in titania-TC oxidation reaction. This result is consistent with the mechanism proposed by Chen *et al.* (2005) in degradation of Acid Orange 7 with TiO₂.

I⁻ are excellent scavengers that can be used to identify the involvement of holes in direct oxidation of organic substrates (Chen *et al.*, 2005). I⁻ can easily capture h⁺_{VB}: (h⁺_{VB} + I⁻ → I₂). In the present study, KI was added to the reaction solution as a source of I⁻ to suppress h⁺_{VB} process. As shown in Fig. 7, photocatalytic degradation of TC was greatly inhibited. Ninety nine percent of TC was degraded in control experiment at an irradiation time of 110 min, while only 78% of TC was degraded in the presence of I⁻. The inhibitive effect of I⁻ indicated that photogenerated holes played an important role in photodegradation of TC in UV/TiO₂ system. It can be attributed to the negative charge of TC, which cause TC tend to be electro statically attracted by the positive charges of h⁺_{VB}. This result is consistent with the mechanism proposed by Palominos *et al.* (2005) for degradation of flumequine with TiO₂.

Benzoquinone can be used to detect O₂^{·-} because it can trap O₂^{·-}, using an electron transfer mechanism (BQ+O₂^{·-}→BQ^{·-}+ O₂) (Palominos *et al.*, 2008; Raja, *et al.*, 2005). Fig. 8 shows a clear effect of the added benzoquinone on photodegradation of TC, although degradation rate of TC in control experiment, at an irradiation time of 110 min, was similar to that in the presence of benzoquinone.

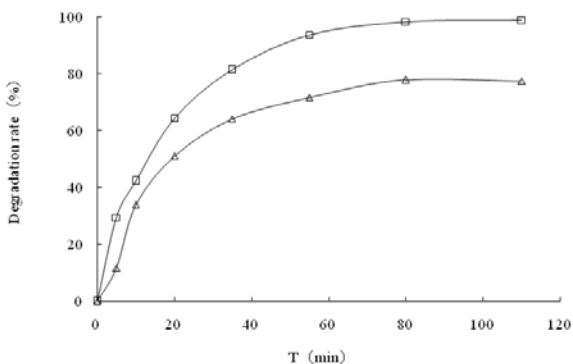


Fig. 7: Effect of f on Titania-TC oxidation. Normal TC concentration (1%). TC in presence of f (0.42 mM) (3%)

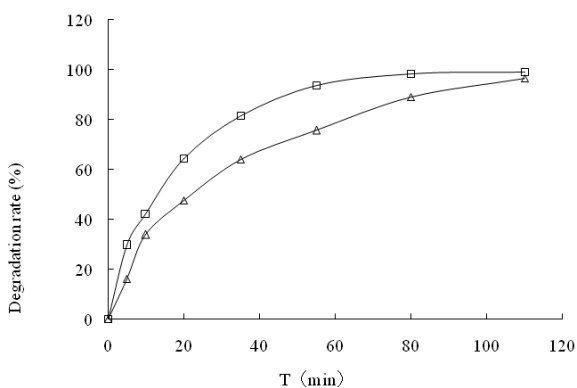


Fig. 8: Effect of bezoquinone on Titania-TC oxidation. Normal TC concentration (1%). TC in presence of bezoquinone (4.2 μ M) (3%)

In conclusion, the present study demonstrates that UV/TiO₂ photocatalysis can be an effective approach for degrading TC. 93.1% degradation efficiency of TC was obtained under optimum degradation conditions. h^+_{VB} with minor participation was responsible for TC oxidation on TiO₂, while \cdot OH played a negligible role in titania-TC oxidation.

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